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Lecture 3: Ensemble Theory

# I. Ensemble Theory Basics

#### A. Microstates and Ensembles

In our discussion of dynamics, we became acquainted with the concept of the phase space. For a system with N particles, phace space is a 6N-dimensional space where the coordinates are the 3N generalized coordinates g; and 3N generalized momenta p; (iGE1, 3N7)

For a given set of initial conditions  $g_i(t=0)=g_{i,0}$  and  $p_i(t=0)=p_{i,0}$ , we will nove with some trajectory in this very high dimensional space. We call a single system a microscopic state or microstate.

The key insight of Josiah W. Gibbs is that instead of thinking about trying to compute the dynamics of microstates, we should focus on ensembles of microstates. An ensemble is a collection of different microstates with different initial conditions. Single microstate Ensemble of N microstates



9i

Pi (Bio, Pi,0)

**S**i

( 2 1 2 ( 2 1 ) Pip)

B. The Ergodic Hypothesis

At first, this seems like it only complicates things. Instead of trying to solve the dynamics of one I.C., we are now trying to solve for the dynamics of NICs! But think back to the harmonic oscillator for a moment. There the phase space trajectory was periodic. If I picked a different initial condition, I was going to get a very similar trajectory.

Harmonic Oscillator

**%** 

e size of circle fixed by system's

Pi Ri nittal energy. R any choice of IC up constant energy will like on this circle.

So, the trajectory of a single microstate is the same as if I picked an ensemble that corresponds to all of the possible initial conditions!

(This has the constraint of having constant energy, but I could always define a different energy and get a new circle if needed.)

This idea is called the Ergodic Hypothesis. It says that the dynamics of a single microstate will visit every possible state, given a long enough time. This is one of the fundamental postulates of statistical thermodynamics. In thermodynamics, we are going to be interested in average quantities. So, for example, we might want the average pressure. If we have a very long trajectory of a single microstate, we could get this average,

T

$$\overline{\mathcal{M}} = \lim_{T \to \infty} \frac{1}{T} \int \mathcal{M}(\underline{X}(t)) dt \qquad \underline{X} = (\underline{P}_i, \underline{Q}_i) \quad i \in [1, 3N]$$

Can we do this? Yes, we can now with computers. One needs to solve the equations of notion for the system. This is notecular dynamics. But, the founders of stat therms couldn't do this. They wanted to be able to do something!

The Ergodic hypothesis of Gibbs says that we don't have to. Instead, we can do an ensemble average,

$$\langle M \rangle = \int M(\underline{x}) g(\underline{x}) d\underline{x}$$
  
 $\Gamma \sim probability density of point \underline{x}$ .

In other words,

<M> = M Ensemble average = time average.

This is a mathematical expression of the Ergodic hypothesis.

<u>- = ] 9 x</u>

C. Phase Space Probability Density

Because of the E.H., we now see that if we know the

probability density of microstates in phase space, we can

compute ensemble averages. How do we get tuis probability density?

Suppose we have N microstales. Let D(X) be the number of microstales per phase space volume, so that

$$N = \int D(\bar{x}) dx$$

The probability density must then be normalized to I, so that

$$\delta(\bar{x}) = \frac{1}{7} D(\bar{x}) = \frac{1}{2} D(\bar{x}) =$$

This is a formal definition of the probability density of microstates in phase space. It seems very "matry." We have just Eicles the can down the road. How can I compute Nor DCE) or gCX)?

## D. Microcanonical Ensemble

I am going to assume a certain kind of ensemble of nicrostates. In this ensemble I will have N particles in a box of volume V. The total system energy will be a constant E. Let's see if we can find the probability density of the nicro states g(X) in this ensemble.

My phase space integral for the NVE-ensemble, or the microcanonical ensemble, is given by

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Using this, the probability density is given by

$$\beta_{NVE}(\underline{x}) = \frac{1}{\Sigma} \delta(H(\underline{x}) - E) = \begin{cases} 5/\Sigma & \text{if energy} = E \\ 0 & \text{if energy} \neq E \end{cases}$$

In other words, there is a uniform probability of microstates in the micro canonical ensemble. This is the second postulate in stattstical thermodynamics. It is sometimes called the principle of equal a priori probabilities.

This isn't that hard of a problem to solve. We will just define some minimum volume of phase space to be our smallest "chunk" that counts as a microstate. Then we can get a discrete number of states by dividing. T (ALLE): size of phase space

Z. (NV,E) : size of phase space Z Z. (NV,E) : minimum volume of Phase Space. IL (NV,E) : number of microsolates

But what is Zo? From a classical mechanics perspective, it is avbitrary. We just need something there. The fact that it is avbitrary is a sign our theory (classical mechanics) is incomplete. But, we know the unation Mechanics! In QM we know that there is an uncertainty principle. Uncertainty says that of the principle.

2.0 🛄

X

Using this principle (month not shown) one can say that a single dimension of  $\chi$  and p give a volume of h in phase space. So, for N particles in three dimensions, we get a factor of  $h^{3N}$ ,

 $\Sigma \propto h^{3N}$ 

 $Q = \frac{N}{M}$ 

F. Gibbs Paradox

There is one more problem with our compiny of microscopic states.

we are overcanting the number of states because of possible

permutations between particles.

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Suppose we have a two particle gas:

particle I: X, P, All I did here is swap

particle 2: 22, pz the labels between

particle I and particle

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2, but these are the

particle 1: 2, P, same m'orostate!

particle 2: 221Pz However, our integral

cants these as two states.

We need to "fix" our integral to not double can't permutations that arent really different states. We could redefine a new integral (hard). Instead, we can just divide by the number we are over counting. This is the other piece that goes into Zo,

Zo ∝ N! ← Factor for overcounting.

Putting this with the quantum correction gives,

 $Z_{0} = h^{3N} N!$  $\Omega = \frac{1}{100} N! Z$ 

Aside: The N. term was initially missing in Eribbs formulation, and it made Entropy not extensive and broke mixing entropy. This was "Gibbs Paradox." with this normalization factor we can write the PMF for the # of microstades like we wanded.

where .....

$$\Omega(N,V,G) = \frac{1}{h^{2N}N!} S(H(X) - G) dX$$

G. Boltzmann's Formula and Entropy

So far we have had two major ideas from Gibbs. These are

two of the three fundamental postulates of statistical thermodynamics.

1) Ergodiaty - we can consider ensemble averages instead of

time averages

2) A priori equal probability - The probability of equal energy

microstocks is uniform and therefore the

probability of nicrostate is inversely proportional

to its degeneracy (number of stoles w/ same energy).

To make the final leap to connect microstates to thermodynamic macrostates we need one more postulate: Boltzmann's

formula,

S & ln SL

entropy # of microstates

R

This idea is probably so familiar to you that you undoubtedly fail to appreciate its significance and revolutionary impact.

In classical thermodynamics, entropy is an abstract guantity that systems posess that always increases. With Boltzmann's and Gibbs' insights we see that entropy is inherently statistical in nature. Entropy is a cant of the number of ways a system can exist-the olume of its phase space. It is something about now "disordered" a system is. How many different ways it can be arranged. How much information the system has ( S & ln(1/p), p21 we have high information /bw surprise).

