To calculate probabilities of obtaining a certain value of an observable, we must first count the number of states with a given value of our observable and divide by the volume of the state space.

**Course-graining:**

Equivalently, if we wanted to speak about values of a macroscopic observable, we would integrate over microstates.

**Density:**

$$P(\theta_1, \ldots, \theta_n, \phi_1, \ldots, \phi_n) = \begin{cases} \frac{1}{\Omega} & \text{if } E < E_{\theta_1, \ldots, \theta_n} < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

Technically, for coarse-graining we should use a $d\theta d\phi$ but it will not end up making a difference in our calculations.

$$P = \int\int_{\text{volume}} \frac{1}{\Omega} \, d\theta_1 \ldots d\theta_n \, d\phi_1 \ldots d\phi_n$$

**QM description:**

Say system is in a pure quantum state $|\psi\rangle$ with probability $P_\psi$. We define a density operator:

$$\hat{\sigma} = \sum_j P_j |\psi_j\rangle \langle \psi_j|$$

where $\sum_j P_j = 1$.

Probability of finding system in state $|\alpha\rangle$ is $\langle \alpha | \hat{\sigma} | \alpha \rangle$.

For basis $|n_1, \ldots, n_s\rangle$:

$$P(n_1, \ldots, n_s) = \langle n_1, \ldots, n_s | \hat{\sigma} | n_1, \ldots, n_s \rangle = \sum_{\psi} P_\psi |\langle n_1, \ldots, n_s | \psi |\rangle|^2$$

$|\psi\rangle$ could be a designation of spins on a lattice or quantum #/s in many potentials in a box $|n_1, n_2, \ldots, n_s\rangle$.

Take into account wave motion of system and allow for interference.
The basic postulate of statistical mechanics (microcanonical ensemble) is that

\[
\langle n_1, \ldots, n_f \mid \hat{H} | m_1, \ldots, m_f \rangle = \begin{cases} 
\frac{1}{\Omega(E)} \delta_{n_1, m_1} \cdots \delta_{n_f, m_f} & \text{if } E < E_{n_1, \ldots, n_f} < E + \delta E \\
0 & \text{otherwise}
\end{cases}
\]

18. No off-diagonal terms in the wavefunction are equally probable if they are consistent with the energy requirement as we did before. We can define

\[
\hat{\Omega} = \frac{1}{\Omega(E)} \delta E
\]

as an average over all states with the same energy.

Aside: In order for ergodicity to hold, there must be small residual interactions (off-diagonal terms) that do not significantly affect \( E_{n_1, \ldots, n_f} \).

All probabilities depend on \( \Omega(E) \) for some energy \( E \).

Q: How does \( \Omega \) change as \( E \) increases?

\[
\Omega(E) = \frac{W(E)}{\Omega(E)} \delta E
\]

\[
W(E) = \frac{\partial \Omega(E)}{\partial E}
\]

For a system with 1 degree of freedom

\[
\Phi \sim e^x \quad \text{where } x \text{ is of order unity}
\]

Ex: S.H.O.

\[
\varepsilon = k \nu (n + \frac{1}{2}) \quad n = 0, 1, 2, \ldots \quad \alpha = 1
\]

\[
\tilde{E} = \frac{k^2}{2m} (\pi n \tau)^2 \quad n = 0, 1, 2, \ldots \quad \alpha = \frac{1}{2}
\]

For system with \( f \) degrees of freedom

\[
\Phi \sim e^{\alpha \tilde{E}} \quad \text{where } E = \frac{\tilde{E}}{\alpha} \quad \text{all states get on equal phase of the energy}
\]

\[
\Omega(E) = \frac{\partial \Phi}{\partial \tilde{E}} \delta \tilde{E} = \frac{\partial \Phi}{\partial \tilde{E}} \delta \tilde{E} = \Phi_0 (\tilde{E}) \frac{\partial \Phi}{\partial \tilde{E}} \delta \tilde{E} = \Phi_0^{f-1} \frac{\partial \Phi}{\partial \tilde{E}} \delta \tilde{E}
\]

\[
\ln \Omega(E) = (f-1) \ln \Phi + \ln \left( \frac{\partial \Phi}{\partial \tilde{E}} \delta \tilde{E} \right)
\]
\[ \frac{\partial i}{\partial E} = \alpha e^{-1} \text{ of order unity} \]

\[ \Phi(E) \text{ is some multiple of } E \text{ but it is certainly smaller than } \Phi(E) \]

since \( \Phi(E) = E \) \& \( \Phi(E) \ll E \)

\[ \text{or} \]

\[ \Phi(E) \sim 3 \alpha \alpha E^{\frac{1}{2}} \]

\( \alpha \) increases very quickly as a function of energy!

