



StatMech Basics



Goal of Stat Mech

- Quantum (Classical) Mechanics – gives energy as a function of “configuration”
- Macroscopic observables (state) $(P, V); (T, S); (\mu, N)$
- Second law tells us that an isolated system goes to a state of maximum entropy...the entropy is the appropriate thermodynamic potential $S(E, V, N)$
- What if you keep a system at constant volume V and temperature T ? This is the Helmholtz Free Energy $A(V, T, N) = U - TS$
- Constant pressure and temperature...Gibbs free energy $G(P, T, N) = A + PV$
- Goal of Stat Mech....Derive thermodynamic potentials from microscopics!



Two Questions

- Consider a mole of mono-atomic gas at NTP...it occupies a box of 22liters; it is well known that the gas molecules are equally distributed in the box...why not all the molecules decide to occupy a small volume (say 2 liter) near the corner?
- Consider a stone placed on a table...why does not the stone cool down and raise up (convert internal energy to gravitational potential energy)?
- Think classically for a minute...both these are systems of interacting particles...There is no fundamental reason from microscopic considerations that prevents the above from happening...but they don't happen!



Plan

- **Stick to classical mechanics to begin with**
- **Understand Macrostates and Microstates**
- **Postulate of Statistical Mechanics**
- **Learn the “Microcanonical Ensemble”**



Recap: Hamiltonian Mechanics

- Hamiltonian (N particles)

$$H(\mathbf{r}_i, \mathbf{p}_i) = \sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} + V(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

- $V(\mathbf{r}_1, \dots, \mathbf{r}_N)$ – Interaction between particles
- Hamilton's equations of motion

$$\frac{d\mathbf{r}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{r}_i}$$

- If initial conditions are specified, we “can” calculate the phase space trajectory of system



But then, a Puzzle!

- Take one gram of copper at NTP...find its properties (specific heat, etc.)
- Now take another sample also one gram of Cu...measure its properties...if you measure correctly, you will find that these the two readings agree!
- Both of these samples of copper have same number of atoms (say!), but they are doing very different trajectories in phase space!
- But then how come they give the same results!!
- It seems, then, that the properties are governed by **MACROSTATE** and not the **MICROSTATE**!



Macrostates and Microstates

- **Macrostate:** A “macroscopic” configuration of a “large” system described by quantities such as (Pressure (P), Volume(V)), (Energy(E), Temperature(T), Entropy(S), (#Particles (N), Chemical Potential (μ)), (Magnetic Field (B), Magnetization (M)) etc.
- **Microstate:** For an N particle classical system it corresponds to a particular volume element in the $6N$ -dimensional phase-space around $(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$
- **Experimentally one only observes macrostates...one only measures the pressure and temperature of a gas in the room, never the positions and velocities of all atoms!**



Macrostates and Microstates

- How are macrostates and microstates related?
- For a given macrostate, there will be many, many microstates possible
- Consider two particles of unit mass in a cubic box of side 1 unit, with total energy 2 units... Thus the macrostate is $(E = 1, V = 1, N = 2)$
- Possible Microstate: $r_1 = (0.5, 0.5, 0.5)$, $p_1 = (1, 0, 0)$ and $r_2 = (0.25, 0.75, 0.25)$, $p_2 = (0, 1, 0)$
- Hey, but there are **MANY** others, e.g.
 $r_1 = (\frac{1}{\pi}, 0.89, 0.42)$, $p_1 = (0, 0, \sqrt{2})$ and
 $r_2 = (0.97, 10^{-16}, 0.11)$, $p_2 = (0, 0, 0)$!
- Key question of stat mech: Given a macrostate, how many microstates are there?



Learn to Count?