To get Boltzmann's equation more precisely, consider the following thought experiment,

 $N_1, V_1, E_1$   $N_2, V_2, E_2$  $Total Energy: E_0 = E_1 + E_2$ 

Total microstates: Sc= 2122

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# Il Heat exchange In

We suppose that the equilibrium state is the one with the most microstates. So, let's maximize to with respect to the energy,

 $\frac{\partial \mathcal{L}_{0}}{\partial \mathcal{E}_{1}} \stackrel{=}{\longrightarrow} at \mathcal{E}_{1} \stackrel{=}{\to} \mathcal{E}_{1}^{*} \text{ the equilibrium energy of } I$   $\frac{\partial \mathcal{L}_{0}}{\partial \mathcal{E}_{1}} \stackrel{=}{=} 0$   $\frac{\partial \mathcal{L}_{0}}{\partial \mathcal{E}_{1}} \stackrel{=}{=} 0$ 

Using the product rule for So,



$$\frac{\partial \Omega_0}{\partial E_1} \Big|_{E_1^*} = \frac{\partial \Omega_1}{\partial E_1} \Big|_{E_1^*} \frac{\Omega_2(E_2^*)}{\Omega_2(E_2^*)} + \Omega_1(E_1^*) (-1) \frac{\partial \Omega_2}{\partial E_2} \Big|_{E_2^*} = 0$$

Divide both sides by R. Rz

$$\frac{1}{\Omega_1(E_1^*)} \frac{\partial \Omega_1}{\partial E_1} = \frac{1}{E_1^*} - \frac{1}{\Omega_2(E_2^*)} \frac{\partial \Omega_2}{\partial E_2^*} = 0$$

$$\frac{\partial \ln \Omega_{1}}{\partial E_{1}} = \frac{\partial \ln \Omega_{2}}{\partial E_{2}} = \frac{\partial \ln \Omega_{2}}{\partial E_{2}}$$

$$\frac{\partial E_{1}}{\partial E_{1}} = \frac{\partial \ln \Omega_{2}}{\partial E_{2}} = \frac{\partial \ln \Omega_{2}}{\partial E_{2}}$$

What is the criteria for thermal equilibrium in classical

thermodynamics?  

$$T_1 = T_2$$
  
 $B = \frac{1}{k_B T}$   
 $S = k_B \ln \Omega$   
 $\frac{\partial S}{\partial E} \Big|_{N,V} = \frac{1}{T}$   
 $\frac{\partial S}{\partial$ 

- H. Connecting Ensembles to thermodynamics
- Boltzmann's equation for connecting the number of microstates to entropy is also consistent with the laws of thermodynamics.
- Oth Law: Definition of temperature, themal equilibrium
  - we just proved this.
- 1st law: conservation of Evergy
  - If we do work on the system (e.g., reversibly change volume), we add internal every, dE= PdV. From our relation above, we know dE= TdS. From thermodynamics, we know that dE= TdS + PdV = SQ + SW
    - Thus we can identify Tds from the microstates as the heat energy.
- 2<sup>nd</sup> law: Entropy of a closed system increases The equilibrium is the maximum number of microstates. This means the system evolves from small Q to large Q. S = ko. In Ω means we evolve from small S to large S, which is the 2<sup>nd</sup> low.
- Stability: perturbations from equilibrium return to it ( $\frac{\partial S}{\partial E^2} < 0$ ) Because the point ( $E_1^*$ ,  $E_2^*$ ) is a makimum, the second derivative  $\frac{\partial S}{\partial E^2}$  must be negative (concave down).

Practically, unat does this man? How do we connect information about microscopic interactions to thermodynamic quantities? Step 1: Determine the Hamiltonian for the system of inderest, H(gi,pi) using molecular potentials.

$$H = \sum_{i} \frac{p_{i}}{2m_{i}} + \sum_{i < j} u_{ij}(q_{i}, q_{j})$$

Step 2: Compute the density of states SC(N, V, E).

$$\Omega(N_{V},G) = \frac{1}{N_{W}} \int S(H(x) - G) dx \qquad x = (g, p)$$

Step 3: Compute S using Boltzmann's formula

S= kg ln S

Step 4: Use thermodynamic relations to find other quantifies of interest.

- · Legendre transforms
  - F= E-TS
  - H= E + PV
  - G = H TS

· Fundamental equations & maxuell veloctions

- dS = + dE + P dV Findamental equation for S
- $P = T\left(\frac{\partial S}{\partial V}\right)_{c}$  Pressure (By inspection)

$$c_{V} = \left(\frac{\partial E}{\partial T}\right)_{V} = \left(\frac{\partial E}{\partial S}\right)_{V} \left(\frac{\partial S}{\partial T}\right)_{V} = T\left(\frac{\partial S}{\partial T}\right)_{V}$$
 Heat capacity

Step 4 (alternate): Use ensemble averages to compute quantifies of interest

$$\langle M \rangle = | M(\underline{x}) \rho(\underline{x}) dx$$

$$\int ANE(X) = \frac{1}{\Sigma} \delta(H(X) - E) dX$$
  
$$Z = \int \delta(H(X) - E) dX$$

This is sometimes written with the PMF instead.  $\langle M \rangle = \frac{1}{h^{3N}N!} \int M(\underline{x}) P(\underline{x}) d\underline{x}$  $P(\underline{x}) = \frac{1}{\Omega} \delta(H(\underline{x}) - E)$ 

$$\Omega = \frac{1}{\sqrt{2}} \frac{1}{$$

I. I deal Gas

Let's apply our procedure to compute the equation of state and the neat capacity of an ideal gas of N particles of equal mass m.

Stepl: Determine H(p,q)For an ideal gas there is no potential between the atoms of the gas,  $U(q_i) = 0$ . So, the Hamiltonian is  $\frac{3N}{p_i} p_i^2$   $i=1 \rightarrow 1x$ 

$$H(3i,pi) = 2 \rightarrow ig$$

$$i = i 2m \qquad 3 \rightarrow ig$$

Step 2: Compute I (the long step)

$$\Omega = \frac{1}{h^{3N}N!} \int S\left[\frac{3N}{2m} - E\right] dp dq \qquad p = EP(3 \ i \in [1, 3N])$$

This is independent of g

$$\Omega = \frac{1}{h^{3N} N!} \int dg \int S \left[ \frac{3N}{Z} - E \right] dp$$

lets do the dg integral

$$\int dq = \int dq_1 \int dq_2 \int dq_3 \dots \int dq_{3N}$$
  
=  $\int dx_1 \int dy_1 \int dz_1 \int dx_2 \int dy_2 \int dz_2 \dots \int dx_N \int dy_N \int dz_N$ 

substitute back into I

P2

= VN

$$\Omega = \frac{V^{N}}{h^{3N}N!} \int S \left[ \frac{3N}{2} \frac{p_{i}^{2}}{2m} - E \right] dp$$

Now, let's do the dp integral. The delta function reduces us to a (BN-1)-dimensional hypersurface in the p phase space - In 2D,

 $P_{1}^{2} + P_{2}^{2} = 2mE$   $A civcle of vadius p = \sqrt{2mE}$   $P_{1} = 2\pi p = 2\pi \sqrt{2mE}$ 

In 3D we get a sphere with a radius  $p = \sqrt{2mE}$  and surface area  $S = 4\pi p^2 = 4\pi (2mE)$ 

For 3N dimensions we got a hypersphere in 3N dimensions. The surface area of a hypershere in a dimensions of radius R is given by 14



 $\frac{\partial S}{\partial V} = \frac{\partial}{\partial V} \sum_{k=1}^{2} \log \ln \left( \frac{V^{N}}{h^{2N} N!} \frac{(2\pi m E)^{3N/2}}{\frac{1}{2} \left[ (2N/2) \right]^{2}} \right)$ 

$$= \frac{2}{2\sqrt{2}} \frac{1}{k_B} N \ln V + \frac{1}{k_B} f(N, E) \frac{2}{5}$$

$$= k_{B} N / V$$

Pluz into formula for P

$$P = T \frac{k_B k_B}{V}$$
 or  $P = \frac{N k_B T}{V}$ 

Now for the heat capacity. Let's use the fact that

$$\begin{aligned} \frac{1}{T} &= \begin{pmatrix} \frac{\partial S}{\partial E} \end{pmatrix}_{V} & \leftarrow & \text{from fundamental equation, other lenn} \\ \frac{1}{T} &= & \frac{\partial}{\partial E} & \frac{2}{2} & k_{B} & ln \left[ \frac{V^{N}}{h^{W}N!} \frac{(2\pi m E)^{3N/2}}{\frac{1}{2}\Gamma(3N/2)} \right]_{V}^{3N/2} \\ &= & k_{B} & \frac{\partial}{\partial E} & \frac{2}{2} & \frac{\partial N}{2} & ln & E & + & f(N,V) & \frac{3}{2} \\ &= & k_{B} & \frac{\partial N}{2} & \frac{1}{E} \\ &= & \frac{\partial N}{2} & k_{B}T \end{aligned}$$

The heat capacity is defined as

$$c_{V} = \left(\frac{\partial E}{\partial T}\right)_{V} = \frac{\partial}{\partial T} \left(\frac{3N}{2}h_{D}T\right) = \frac{3NL_{D}}{2}$$