Let us do an Example: 

**Problem in a box**

\[ \frac{\Phi M}{k} \leq \frac{n^2 \pi^2 k^2}{2mE} = E_n \ldots E_f < E ? \]

\[ \leq n^2 < \frac{2mE L^2}{\pi^2 k^2} \]

\[ \Phi(E) = \frac{1}{2} \left( \frac{2mE L^2}{\pi^2 k^2} \right)^n \]

Quantum only positive \( n \)

\[ \Phi(E) = \text{Volume of sphere with radius } R \text{ in } n \text{ dimensions} \]

In both cases this problem reduces to calculating the volume of a sphere in \( n \) dimensions.

**Math Aside:** \( T \) functions

\[ T(n) = \int_0^\infty e^{-x} x^{n-1} \, dx = -\int_0^\infty x^{n-1} e^{-x} \, dx = -x^{n-1} e^{-x} \bigg|_0^{(n-1)} + (n-1) \int_0^\infty x^{n-2} e^{-x} \, dx \]

\[ T(n) = (n-1) T(n-1) \quad \text{or} \quad T(n) = (n-1)! \quad T(1) = 0! = 1 \]

\[ T(\frac{1}{2}) = \int_0^\infty e^{-x} x^{\frac{1}{2}} \, dx = 2 \int_0^\infty e^{-y^2} \, dy = \sqrt{\pi} \]

\[ T(m+\frac{1}{2}) = (m-\frac{1}{2})! = \frac{(2m-1) \cdot (2m-3) \ldots 3 \cdot 1}{2^m} \pi^{\frac{1}{2}} \]

\[ T(\frac{3}{2}) = \frac{3!}{2^3 \sqrt{\pi}} \]

\[ T(\frac{5}{2}) = \frac{5!}{2^5 \sqrt{\pi}} \]
Volumes of spheres in \( n \)-dimensions

\[ V_n(R) = C_n R^n \quad \text{trick is to determine } C_n \]

\[ dV_n = S_n(R) dR = nC_n R^{n-1} dR \]

where \( S_n(R) \) is the surface area of the sphere

Recall \( \int_{-\infty}^{\infty} e^{-x^2} dx = \pi^{1/2} \)

\[ \pi^{n/2} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\sum_{i=1}^{n} x_i^2} dx_1 dx_2 \cdots dx_n \]

\[ \pi^{n/2} = \int_{0}^{\infty} \cdots \int_{0}^{\infty} e^{-R^2} nC_n R^{n-1} dR \]

\[ \pi^{n/2} = nC_n \int_{0}^{\infty} e^{-R^2} R^{n-1} dR = nC_n {\frac{1}{2}} T\left( {\frac{n}{2}} \right) = \left( {\frac{n}{2}} \right)! C_n \]

\[ C_n = \frac{\pi^{n/2}}{\left( {\frac{n}{2}} \right)!} \]

\[ V_n(R) = \frac{\pi^{n/2}}{\left( {\frac{n}{2}} \right)!} R^n \quad \text{and } S_n(R) = C_n \left( {\frac{n}{2}} \right)! R^{n-1} \]

Try this for dimensions we are familiar with: \( 1, 2, 3 \)

\[ V_3(R) = \frac{\pi^{3/2}}{\left( {\frac{3}{2}} \right)!} R^3 = \frac{4}{3} \pi R^3 \quad S_3 = 2 \pi \frac{3}{2} R^2 = \frac{2}{3} T\left( {\frac{3}{2}} \right) R^2 \]

\[ V_2(R) = \pi R^2 \quad S_2 = 2 \pi R \]

\[ V_1(R) = 2R \quad S_1 = 2 \]

±0 or odd points
Back to our counting of states,

$$\Omega(E) = \frac{1}{\sqrt{\pi}} \frac{9}{2} \left( \frac{2mL^2E}{\hbar^2} \right)^{3/2} \frac{f}{2}!$$

Use Stirling's formula

$$n! = \sqrt{2\pi n} \; n^n e^{-n} \quad (A.6)$$

$$\Phi(E) = \left( \frac{4mL^2\pi Ee}{\hbar^2} \right)^{3/2} \left( \frac{1}{\sqrt{\pi f}} \right)$$

Indeed, $$\Phi \sim \left( \frac{E}{f} \right)^{3/2}$$

So our argument holds

and $$\Omega(E) \propto E^{3/2}$$

Other examples of counting states:

- Polyethylene
  \[ \{C\}_N \]
  - Film, bottles, cellophane, electrical insulators
- Polystyrene
  \[ \{C - H\}_N \]
  - Coffee cups, packaging

Polymers in 2D: We like random walkers in 2-D taking steps a:

Pascal's Pyramid

\[ \langle r^2 \rangle_2 = \frac{4}{6} x + \frac{4}{16} x(15) + 4x(2) = 2 \]

\[ \langle r^2 \rangle_4 = \frac{36}{6^2} + \frac{4}{24} x(15) + 4x2^2 + 4x6(6) + 8x9(5\times) + 4x^2 \]

\[ \approx 4 \]

In the limit of large #s, 

$$\rho(r) = \frac{1}{\pi Na^2} e^{-r^2/Na^2} \right\}$$
We've now looked at single particles & systems of many particles.
Next, let's discuss Interactions Between Macroscopic Systems.

Two Systems A & A'

Total energy of combined system \( A^{(0)} \) + Stating Constant

Energy can be transferred in two ways: heat \( Q \) & work \( W \)

Let's first discuss heat

\[ Q = \Delta E \] The change in the mean energy of system A is the heat \( Q \) absorbed

\[ \Delta E + \Delta E' = 0 \] Conservation of energy

\[ Q + Q' = 0 \] or \( Q = -Q' \)

heat gained by one system equals heat lost by other system

Work only (no heat) Removable isolated

\[ W = \Delta E \] work done by the system

\[ W + W' = 0 \] or \( W = -W' \) Conservation of energy

work done by one system must equal to the work done on other system

Heat + Work

\[ \Delta E = Q - W \]

\[ Q = \Delta E + W \]

See overall change in energy

\[ \Delta Q = \Delta E + \Delta W \]

Infinite amount of heat absorbed

Infinite amount of work done by system

Path dependent
Exact vs. Inexact differentials

\[ F = F(x, y) \]
\[ \frac{dF}{dx} = A(x, y) \frac{dx}{x} + B(x, y) \frac{dy}{y} \]

\[ \Delta F = F_1 - F_0 = \int dx = \int (A(x, y) dx + B(x, y) dy) \]

\[ \text{all infinitesimal quantities that can be written as sums of derivatives in } x, y \text{ are exact differentials} \]

Need a smooth (Controll derivatives) & single valued

\[ F \]

\[ G \]

Double valued or kinked

Cannot write derivatives as exact differentials

All our thermodynamic energies will be exact differentials

Our variables \( \frac{dx}{x}, \frac{dy}{y} \) may be inexact but their sum will be exact

Think object in a gravitational field

From a microscopic point of view

\[ \Omega \text{ isolated systems are in a state Constrained} \]

\[ \Omega = \Omega(y_1, \ldots, y_n) \text{ Constraints} \]

Value of the

The macroscopic variables/observables associated with the new phase space are the equilibrium volume

\[ \Omega \]

\[ \Omega \]

\[ \Omega \]

Gas in a room

Constraint: all molecules are on right half of the room

Once we lift the constraint what is the probability that

the molecules all stay on the right side of the room?

\[ \rho_i = \frac{\Omega_i}{\Omega} \]

\[ \Omega \text{ states on right side} \]

\[ \Omega \text{ states for full room} \]
Regardless of how we split up the phase space of the molecules, we explore twice as many states in the full internal energy. Note: it does not matter what we choose as our average radius $R$.

$P_i = \left(\frac{1}{2}\right)^i$ for large $N$ this is a very small $P_i$.

Other examples:
- Thermal equilibrium
- Pressure equalization

If some constraints of an isolated system are removed, the parameters of the system readjust so that

$\Omega(y_i)$ approaches a maximum.

$\Omega_f \geq \Omega_i$

if $\Omega_f = \Omega_i$ process is reversible,

if $\Omega_f > \Omega_i$ process is irreversible - we would need to do work to get system back into initial state.

If we consider $\Omega$ for system + machine, it increases during the process.

Why does a stretched rubber band recoil once you let go?

Time Scales

Every system has a relaxation time. Silly puts clemo.

Debora #: Panta Rei - everything above.

$\tau \ll T_{exp}$ System equilibrates very quickly.

$\tau \gg T_{exp}$ Treated system as though constraints are there (this scales time of the time) show constraint.

$\tau \sim T_{exp}$ bond, sheared colloidal particle.