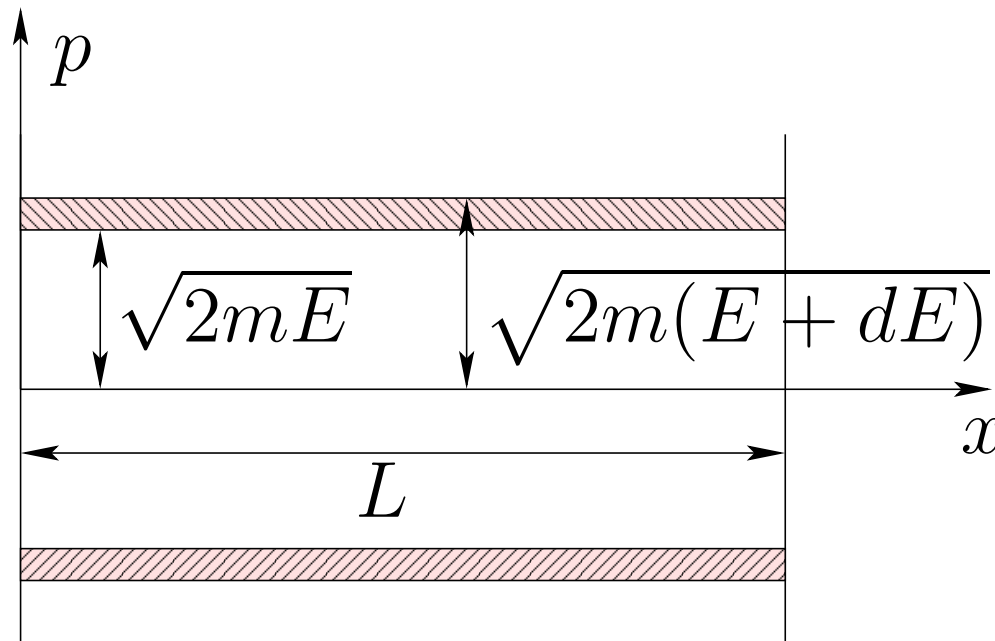
- How do you count microstates corresponding to a given macrostate?
- We will first work with the macrostate defined by (E, V, N) ...total energy, volume and number of particles are fixed...strictly we will think of energy E between E and $E + dE$!
- Rule for calculating number of states in s dimensions

$$\Omega(E, V, N)dE = \frac{1}{h^{sN} N!} \text{“phase-spc.-vol.” betwn. } E \text{ \& } E + dE$$

- Stick to classical mechanics and look at examples:
Particle in a 1D Box 1D-Harmonic Oscillator, Particle in a 3D Box, Ideal gas of N atoms!

of Microstates: Particle in 1D Box

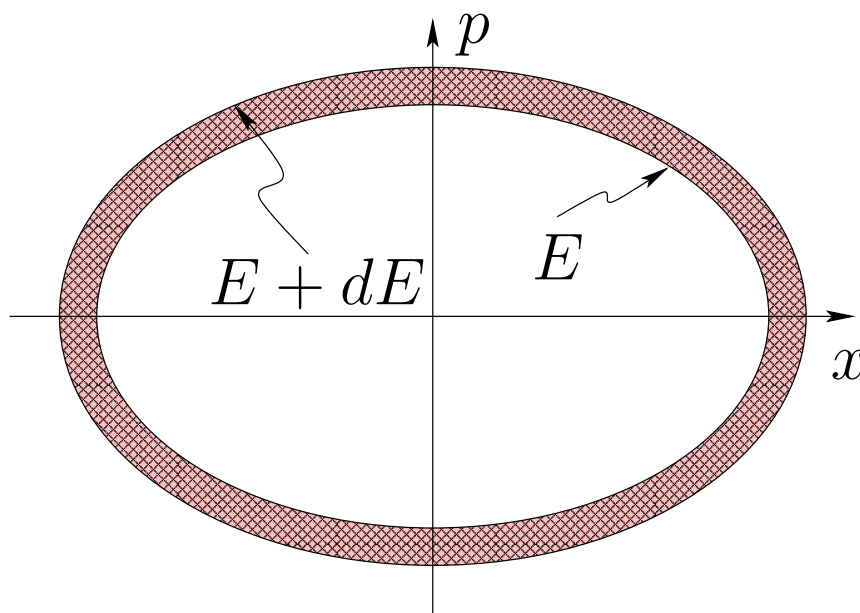
- A particle in a 1D box of size L in macrostate (E, L)
- Phase portrait (x, p)



- Total volume of phase space between E and $E + dE = L\sqrt{\frac{2m}{E}}$ implies $\Omega(E, L) = \frac{L}{h} \sqrt{\frac{2m}{E}}$

of Microstates: Harmonic Oscillator

- Harmonic oscillator ($H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$) in macrostate (E)
- Phase portrait (x, p)



- Total volume of phase space between E and $E + dE = \frac{2\pi}{\omega}$ implies $\Omega(E) = \frac{2\pi}{\hbar\omega}$



of Microstates: Particle in a 3D Box

- Particle in cube of volume V ($H = \frac{\mathbf{p} \cdot \mathbf{p}}{2m}$), macrostate (E, V)
- Phase portrait is six dimensional...cannot draw! But not difficult!
- $\frac{\mathbf{p} \cdot \mathbf{p}}{2m} = E$ is an equation of the sphere in the momentum subspace of the phase-space...its volume is $\frac{4\pi}{3}(2mE)^{3/2}$
- Therefore, the total phase space volume up to energy E is $V \frac{4\pi}{3}(2mE)^{3/2}$
- Thus the phase space volume between E and $E + dE$ is $2\pi(2m)^{3/2}V\sqrt{E}dE$
- $\Omega(E, V) = \frac{2\pi(2m)^{3/2}}{\hbar^3}V\sqrt{E}$