 $C_{V} = \frac{3Nk_{B}}{2}$ 

What did we do? We derived all of the thermodynamic properties of a monoadomic ideal gas from first principles! Molecules to bulk properties. Complete theory! Matches empirical results with dilute gases. Teaches us what an ideal gas is! If is a gas with U = 0. J. Quantum Corrections and Absolute Density of states I want to use the ideal gas entropy to make two points about statistical thermo. First we need to do some math. Starting with the expression we had for the entropy of an ideal gas,

$$S = k_{B} ln \left[ \frac{V^{N}}{3^{N} N!} \frac{(2\pi m E)^{3N/2}}{\sum_{n=1}^{3N} \Gamma(3N/2)} \right]$$
  
= k\_{B} ln \left[ \frac{2V^{N}}{N! \Gamma(3N/2)} \left( \frac{2\pi m E}{n^{2}} \right)^{3N/2} \right]

$$S/k_{B} = ln \vee N - ln N! - ln \int (3N/2)$$
  
+ ln  $\left(\frac{2\pi mE}{h^{2}}\right)^{3N/2} + ln 2$ 

Stirling's formula for the Gamma function: r note the minus sign blc (h-1)!  $h \Gamma(3) = (2 - \frac{1}{2}) h = \frac{3}{2} + \frac{1}{2} h (2\pi)$  Also valid for confinuous numbers  $h \Gamma(\frac{5N}{2}) = (\frac{3N}{2} - \frac{1}{2}) h \frac{3V}{2} - \frac{3V}{2} + \frac{1}{2} h 2\pi$  and in the complex  $g \frac{3N}{2} h \frac{3N}{2} - \frac{3N}{2}$ 

$$\frac{S/k_{0}}{k_{0}} = N \ln V - N \ln N + N - \frac{3N}{2} \ln \frac{3N}{2} + \frac{$$

$$S = \ln V - \ln N + 1 - \frac{3}{2} \ln \left(\frac{3N}{2}\right) + \frac{3}{2}$$

$$+ \frac{3}{2} \ln \left(\frac{2\pi m \overline{U}}{h^{2}}\right) + \frac{3N}{N}$$

$$= \ln \left(\frac{7}{N}\right) + \frac{3}{2} + \frac{3}{2} \ln \left(\frac{2\pi m \overline{E}}{h^{2}} \cdot \frac{2}{3N}\right)$$

$$S = \ln \left(\frac{7}{N}\right) + \frac{3}{2} \ln \left(\frac{4\pi m \overline{E}}{3Nh^{2}}\right) + \frac{5}{2}$$

$$S = S + \frac{3}{2} \ln \left(\frac{4\pi m \overline{E}}{3Nh^{2}}\right) + \frac{5}{2}$$

$$S = S + \frac{3}{2} \ln \left(\frac{4\pi m \overline{E}}{3Nh^{2}}\right) + \frac{5}{2}$$

$$S = S + \frac{5}{2} + \frac{3}{2} \ln \left(\frac{4\pi m \overline{E}}{2}\right) + \frac{5}{2}$$

$$S = S + \frac{5}{2} + \frac{5}{2}$$

Recall that the total momentum p is given by,

$$P^{2} = P_{1x}^{2} + P_{1y}^{2} + P_{1z}^{2} + P_{2x}^{2} + \dots = 2mE \quad (101a) \quad system \\ energy \quad energy$$

What is the average momentum per atom ? The average momentum is given by

$$\langle p \rangle = \sqrt{\frac{2\pi}{3}} p_{rms} \ll root-mean square$$
  
 $p_{rms} = \sqrt{\frac{p^2}{N}} \ll \frac{p^2}{s} \frac{s}{s} \frac{s}{s}$ 

If we know the average momentum, we can define the average

de Broglie wave length,

$$\lambda_{\text{th}} = \langle \lambda \rangle = \frac{h}{\langle p \rangle} = \frac{h}{\frac{\mu r}{\sqrt{\mu r}}} = \int \frac{3Nh^2}{4\pi mE}$$

Aside: Thermal wave length

The thermal wavelength is the debroit wavelength of gas atoms with  
energy 
$$E/N$$
. We usually substitute  $E = \frac{3}{2} N \log t$  to get  
 $\frac{2}{N \ln} = \frac{3Nh^2}{4\pi m E} = \frac{8Mh^2}{4\pi m (\frac{2}{2} \text{ plot})} = \frac{h^2}{2\pi m \ln t}$ 

λth = \_\_\_\_\_ Size of wave packet of an atom 2trmkgT with mass m and temperature T

Note the correspondance with the termin parentheses in the Sackur - Tetrode equation!

$$\frac{S}{Nk_{B}} = ln\left(\frac{V}{N}\right) + \frac{3}{2}ln\left(\frac{4\pi mE}{3Nh^{2}}\right) + \frac{5}{2}$$

$$\frac{S}{Nk_{B}} = ln\left(\frac{V}{N}\right) + \frac{3}{2}ln\left(\frac{1}{\lambda_{2}^{2}}\right) + \frac{5}{2}$$

$$= ln\left(\frac{V}{N}\right) + ln\left(\frac{1}{\lambda_{3}^{2}}\right) + \frac{5}{2}$$

$$\frac{S}{Nk_{B}} = ln\left(\frac{V}{N\lambda_{3h}}\right) + \frac{5}{2}$$

$$\frac{S}{Nk_{B}} = ln\left(\frac{V}{N\lambda_{3h}^{2}}\right) + \frac{5}{2}$$

Now we can make a comment about quantum corrections. When is the Sackur-tetrode, the equation for a classical ideal gas, val.b? When the de Broglie wave length is small? How "small"? We have another notwal length scale. The average distance between atome in the gas  $l = \left(\frac{V}{N}\right)^{V_3}$ V : volume per atom. units length?

So when l >> N the, the grantim effects should be small. If l~ hith then I can have grantim effects. If l ~ high then I have to tote into account spin degrees of freedom. If they have integer spin, they are bosons (e.g., photons) and the gas is a "lose gas." If they have half-integer spin, they are fermions (e.g., electrons) and the gas is a "fermi "gas. Most matter (e.g., atoms) are fermions. But some can be bosons (e.g., solium atoms can form a Box - Etnotein condensate).

Wait a minute, then is our I wrong? If so, why doesn't it maker? The answer is that I neglects smaller scale degrees of freedom. So in this sense if is "wrong." We could get a new I with more microstates,

Scomeded = Stor Stapin Bose or Fermi

But it turns out this doesn't matter at lange (YN)<sup>3</sup>. Why? One of the most important points to learn here is that there are always smaller D.O.F we could account for! we can have more microstates for string theory too! By ignoring these, AKA by setting Despin = [ (or any small DOF), we are choosing a reference state. We are snying theat S=O at some point.

As we know, in thermodynamics, our results don't depend on the reference state! So, we are of when we do this. What matters is how  $\Omega = \Omega(N, V, E)$ . Or how  $\Omega$  depends on the system constraints. So, in the case of a Bosel Fermi gas, the dependence of Son N, V, E is only a flected when L ~ Z. Otherwise those D.O.F. are irrelevant.

The other point to make here is funt the absolute value of  $\mathcal{A}$  is not very important then. We really only care about  $\mathcal{A}(\mathcal{A}_{0})$ , where  $\mathcal{A}_{0}$  is our reference state (where S=0).

Finally, it is impractical to cant microstodes numerically, these are impossibly large numbers. Lets do a quick calculation with the Sacker-Tetrode equation to see thy.

 $S = kg ln \Omega \rightarrow \Omega = exp(s/ke)$ 

$$\frac{S}{keN} = ln\left(\frac{V}{N\lambda_{yn}^3}\right) + \frac{S}{2} \qquad \lambda_{yth} = \frac{h}{\sqrt{2\pi rm k_BT}}$$

Example: He atoms at 300% and 1 bar in 1 cm3

m = 4.9/mol  $h = 6.626 cco^{-34} Ts$  T = 300 k

lens = 8.314 J/molk P= 1 bar = 105 J/m3

 $P = \frac{N k_{B}T}{V} \frac{N}{V} = \frac{P}{k_{B}T} \frac{10^{5} J/m^{3}}{8.314 \cdot 300 \frac{J}{m01}} = 40.09 \frac{mal}{m^{3}} \cdot \frac{6.02 x c0^{23}}{10001}$   $= 2.41 x c0^{25} m^{-3}$ 

$$\frac{1}{2 \text{ tr} \text{ mkgT}} = \frac{2 \cdot \text{tr} \cdot 4 \text{s}}{\text{mol}} \cdot \frac{3 \cdot 314}{\text{mol}} = \frac{1}{2 \cdot 2 \text{cos}} \cdot \frac{1}{1000 \text{s}} \cdot$$

$$= \frac{6.626 \times 10^{-344} \text{kgm}_{5}^{2}}{(6.02 \times 10^{23})^{2} (0^{3})^{2}} \cdot \frac{\text{kg} \cdot \text{kgm}_{5}^{1}}{(5.2 \times 10^{23})^{2} (0^{3})^{2}}$$



In summary:

- · Absolute density of states is not necessary and impractical.
  - There are always smaller scale degrees of freedom.
  - Thermodynamics depends on the difference between two states.
  - The density of states is an impossibly large number.
- · By setting the degrees of freedom we are neglecting, we are setting the reference state.
- The dependence of SC on the constraints SC(N,V,E) determines
   the thermodynamic behavior.