Kivelson's paper on glasses.
Partial derivatives & independent variables

\[ Z = Z(x, y) \quad \text{Exact differential} \]

\[ \frac{dZ}{dx} = \frac{\partial Z}{\partial x} \, dx + \frac{\partial Z}{\partial y} \, dy \]  

(1)

\[ dx = \left( \frac{\partial x}{\partial y} \right)_z \, dy + \left( \frac{\partial x}{\partial z} \right)_y \, dz \]

to evaluate \( \frac{dx}{dy} \), set \( dz = 0 \)

\[ 0 = \left( \frac{\partial x}{\partial y} \right)_z \, dy + \left( \frac{\partial x}{\partial z} \right)_y \, dy \]

(2)

Note that \( \frac{dx}{dy} = -\frac{\partial z/\partial y}{\partial z/\partial x} \)

\[ \frac{1}{\left( \frac{dx}{dy} \right)_z} = \frac{dy}{dx} \]

Note also \( \frac{1}{\left( \frac{dx}{dy} \right)_z} = \frac{dy}{dx} \)

\[ \begin{vmatrix} \frac{\partial z}{\partial x} & \frac{\partial z}{\partial y} \\ \frac{\partial x}{\partial y} & \frac{\partial x}{\partial z} \end{vmatrix} = -1 \]

(3)

\[ \frac{d^2 z}{dx \, dy} = -\frac{d^2 z}{dy \, dx} \]

Comes from path independence

Curvature is well defined

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Back to \( \Omega \) & counting states

Recall \( \Omega \) is a very rapidly increasing function of \( E \)

\[ \Omega \sim E^{\infty} \]

Let's take two systems & put them in contact

\[ \begin{array}{c|c}
A & A' \\
\hline
E & E' \\
\hline
A^o & A'^o \\
\hline
\end{array} \]

If we put them in contact these systems will exchange energies & the state of each system will change

\[ \Omega^{0}(E') = \frac{\Omega(E) \Omega'(E' - E)}{A} \]

where does \( \Omega^0 \) go?
\[ \frac{\ln \Omega(E)}{dE} = \frac{d\ln \Omega(E)}{dE} + \frac{d\ln \Omega(E^0)}{dE} \cdot \frac{E-E^0}{E-E'} \]

\[ \frac{\ln \Omega(E^0)}{dE} = \frac{d\ln \Omega(E^0)}{dE} \cdot \frac{E}{E'} \]

\[ \ln \Omega(E) = \ln \Omega(E') \]

\[ \beta(E) = \beta'(E') \quad \text{This is what temperature does!} \]

\[ \beta = \frac{1}{kT} \]

\[ S = k \ln \Omega \]

\[ S + S' = \text{maximum at equilibrium} \]

If we start with systems out of equilibrium we are not at the most likely \( \Omega(E^0) \)

\[ S_{\text{total}} = S_i + S_2 \quad \text{so if we bring two systems together} \]

\[ S_i + S_2 \geq S_{1i} + S_{2i} \quad \text{or} \]

\[ \Delta S + \Delta S' \geq 0 \quad \text{entropy always increases} \]

by Conservation of Energy

\[ Q = E_f - E_i \quad Q' = E_f' - E_i \quad Q + Q' = 0 \]
2 cases:

1) Initial energies are such that \( \beta_i = \beta' \) \( \Rightarrow E = E' \) \( \Rightarrow \beta_s = \beta_s' \) \( \Rightarrow E_s' = E' \)

Stat is already maximized

2) \( \beta_i \neq \beta' \) then \( E_i \neq E' \) then systems are in a very improbable, non-equilibrium situation

as time progresses, Stat is maximized if \( \beta_s = \beta_s' \) and \( E_s = E' \)

If we allow volume to change, \( \Omega = \Omega(E, V) \)

\[ \Omega(E, V) = \Omega'(E', V') \]

\[ \ln \Omega' = \ln \Omega + \ln \Omega' \]

\[ \frac{d \ln \Omega}{dE} = \frac{d \ln \Omega}{dE} + \frac{d \ln \Omega'}{dE} \]

\[ \frac{d \ln \Omega}{dV} = \frac{d \ln \Omega}{dV} = \frac{d \ln \Omega'}{dV} \]

\[ \ln \Omega = (\beta - \beta') dE + (\frac{d \ln \Omega}{dV} - \frac{d \ln \Omega'}{dV}) dV \]

\[ \frac{d \ln \Omega'}{dE} = \beta' \]

\[ \frac{d \ln \Omega'}{dV} = \beta' \]

\[ \frac{d \ln \Omega}{dE} = \beta \]

\[ \frac{d \ln \Omega}{dV} = \beta' \]

For equilibrium, \( \frac{d \ln \Omega}{dE} = 0 \)

\( \beta = \beta' \)

\( \beta' = \beta' \)