of Microstates: Ideal Gas

- N non-interacting particles in a cube of volume V ,
($H = \sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m}$); macrostate (E, V, N)
- Phase portrait is six N dimensional...cannot draw! But not certainly not difficult! Easy, in fact!!
- $\sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} = E$ is an equation of the sphere in the $3N$ -dimensional momentum subspace of the phase-space...its volume is $C_{3N}(2mE)^{3N/2}$
- Therefore, the total phase space volume up to energy E is $V^N C_{3N}(2mE)^{3N/2}$
- Thus the phase space volume between E and $E + dE$ is $\frac{3N}{2} C_{3N}(2m)^{3N/2} V^N E^{\frac{3N-2}{2}} dE$
- $\Omega(E, V, N) = \frac{1}{h^{3N} N!} \frac{3N}{2} C_{3N}(2m)^{3N/2} V^N E^{\frac{3N-2}{2}}$



Story So Far

- “Thermodynamic” properties depend only on macrostates
- For a given macrostate, there are many possible microstates
- Counting principle (E, V, N) :

$$\Omega(E, V, N)dE = \frac{1}{h^{sN} N!} \text{“phase-spc.-vol.” betwn. } E \text{ \& } E +$$

- Next on line...the basic “principle” of statistical mechanics!



Taking Stock!

- The goal of Stat Mech is to derive thermodynamic potentials from the “microscopics” of the given system
- To this end, we introduced “Macrostate” and “Microstates”
- Many macrostates corresponding to given microstate...How many?
- If system is in (E, V, N) , then # of microstates is $\Omega(E, V, N)dE$
- Ok! Lets go back to thermodynamics for a minute



Back to Thermodynamics

- **First Law :** $dU = TdS - PdV + \mu dN$
- **We can clearly see the following**

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

- **If we know entropy function $S(E(U), V, N)$, it seems we can calculate essentially any thermodynamic function!**
- **But, what really is entropy?**
- **If Stat Mech can help us calculate it, then we are through...we can get all thermodynamics! So back again to Stat Mech, but do remember the three relations above!**



And Back again to Stat Mech!

- We know that given a macrostate (E, V, N) , then there are $\Omega(E, V, N)dE$ microstates
- We have seen how to obtain $\Omega(E, V, N)$ for some simple systems...now we assume that $\Omega(E, V, N)$ is known for the general system and proceed
- Question: give that the system is in a macrostate (E, V, N) , which microstate is it in?
- This is not question that we can ever answer experimentally...(nor is it worthwhile doing so! But worthwhile conceptually!!)
- But we cannot ignore microstates...all the details of the system is hidden in $\Omega(E, V, N)$...we need something more to proceed the connection between microscopics and macroscopics!



The Postulate of Stat Mech

- We give up trying to decide which precise microscopic state it is in...and move over to a completely probabilistic description...therefore the detailed dynamics of the system is accounted only via $\Omega(E, V, N)$!
- Equal Apriori Probability Postulate (EAPP): Every microstate consistent with the given macrostate is equally probable!
- The word apriori means “before-hand”...what is meant is that when we start with we don’t know anything about the system (except $\Omega(E, V, N)$), so we take that every possible state is an equally likely candidate!
- “Probability” here is to be interpreted carefully...it is not like the probability in QM...think of dice!