# II. Canonical Ensemble

A. Canonical Ensemble Probability Density

We saw that we could define an ensemble of systems that had a fixed number of particles N, volume V, and energy E. However, energy and temperature are thermodynamic conjugates. E is not privileged over T. Also, it is more common for us to experimentally encounter a system that is at constant T. So, we would like to construct an ensemble with constant N, N, and T. This type of ensemble is called a canonical ensemble.

For the microcanonical ensemble, we

1. Postulated a probability density

(uniform density of configurations with equal energy)

2. Used the probability density to find the density of stades D(E).

3. Used the Boltzmann formula to find the entropy.

S= le ln D

we want to follow an analogous procedure for the canonical ensemble. Let's first find the probability density.

In this case, we need to use our result for the microcanonical ensemble. We don't want any new postulates.

So, we are going to construct a cononical easemble as follows.



- The other systems act as a heat both for the NVT system, keeping if at a constant temperature.
- · There are M "little systems" making up the ensemble.

$$N = MN$$
,  $N = MV$ 

- The energy of the NVT system can fluctuate and is a random variable, Ei.
- In the M members of the ensemble, there will be m; that have energy E;.

$$m_{j} = \sum S(E_{i}, E_{j}) \qquad m_{j}: occupation number$$

$$i=1 \qquad J: number of energy leve
$$E_{i} = E_{j} \qquad S(E_{i}, E_{j}) = \sum I \quad if \quad E_{i} = E_{j}$$

$$O \quad of urwayse$$$$

· The total energy and total number of encembles are constrained

$$\sum_{j} m_{j} E_{j} = E \qquad \underline{m} = \frac{2m_{j}}{2}, \text{ vector of all}$$

$$\sum_{j} m_{j} = M \qquad \text{Occupation } \pm \frac{1}{2}$$

2l

With the above in mind, he want to find the probability of finding one of the members of our NVT ensemble at energy Ej

$$P_{j} = P_{NVT}(E_{j}) = ?$$

If we could look at the statistics of our ensemble, we would see that

There are many different ways we could arrange all of the energies. Example:

- $M = 6 = E_1 = 8 = T = 4 = E_j = 20,1,2,3\xi$
- Distribution I
- $\sum_{i} m_{i} = 0 + 4 + 2 + 0 = 6 = M \sqrt{1}$
- $\sum_{i} m_{j} E_{j} = 0 \cdot 0 + 4 \cdot 1 + 2 \cdot 2 + 0 \cdot 3 = 4 + 4 = 8 = E_{i} \vee$
- $\sum_{j} w_{j} = 1 + 3 + 1 + 1 = 6 = M J$
- $\sum m_j E_j = 1.0 + 3.1 + 1.2 + 1.3 = 3 + 2 + 3 = 8 = E_j \sqrt{2}$

In the microcanonical ensemble, we said that any configuration with energy E was equally probable (principle of equal a priori probability). Here, the big system is an NVE ensemble. That means that any vector <u>m</u> where  $\sum m_i E_i = E_i$  is equally probable. So, we just to cant the number of ways we can arrange the energy in the M bins. This will tell us the probability distribution.

$$W(\underline{M}) = \underbrace{M!}_{m_1! m_2!} = \underbrace{M!}_{m_1! m_2!} M!$$

$$M(\underline{M}) = \underbrace{M!}_{m_2! m_2!} = \underbrace{M!}_{m_1! m_2!} M!$$

Example:  $B_{xample}$ :  $D_{xample}$ :  $D_{yample}$ :  $D_{yample$ 

\$of ways to arrange the 4 x E=1 and 2x E=2 into 6 bins.

Distribution 2: m = [1,3,1,1], M = 6

 $W(\underline{m}) = \underbrace{\frac{6!}{1!3!1!5!}}_{1!3!1!5!} \underbrace{\frac{6-5\cdot 4\cdot 3\cdot 2\cdot 1}{3\cdot 2\cdot 1}}_{3\cdot 2\cdot 1} = 6\cdot 5\cdot 4 \cdot 120$ 

Many more ways to come up with this distribution of erersics

Using W(M) we can write a probability mass function for a configuration,

Using this probability mass function we can find the average  

$$P_{j} = \frac{\langle m_{j} \rangle}{M} = \frac{1}{M} \sum_{m} P(m) m_{j}(m) = \frac{1}{M} \frac{\sum_{m} W(m) n_{j}(m)}{M} \frac{\sum_{m} W(m) n_{j}(m)}{\sum_{m} W(m)}$$
Rewriting (A) using  $W(m)$ 

(my= o in Dist | and my= 1 in DistZ.)

OK, this is all great, but what do I do when  $M \rightarrow \infty$  (large ensemble) and J is big (large number of energies). Computing the nultinomial coefficient will be very hard.

Answer: when the  $m_j \rightarrow \infty$ , the multinomial coefficient becomes a very sharply peaked normal distribution around  $m_j = m_j^* = M_J$ . So sharp that it becomes a Dirac delta function  $S(m_j - m_j^*)$  and only the most probable configuration matters.

Because the distribution is so sharp, the average is the same as the most likely stock ut. <m;> = m; There fore, our probability becames

$$P_{NT,S} = M_{j}^{*}$$





What is the distribution as M>00?

 $G(z) = E[z^m]$ 

$$P(m) = \binom{M}{m} = \frac{1}{2}\binom{M}{m}$$
$$= \frac{1}{2}\binom{M}{m}$$

To find the distribution of large M, we will look at
 the cumulant generating function.

· Find the probability generating function first

$$G(2) = \frac{M}{Z} \stackrel{[]}{=} \frac{M}{2^{M}} \begin{pmatrix} M \\ m \end{pmatrix} \stackrel{[]}{=} \frac{1}{2^{M}} \begin{pmatrix} 1+2 \end{pmatrix}^{M} = \begin{pmatrix} 1+2 \\ -2 \end{pmatrix}^{M}$$

• The moment generating function is  $M(s) = E(e^{sm}) = G(e^{s})$  $= (\underbrace{I+e^{s}}_{2})^{M}$ 

· The cumulant generative function is

$$K(s) = \ln M(s) = \ln \left[ \left( \frac{1+e^{-}}{2} \right)^{H} \right] = M \ln \left( 1+e^{s} \right) - M \ln 2$$

m\* = M/2

• Now Find camulants

$$k_{1} = \mathcal{M} = \frac{d}{ds} \Big|_{s=0} = \frac{\mathcal{M}}{1+e^{s}} \Big|_{s=0} = \frac{\mathcal{M}(c)}{(+1)} = \mathcal{M}_{2}$$

$$(+1)$$

$$\mathcal{M}_{1} = \mathcal{M}_{2}$$



(used Mathematica for ky,...)

 $k_3 = 0$   $k_4 = -M/8$   $k_5 = 0$   $k_6 = M/4$ 

· Series solution

 $K(s) = \frac{M}{2}s + \frac{M}{4}\frac{s^{2}}{2!} - \frac{M}{8}\frac{s^{4}}{4!} + \frac{M}{4}\frac{s^{6}}{1!} + \frac{M}{4!}\frac{s^{6}}{1!} + \frac{M}{4!}\frac{s^{6}}{1!}$ 

· Compare to normal (Gaussian):

 $k_{Gauss} = MS + \frac{\sigma^2}{2}S^2$ 

• Do the higher order terms matter as  $M \rightarrow \infty$ ? (No) S is of the order of M ( $e^{Sm}$ ). let's rescale. [et S = M = -7  $S = \frac{3}{M}$  $K(S) = \frac{M}{2} \frac{S}{M} + \frac{M}{4} \frac{S^2}{2M^2} - \frac{M}{8} \cdot \frac{S^4}{24M^4} + \frac{M}{4} \frac{S^6}{720M^6}$ 

 $k(\vec{s}) = \frac{1}{2}\vec{s} + \frac{1}{8M}\vec{s}^{2} - \frac{1}{192M^{3}}\vec{s}^{4} + \frac{1}{2880M^{5}}\vec{s}^{6}$ 

The width These derms will drop out will also go y very quickly as M=> 00



30, we want to find the most probable configuration for  
the multidimensional 
$$W(m)$$
 subject to the constraints  
 $Z_{n_j} = M \leftarrow total # of ensembles$   
 $Z_{n_j} E_j = E_i \leftarrow total energy$ 

We will use the method of Lagrange multipliers for the constraints. Let:

$$f(m) = \ln W(m) - \alpha \left( \sum_{j=1}^{m} u_{j} - M \right) - \beta \left( \sum_{j=1}^{m} u_{j} = E_{j} \right)$$

Find the extremen:



$$33$$

$$3: \frac{d}{dm_{j}} \left( \sum_{j} m_{j} E_{j} - E_{j} \right) = \frac{1}{dm_{j}} \left( m_{i} E_{i} + m_{2} E_{i} + \dots + m_{j} E_{j} + \dots + m_{j+} E_{j+1} + m_{3} E_{j} - E_{i}^{4} \right)$$

$$= E_{j}$$
Put it trogether:
$$\frac{df}{dm_{j}} \left| \begin{array}{c} = -bn \ m_{j}^{*} - \alpha - \beta E_{j} = 0 \\ \frac{dm_{j}}{dm_{j}} \right|_{m_{j} = m_{j}^{*}}$$

$$0k_{j} \ finally, lets \ get two distribution$$

$$P(e_{j}) = \frac{m_{j}^{*}}{M} = \frac{e^{-\alpha} e^{-\beta E_{j}}}{M}$$
Summing over all the systems allows us to find  $x_{j}$ .
$$\sum_{l=1}^{M} P(E_{l}) = 1$$

$$\sum_{l=1}^{M} \frac{e^{-\alpha} e^{-\beta E_{l}}}{M} = 1 \Rightarrow \frac{e^{-\alpha} M_{j}}{M} = e^{-\beta E_{l}} = 1$$

$$e^{-\alpha} = M \sum_{l=1}^{M} e^{-\beta E_{l}}$$
Putting it all together gives us the probability density!
$$\frac{e^{-\beta E_{l}}}{M} = e^{-\beta E_{l}}$$

$$\frac{e^{-\beta E_{l}}}{M} = e^{-\beta E_{l}}$$

 $P_{AVT}(E_i) = \frac{e^{pe_i}}{\sum_{i=1}^{M} e^{-BE_i}} \qquad B \quad cole will see that$   $E_{AVT}(E_i) = \frac{e^{-BE_i}}{\sum_{i=1}^{M} e^{-BE_i}} \qquad B = \frac{1}{2} \sum_{i=1}^{N} e^{-BE_i}$ 

Summary of derivation

- We create an ensemble of NVT distributions that gives a total NVE system.
- · Each NVT system has a random energy Ej.
- · Any distribution of the energies, E; that sums to E is equally
  - likely to occur, but some of them occur many ways.
- For a large ensemble, only the most likely way to distribute the energies (the one with the most ways) will accur.
- · we can solve this by maximizing the system, keeping the #
- of ensembles and energy constant.
- · This gives the Boltzmann Listribution.

B. The Partition Function

We have a probability mass function for the canonical ensemble,

Sometimes you will see the PME willow differently.

Analogous to the NVE ensemble, the denominator, the "constant" that normalizes the probability plays a special role. In the NUT ensemble, this quantity is called the canonical partition function,

$$Q = \sum_{i=1}^{M} e^{-\beta E_i} = \sum_{i=1}^{T} \Omega_i e^{-\beta E_i}$$

We would also like the probability density for the classical statistical mechanics that relies on continuum classical mechanics. The probability density is

$$\sum_{x} = \frac{\exp(-\beta H(x))}{\int \exp(-\beta H(x))} \qquad \begin{array}{c} x = \frac{2}{2} p, \frac{3}{2} \\ H(x) : Hamiltonian \\ \Gamma : phase space volume. \end{array}$$

Analogous to our previous work in the NVE ensemble, we define

the canonical partition function as,

$$Q = \frac{1}{h^{3N}N!} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \qquad \text{weighted sum of the} \\ \frac{1}{T} \int e^{-\beta H(\underline{x})} \\qquad \frac{1}{T} \int e^{-\beta H(\underline{x})} \\qquad \frac{1}{T} \int e^{-\beta H(\underline{x})} \\qquad \frac{1}{T} \int e^{-\beta H(\underline{x})}$$

We can also define ensemble averages.

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$$\langle M \rangle = \int M(\underline{x}) p(\underline{x}) d\underline{x}$$

Or, equivalently

$$\langle M \rangle = \frac{1}{h^{3N}N!} \int M(x) \frac{1}{Q} e^{-\beta H(x)} dx$$
  $Q h^{3N}N! = \int e^{-\beta H} dx$   
 $P(x) = \frac{1}{Q} e^{-\beta H} (PMF)$ 



$$\Rightarrow \langle BH \rangle = B\langle H \rangle \leftarrow average cnergy$$

$$\langle H \rangle = U \leftarrow internal energy$$

$$BU = \frac{1}{Qh^{2N}N!} \int BH e^{-BH} dX$$

C. Connecting the NUT ensemble to thermodynamics We want to connect this to thermodynamics. For the microcanonical engemble, we said that

the do we generalize this for a case where the number of Microstocles is weighted by a femperature? We need a more muanced version of Boltzmann's equation for entropy.

In our NVE interpretation of entropy, we said entropy was related to the carn't of microstates (with a logarithm so that entropy is extensive, i.e. doubling volume = squaring # microstates = doubling entropy).

But what if we think in terms of the probability density? We can think of entropy as a measure of how broad the probability distribution is over the microstates. If the

Let's use this idea to define entropy and show that it is equivalent to Boltzmann's formula for the NVE ensemble.

recall 
$$\langle M \rangle = \frac{1}{N^{3N}N!} \int M P(y) dx$$

For the NVE ensemble  $P = Y_{\Omega}$ . Subbing into our new definition,

$$S = -\frac{k_B}{h^{2W} N!} \int \frac{1}{n} \ln\left(\frac{1}{n}\right) dx \qquad \Omega \text{ is a constant}$$

$$= \frac{-k_{B}}{h^{2}} \frac{1}{R} \frac{1}{R} \int dX \qquad \int dX = \sum = h^{2} N! \Omega$$

$$S = -k_0 \perp l_n \perp Z = -k_0 l_n \perp = l_{l_0} l_n \Omega \vee$$

Example: Intuition about probability - defined entropy

Fair Die: 
$$\Omega = 6$$
,  $S = l_B ln 6$   
 $P = \frac{1}{6}$ ,  $S = -\frac{1}{6}g \langle ln \frac{1}{6} \rangle$   
 $= -\frac{1}{6}g \langle ln \frac{1}{6} \rangle$ 

(PMF)



Uniform distribution. More states = more sprendout = larger entropy A die wich more sides -> bigger S.

Now we can't just count microstates.

$$S = -k_{0} < ln P > = -k_{0} \sum_{i} P_{i} ln P_{i} = -k_{0} \cdot \left(S \cdot \frac{1}{20} ln \frac{1}{20} + \frac{3}{4} ln \frac{3}{4}\right)$$

$$= -k_{0} \left(\frac{1}{4} ln \frac{1}{20} + \frac{3}{4} ln \frac{3}{4}\right)$$

$$= -\frac{1}{4} k_{0} ln \left(\frac{1}{20} \cdot \frac{3^{3}}{4^{3}}\right) = -\frac{1}{4} k_{0} ln \left(\frac{9}{1280}\right)$$

$$= \frac{k_{0}}{4} ln \left(\frac{1280}{9}\right) \approx 1.24 k_{0}$$

Unfair die has lower S, because we have more concentrated probability in one state More certainty. less uncertainty.