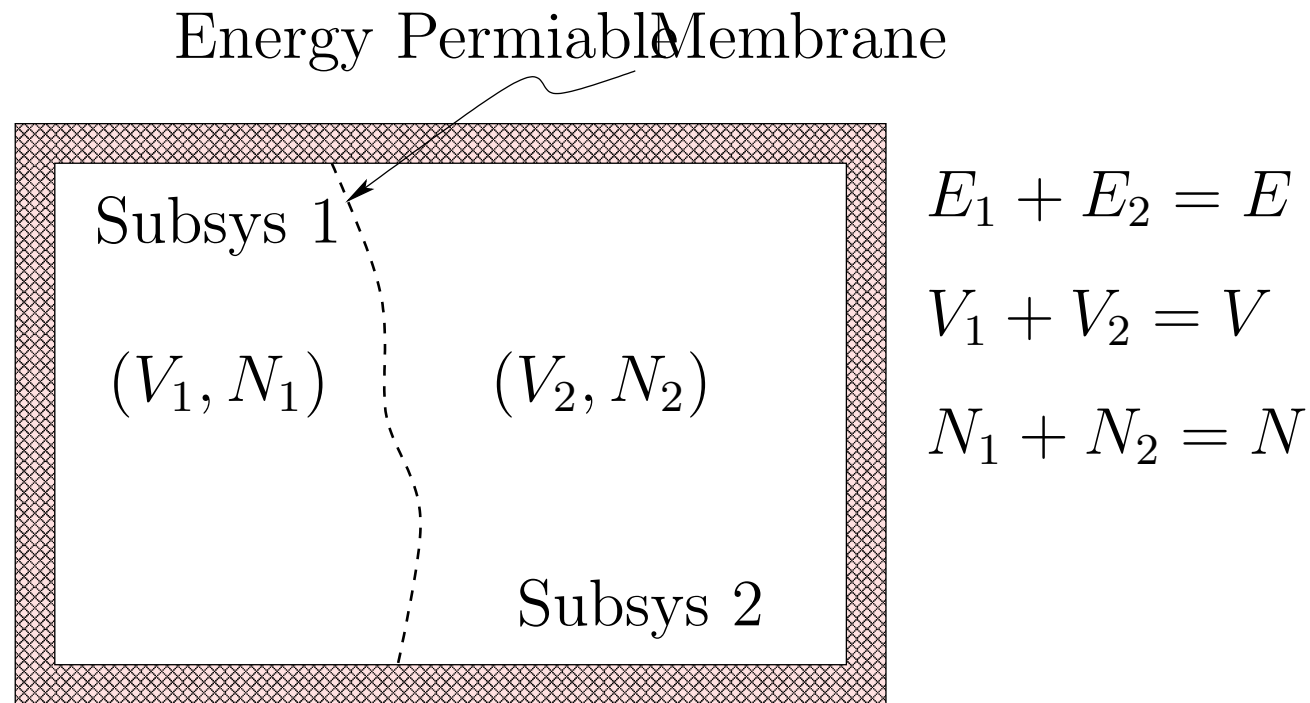


The Postulate of Stat Mech

- The postulate is just what it is...a postulate...NOT a law of nature!
- There are systems that will readily agree to this postulate...most practical system do!
- Thinking dynamically, we would expect this to be valid, if our time scale of observation is such that the system “can sample” all possible microstates...this is related to the so called “ergodic hypothesis”!
- There are real life systems where this is really not true...glasses! Can understand this from a simple two well potential...
- All good, but what about entropy, temperature?

Microcanonical Ensemble

- Consider a system of N particles occupying volume V with total energy E with $\Omega(E, V, N)dE$ as number of states



- The system is made up of two subsystems (1 & 2) separated by an “energy permeable membrane”...



Microcanonical Ensemble

- Question: How will the two subsystems share the energy E ?
- Say, subsystem 1 has energy E_1 and 2 has $E_2 = E - E_1$
- We ask: what is the most likely value of E_1 ?
- In how many ways can the system exist such that subsystem 1 has energy E_1 and 2 has $E_2 = E - E_1$?
Clearly, this is equal to $\Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_2)dE$
- By EAPP, the probability that subsystem has energy E_1 ,
$$P(E_1) = \frac{\Omega_1(E_1, V_1, N_1)\Omega_2(E_2, V_2, N_2)}{\Omega(E, V, N)}$$
- The most likely state is the one that will have maximum probability: we maximise $P(E_1)$ with respect to E_1 (noting $E_2 = E - E_1$)



And now, Entropy! Temperature even!!

- A bit of algebra shows that the most probable value of E_1 is such that $\left(\frac{\partial \ln \Omega}{\partial E}\right)_1 = \left(\frac{\partial \ln \Omega}{\partial E}\right)_2$!!
- Recall now that $\frac{\partial S}{\partial E} = \frac{1}{T}$ from thermodynamics...
- Suppose now we take $S \sim \ln \Omega$, then the condition above will be like saying two systems in equilibrium have same temperature!!
- THIS IS IT!...the connection between microscopics and macroscopics! Entropy $S = k_B \ln \Omega$...the result of Stat Mech!
- And temperature is the energy derivative of entropy!



But, then...

- You may wonder...this is the “most probable situation” ...Not to worry....the probability distribution is **VERY HIGHLY PEAKED** around E_1 satisfying the condition of equal temperatures...this is why thermodynamics works...all other situations are possible but **HIGHLY IMPROBABLE!**
- Perhaps you realise...we are through with Stat Mech at a conceptual level!!!
- To derive thermodynamics all we do is count states $\Omega(E, V, N)dE$...everyone of them is equally likely...Entropy is $k_B \ln \Omega$
- Once we have entropy, we have **ALL** thermodynamics...its **OVER!**
- ~~And, thus things really begin now!~~



Summary

- **EAPP...every microstate is equally likely**
- **Entropy is a measure of the number of microstates corresponding to the macrostate**
- **Once we know the entropy (calculated from microscopics), we “can derive” all thermodynamics!**
- **In essence, all the detailed dynamics of the system does not matter...it comes into the picture only in terms of determining the number of microstates available $\Omega(E, V, N)$!**