Ok, so we have a more general definition of entropy that we can apply to the canonical ensemble.

$$S = -k_B \langle 0nP \rangle P = \frac{1}{Q} e^{-BH} (PMF)$$

$$S = -\frac{k_{B}}{h^{3N}N!} \int P \ln P d\underline{X} = -\frac{k_{B}}{h^{3N}N!} \int \frac{1}{Q} e^{-\beta H} \ln \left(\frac{1}{Q} e^{-\beta H}\right) d\underline{X}$$

$$= -\frac{k_{B}}{\int e^{BH}} \int \frac{e^{BH}}{e^{BH}} \left( \frac{1}{\alpha} \right) + e^{-BH} \left( e^{-BH} \right) dx$$

$$h^{3M} N! Q \int \frac{1}{1} \left( \frac{1}{\alpha} \right) + e^{-BH} \left( \frac{1}{\alpha} \right) dx$$

$$= -\frac{1}{8} \int \frac{-2nQ}{Q} \frac{1}{h^{3}N} \int \frac{e^{-BH}}{e^{-BH}} \frac{1}{h^{3}N} \int \frac{-BH}{h^{3}N} \frac{e^{-BH}}{h^{3}N} \frac{1}{h^{3}N} \frac{1}{h^{3}N}$$

Definition of Q < BH> = BU (Internal Energy)

$$= -k_{\beta} \left( -ln Q \cdot \frac{Q}{Q} + \beta u \right) = k_{\beta} ln Q - k_{\beta} \beta u$$

S= kg ln Q - kg BU

This seems like a little nessy. There is a better relationship. Recall that the Helmholtz free energy is,

$$A = U - T(k_0 ln Q - k_0 pu)$$

 $A = -k_{BT} \ln Q$ 

We can also get U in terms of Q.

 $U = \int \int dH e^{-\beta H} dX$  $-He^{-BH} = \frac{\partial(e^{-BH})}{\partial\beta}$  $U = \frac{i}{h^{3N}} \int \frac{\partial (e^{-\beta H})}{\partial \beta} dX = \frac{-i}{h^{3N}} \frac{\partial}{\partial \beta} \int e^{-\beta H} dX$  $u = \frac{1}{2} \frac{2}{2} \alpha = -\frac{2m\alpha}{2\beta}$ = -<u>27</u> 2JmQ 28 2T  $B = \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} \frac{2T}{2T} \\ \frac{2T}{2T} \end{pmatrix} = \begin{pmatrix} \frac{2B}{2T} \end{pmatrix}^{-1}$  $\frac{\partial \beta}{\partial T} = -(k_{\theta}T)^{-2}k_{\theta} = -\frac{1}{L_{\phi}T^{2}} \Rightarrow \frac{\partial T}{\partial \beta} = -k_{\theta}T^{2}$  $U = k_{B}T^{2} \frac{\partial h_{Q}}{\partial T} = -\frac{\partial h_{Q}}{\partial \beta}$ Plug back into entropy,  $S = k_3 \ln Q + \frac{k_0}{k_0 T} \cdot \frac{k_0 T^2}{\partial T} \frac{\partial \ln Q}{\partial T}$ 

S = kg ln Q + kg T  $\frac{\partial ln Q}{\partial T}$  for imperature dependence

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Can now get things like pressure and heat capacity



<u>D. The total Gas</u> We already solved the ideal gas in the NVE ensemble, so we will be quick. But it is still an important derivation to see. Stepl: Determine the Hamiltonian

Recall that

$$H(q,p) = \frac{2n}{2m} \frac{p_i^2}{2m}$$
 Ideal Gas Hamiltonian for particles  
 $i \in i$  of equal mass, m.

Step 2: Compute the partition function

$$Q = \frac{1}{h^{3N}N!} \int_{a} \int_{a} \int_{b} dp \exp(-\beta H)$$

Recall Jdg = VN

$$= \frac{\sqrt{N}}{h^{3N}} \frac{3N}{N!} \left( \frac{dp}{i=1} \exp \left(-\frac{pp_{i}^{2}}{2m}\right) \right)$$

This is a Gaussian integral

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$$\int_{\infty} e_{x} e_{x} \left( -\frac{x^{2}}{2\sigma^{2}} \right) = \sqrt{2\pi} \sigma \qquad \sigma^{2} = m/\beta$$

$$\int exp(\frac{-\beta pi^2}{2m}) = \sqrt{\frac{2\pi m}{\beta}} = \sqrt{2\pi m k_s T}$$

$$Q = \frac{V^{N}}{h^{N}N!} \frac{3N}{i=1} \left( 2\pi m k_{BT} \right)^{V_{2}} = \frac{V^{N}}{h^{2N}N!} \left( 2\pi m k_{BT} \right)^{3N/2}$$

Remember the thermal wavelength?

$$\lambda_{\text{th}} = \frac{h}{(2\pi m \, k_{\text{B}} T)^{\frac{1}{2}}} \qquad \lambda_{\text{th}} = \frac{h}{(2\pi m \, k_{\text{B}} T)^{\frac{3}{2}}}$$



Step 3: Relate Q to A.

$$A = -k_{\text{B}} t \ln Q$$

$$= -k_{\text{B}} t \ln \left(\frac{v^{N}}{\lambda_{\text{M}}^{2N}}\right)$$

$$= -k_{\text{B}} t \ln v^{N} + k_{\text{B}} t \ln \lambda_{\text{M}}^{2N} + k_{\text{B}} t \ln N!$$

$$N \ln N + N$$

$$= N k_{B} T \left( -ln V + ln \lambda_{in}^{3} + ln N - l \right)$$

$$A = N k_{\theta} T \left[ ln \left( \frac{N \lambda_{11}^3}{V} \right) - 1 \right] \qquad \lambda_{11} = \frac{h}{\left( 2\pi m k_{\theta} T \right)^{1/2}} \propto T^{-1/2}$$

$$dA = -S dT - P dV$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V}$$

$$S = -\frac{\partial}{\partial T}\left[N \log \left(\frac{N \chi_{gn}^{3}}{V}\right) - 1\right]$$

$$= -N \log\left[\ln\left(\frac{N \chi_{gn}^{3}}{V}\right) - 1\right] - N \log \left[\ln\left(\frac{N \chi_{gn}^{3}}{V}\right) - 1\right]$$

$$= -N \log\left[\ln\left(\frac{N \chi_{gn}^{3}}{V}\right) - 1\right] - N \log \left[\ln\left(\frac{N \chi_{gn}^{3}}{V}\right) - 1\right]$$

$$\frac{\partial \lambda_{\text{LM}}}{\partial T} = \frac{\partial \lambda_{\text{LM}}}{\partial T}$$

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# III. Other Ensembles and Fluctuations

# A. The Grand Canonical Ensemble

We sow that we could define the microcanonical (NVE) ensemble and get thermodynamics, and we can define the canonical (NVT) ensemble to get thermodynamics. Are there other ensembles? Yes! The ensemble with constant MVT, where  $\mu$  is the chemical polontial is the Grand canonical ensemble. Note that  $\mu$  is the thermodynamic conjugate variable to N. As before, there is no reason why we have more/less information with either Nor  $\mu$ .

We can construct a MVT-ensemble in a way that is similar to now we obtained an NVT ensemble from an NVE ensemble



- · Now, both the energy and number of molecules in each bin
  - Can vary: Ni,Ei
- · The occupation number can now make a 20 matrix:

$$m_{jk} = \sum_{i=1}^{N} \delta(E_i - E_j) \delta(N_i - N_k) \quad j \in \{1, J\} \quad J: \text{ the fearsy levels}$$

$$k \in \{1, k\} \quad k: \text{ the fear ficks (possible)}$$

$$\begin{array}{l} \underline{m} = m_{jk} = matrix \text{ of occupation} \\ \underline{m} = m_{jk} = matrix \text{ of occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ of } m_{k} \text{ occupation} \\ \underline{m} = m_{jk} = matrix \text{ occupation} \\ \underline{m} =$$

M: total # of ensembles 
$$S(v_i - N_k) = 3(i + N_i - N_k)$$

Similar to before, we want to find the probability mass

function

$$P_{\mu\nu\tau} = \frac{\langle m_{jk} \rangle}{M}$$

Using the now-familiar logic, we know that the number of ways we can arrange the occupation of particles and energy is going to be almost certainly the maximum.

$$\langle m_{jk} \rangle \approx m_{jk}^{*} = most likely distribution$$
  
 $P_{\mu\nu\tau} = \frac{m_{kj}^{*}}{M}$ 

To find the most probable distribution, we are being to maximize the thof ways of distributing both energy and mass subject In the NVE constraints.

$$W(\underline{m}) = \frac{M!}{\frac{J}{J} + \frac{J}{J} + \frac{J}{J}$$

$$\sum_{j=1}^{K} m_{jk} = M$$

$$\sum_{j=1}^{j=1} k m_{jk} E_{j} = E_{j}$$

$$\sum_{j=1}^{K} m_{jk} N_{k} = N$$

$$\sum_{j=1}^{j=1} k m_{jk} N_{k} = N$$

Accordingly we define

$$f(m_{jk}) = ln W(m_{jk}) - \alpha \left[ \sum_{j \in k} m_{jk} - M \right]$$
$$- \beta \left[ \sum_{j \in k} m_{jk} E_{j} - E_{j} \right] - \delta \left[ \sum_{j \in k} m_{jk} N_{k} - N \right]$$

And we seek the solution to

$$\frac{df}{dm_{jk}} = 0$$





Putting It all together gives

$$\frac{df}{dm_{i\ell}} = -\ln m_{jk}^* - \alpha - \beta E_j - \delta N_k = 0$$

$$ln \underset{jk}{\mathsf{m}} = -\alpha - \beta E_j - \delta N_k$$

$$m_{jk} = e e e^{-\beta E_j} - \delta N_k$$

$$m_{jk} = e e^{-\beta E_j} - \delta N_k$$

$$f_{jk} = e e^{-\beta E_j} - \delta N_k$$

$$f_{jk} = e^{-\beta E_j} - \delta N_k$$

The probability mass function is



$$P_{\mu\nuT} = \underbrace{e^{-\beta E_j} e^{-\beta N_k}}_{\sum e^{-\beta E_j} e^{-\gamma N_k}} \quad PMF \text{ for the Grand} \\ \sum e^{-\beta E_j} e^{-\gamma N_k} \quad Canonical ensemble.$$

what are p and 8? We will get this in the next section. But (spoiler alert) B= 1/20T and 8=-14 LoT

The denominator is the Grand (Canonical) Partition function

$$\equiv (\mu, \nu, \tau) = \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} e^{-\beta G_{j}} - \frac{\partial N_{k}}{\partial k} = \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} e^{-\beta G_{j}} - \frac{\partial N_{k}}{\partial k}$$

sometimes caligraphic Zi = ZQ(NE,V,T) e-NE k Cnole the similarity with how

we wrote Qin terms of SZ.

mechanics?

$$= \sum_{k} \frac{e^{-0Nk}}{h^{3N}N!} \int e^{-\beta H(x)} dx \qquad y = -\beta \mu$$

$$= \sum_{k} \frac{e^{\beta\mu N}}{h^{3N}N!} \int e^{-\beta H(x)} dx \qquad z \to \overline{z}$$

$$= \sum_{k} \frac{e^{\beta\mu N}}{h^{3N}N!} \int e^{-\beta H(x)} dx \qquad z \to \overline{z}$$

$$= N = 0 \qquad h^{3N}N! \int e^{-\beta H(x)} dx \qquad z \to N = 0$$

$$\overline{\Xi} = \overline{\Xi} (\mu_1 \vee, T)$$
 sometimes written  $H_N(\underline{X})$   

$$\underline{\Xi} = \underbrace{\sum_{N=0}^{\infty} \underbrace{\sum_{n=0}^{N} \int_{1}^{\infty} e^{-\beta H(\underline{X})} d\underline{X}}_{\Gamma}$$
 to denote this explicitly.  

$$\underline{Z} = e^{\beta \mu} \int_{1}^{\infty} e^{-\beta H(\underline{X})} d\underline{X}$$
 to denote this explicitly.  

$$\underline{Z} = e^{\beta \mu} \int_{1}^{\infty} e^{-\beta H(\underline{X})} d\underline{X}$$
 
$$\underline{Z} = e^{\beta \mu} \int_{1}^{\infty} e^{-\beta \mu} d\underline{X}$$

What about the probability density?

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$$g(\underline{x}) = \underbrace{e^{\beta\mu N} e^{-\beta H(\underline{x})}}_{N=0} = \operatorname{probability}_{h^{3}N, N!} = e^{\beta\mu N} \int e^{-\beta H(\underline{x})} d\underline{x} \quad \text{if is missing two corrections for over camfing in numerator and denonination of the state of the sta$$

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To connect the GCE to thermo dynamics, we need the Gribbs entropy formula,

Aside: There is a correction that need to be accounted for in the Gibbs entropy formula. Jaynes discovered it in the Go's. Let me explain.

The discrete version of Gibbs Formula is correct.

S= - Ro Z Pi lu Pi Pi Pi PMF (\*)

But when we go to the confinuous probability density function, we have a problem.  $P(a < x \le b) = \int g(x) dx$  (Assume (D for a moment))

For Dx = b-a <<1, this reduces to

Pi 2 g(x) Ax

Substituting into (XF) gives

S=- 20 Z gw) Ax ln [pw) sx]

In the limit that  $Ax \rightarrow 0$ , we get As  $dx \rightarrow 0$ ,  $m \rightarrow -\infty$ !

 $S = -k_B \int g(x) \ln [g(x) dx] dx$ 

This looks wrong. We have a problem.

To fix this, we need to divide by the "measure" or the dx,

to make this cancel out.

we have one more issue, we said our probability densities needed

to account for quantum effects.

 $\frac{2}{3} = \frac{1}{2} = \frac{1}{3} = \frac{1}$ 

 $\frac{g_{\text{NVT}}}{g_{\text{NVT}}} = \frac{e^{-\beta H}}{\int e^{-\beta H} dX} = \frac{1}{h^{2N}N!} \frac{e^{-\beta H}}{e^{-\beta H}} \frac{g_{\text{H}}}{Q} = \frac{1}{h^{2N}N!} \int e^{-\beta H} dX$ 

So, to properly normalize our probability dusities we have a

weight of w= / www. in the measure. In other words,

 $\int \tilde{\varphi}(x) \, \omega(x) \, dx = l \qquad \omega = (h^{3W} N!)^{-1} \, \rho(x) = \tilde{\varphi}(x) \, \omega(x)$ 

Measure

39,

Pi & gexi) w(xi) dx as Ax ->0

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· this changes the definition of the ensemble armse

$$\langle M \rangle = \int M \tilde{\beta} \frac{1}{h^{2}N} dX$$

OK, back to finding our connection to thermodynamics, now that we have worked that out.

$$S = -k_{B} \leq ln \vec{g}$$
  
=  $-k_{B} \sum_{N=0}^{\infty} \int \vec{g}(x) \ln \vec{p}(x) \cdot \frac{1}{h^{2W}N!} dx$ 

$$= -i_{B} \sum_{n=0}^{\infty} \int = e^{-\beta H + \beta \mu n} \int \frac{1}{2} \int$$

$$= -\mathbf{i}_{\mathcal{B}} \mathbf{e}_{\mathcal{A}} \left( \frac{1}{\Xi} \right) = \frac{1}{2} \sum_{N=0}^{\infty} \int_{\Gamma} \frac{-\mathbf{i}_{\mathcal{B}}}{\mathbf{h}_{\mathcal{A}}} \frac{1}{\mathbf{h}_{\mathcal{A}}} \frac{1}{\mathbf{h}_{\mathcal{A}}} \frac{1}{\mathbf{h}_{\mathcal{A}}}$$

$$-k_{\theta} \stackrel{!}{=} \sum_{N=0}^{\infty} \int (-p_{H} + p_{MN}) e^{-p_{H} + p_{MN}} \prod_{N=0}^{1} dx$$

 $\langle -BH + MN \rangle = -B \langle H \rangle + B \mu \langle N \rangle$ 

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There is a more compact way.

- A= U-TS Helmholtz Free Energy
- Φ= A-μN Grand Potential

$$A = U - T \left[ k_B \ln \Xi + \frac{U}{T} - \frac{\mu N}{T} \right]$$
  
=  $V - k_B T \ln \Xi - \frac{\mu}{L} + \mu N$   
$$A = -k_B T \ln \Xi + \frac{\mu N}{L} + \frac{\mu N}{L}$$

what is the Grand potential \$?

$$\overline{\Phi} = A - \mu N \qquad G = A + PV \qquad G = \mu N$$
$$= A - G = -PV \qquad !$$

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$$FV = k_{BT} ln \equiv Grand Canonical relation
For thermodynamics.
Persy by get put E.O.S. 
$$F = F(\mu, \nu, T)$$$$

# C. The NPT Ensemble

The last ensemble that we commonly encounter has a fixed value of N, P, IT. The new thing here is that volume can fluctuate. This is called the isothermal - iso baric ensemble. Walls can change volume

I will not derive the probability density, but I will give it.

 $P_{NPT} = \frac{e^{-\beta E_i} - \beta P^V}{\sum_{i} e^{-\beta E_i} e^{-\beta P^V}}$ (PMF)

A Gibbs free energy G=A+PV

D. Connections Between Ensembles

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Normalized Prob. Density Partition Function Thermo Connection

microcanonical ensemble : fires N, V, E

canonical ensemble: fixed N, V, T

-BH

grand canonical ensemble : fixed u, V, T

$$\vec{\beta}(\mu, V, T) = \underbrace{e^{\beta(H-\mu N)}}_{=} = \underbrace{\sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{h^{N} N!}}_{N=0} \int e^{\beta H} dx \quad PV = k_{0}T \ln \Xi$$

Isobanic - Isotnermal ensemble: fixed N, P, T

$$\widetilde{\mathcal{F}}(N,P,T) = \frac{e^{-\mathbf{k}}}{\Delta} \qquad \Delta = \frac{1}{h^{*}} \int e^{-\mathbf{k}} (H + PV) dx \qquad G = -\mathbf{k} \cdot \mathbf{k} \cdot \mathbf{k} \cdot \mathbf{k}$$

An interesting note: The portition functions can be obtained by Laplace transforms and the connection formulas by legendre transforms.

Laplace Transform Legendre Transform

Micro anonical -> canonical

$$Q = \int \Omega e^{-\beta E} dE \qquad A = U - TS$$
  

$$\int Iaplace vanishle : E \to U$$

canonical -> grand canonical

cononical -> isobaric-isothermal

$$\Delta = \int Q e^{-\beta PV} dV \qquad G = A + PV$$

Laplace fransforms and legendre transforms switch between functions with identical information. So, all ensembles have equivalent information.

E. Fluctuations

Ok, so we've looked af ensemble averages, but what do fluctuations Look like?

For example, in the NVT (canonical ensemble) we have N, V, and T that are fixed, but M, P, and E can fluctuate. We already know the whole PDF, so we should be able to figure out what the variance of these grantities are.

 $E \times ample : NVT O_{E}^{2}$ , variance of energy

 $\sigma_{E}^{2} = \left\langle \left(H - \left\langle H \right\rangle\right)^{2} \right\rangle^{2}$  $= \int \vec{p} \left(H - \left\langle H \right\rangle\right)^{2} d\vec{x}$ 



Sh



# $\sigma_{E}^{2} = k_{0}T^{2} \frac{\partial \langle H \rangle}{\partial T} + \langle H \rangle \langle H \rangle - \langle H \rangle^{2}$ $(H) = U, \quad \frac{\partial U}{\partial T} = C_{V}$ $T = k_{0}T^{2}C_{V} \quad Eheron \quad Clucturation$

 $\sigma_E^2 = k_B T^2 C_V$  Energy fluctuations are proportional to the heat capacity!

We are interested in the magnitude of these fluctuations as  $N \rightarrow \infty$ . As we have said many times  $N \approx 10^{23}$  in many cases. The limit  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ , N/U = constant is called the "Inermodynamic limit" (TL"). This is called the thermodynamic limit because the fluctuations in the system variables:  $P_{V}, V_{J}T, \mu, N$  become negligible in this limit. If it were not so, then we could not define state variables in thermodynamics. Or, alternatively, our different easenbles would not give consistent answers if there was no T.L.

I will derive a formal expression for the fluctuations in a moment, but I want to make two quick points:

i) the fluctuations don't go to zero, but the relative value of the fluctuations becomes negligible.

Example:  $\lim_{N \to \infty} \sigma_E \neq 0$   $\lim_{N \to \infty} \frac{\sigma_E}{U} = 0$ 

ii) Fluctuations are still important at small scales (small N, N).

ici) The thermodynamic limit is a manifestation of the contral limit pheorem for statistical mechanics. 58

Proof of the moment generating function for 
$$\beta_{NVT}$$
 (E).  
Calculate the moment generating function for  $\beta_{NVT}$  (E).  
 $\beta_{NVT}$  (E) =  $e^{-\beta H}/Q$   $Q = \int e^{-\beta H} d\tilde{z} = \int \Omega e^{-\beta E} dE$   
 $= \Omega(E)e^{-\beta E}/Q$   $\tilde{Z} = \int_{N}^{\infty} N! \tilde{z}$  1  
 $M(s) = \langle e^{SE} \rangle = \int_{Q}^{\infty} \int_{Q}^{SE} \Omega(E) e^{-\beta E} dE$  The "Laplace Transform"  
 $= \int_{Q}^{\infty} \Omega(E) e^{-\beta E} dE$ 

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write the cumulant generating function.

$$k(s) = ln M(s) = ln \left[ \frac{1}{2} \int \Omega(E) e^{(s-p)E} dE \right]$$

Recall that derivatives of K(5) are related to cumulants

$$\frac{d^{n}k}{ds^{n}}\Big|_{s=0} = k_{n} \ll n^{th} \quad cumulant$$

$$k(s) = k_{1}S + k_{2} \frac{s^{2}}{2!} + k_{3} \frac{s^{3}}{3!} + \dots \ll cumulant \quad expansion$$

Now, calculate expressions for the cumulants

$$k_{i} = \frac{d}{d\epsilon} \int \ln \left[ \frac{1}{Q} \int \Omega(E) e^{(S-B)E} dE \right] \int_{S=0}^{S=0}$$
$$= \frac{d}{ds} \int \ln \int \Omega e^{(S-B)E} dE - \ln Q \Big]_{S=0}$$
$$= \frac{d}{ds} \int \ln \int \Omega e^{(S-B)E} dE \Big]^{-1} \frac{d}{ds} \left[ \int \Omega e^{(S-B)E} dE \right] \int_{S=0}^{S=0}$$

integral & D don't depend on s









Main takeaway: At large N, ensemble averages grow proportional to N, but fluctuations only grow like  $N^{1/2}$ . Thus, the relative size of the fluctuations  $\sigma_{N}/\langle N \rangle \propto N^{1/2}$ . (when  $N = co^{23}$ , these fluctuations are really small.



Note: These are fluctuations in the quantities in the ensemble that can vary. In canonical N, V, & T are fixed and M, P, and E have distributions. The fact that the distribution becomes a dirac dilta for E (or provP) shows that all ensembles are equivalent in the thermodynamic limit.

### F. Reversibility

In thermodynamics, we learn that systems tend to maximize their entropy and minimize their free energy (Helmholtz or Gibbs). We algo learn that systems move spontaneously from lower entropy to higher entropy and higher free energy to lower free energy. What can statistical thermodynamics teach us about these concepts? It teaches us that probability drives entropy maximization. Consider an ideal gas in an NVE ensemble where N molecules are initially prepared in a volume of Vi=1cm<sup>3</sup>. We open this container in a volume of V2=1m<sup>3</sup>. The probability of a single microstate having all of the molecules located in the original volume, V1=1cm<sup>3</sup> is the exact same as a single microstate where the molecules are spread throughout V2=1m<sup>3</sup>. This might seem conter infaitive, but it is a consequence of our assumption of a priori equal probabilities. However, there are many more microstates unere the molecules are spread out! So, if each one is egrally likely, the system will more to the most frequently encountered microstates.

This can still be subject to fluctuations at low N. If N < 10, then it is quite possible for all of them to suddenly appear in  $V_1$ again. But for  $N \rightarrow \infty$ , it becomes virtually impossible.

Consider the plot I've made (see python plot) for the number of microstates Q(V) relative to Q(1m²) for different values of N.

Example: Ideal gas entropy in NVE ensemble



Stirlings approximation:



confine itself to a smaller volume. This is why entropy is

maximized. The system will always find itself in the most

frequently occuring set of microstates!