- We see that macroscopic bodies, like ideal gasses, are made of a huge number of particles ($\sim 10^{23}$).

- A question then arises naturally. How can we study the properties of macroscopic bodies in terms of their microscopic particles.

  - Computationally speaking, it is impossible to solve the equation of motion for 10^{23} Objects (Just think of the amount of memory you need to save the coordinates of each atom!).

  - At the macro-level, we actually <u>do not</u> care about the exact state of each particle (coordinate & velocity).

  - Then, what are the quantites we care about?

  - Some of them are obvious extensions of analogous quantities in systems made by a small number of particles:

    1) The total number of particles, N
    2) The volume occupied by the system, V

- As we mentioned before, N is typically huge ($N \simeq 10^{21}$ in $1\,mm^3$ of Gas)

- Mathematically, we will often consider the limit $N \to \infty$, with $V \to \infty$ such that $n = \frac{N}{V}$ stays constant (Thermodynamic limit)
  $n \to$ particle # density.

3) Another extension of mechanical quantity for few body systems is the total energy E

- For a quantum mechanical system in a finite volume, only a discrete spectrum ε_i ($i = 1, 2, \ldots$) of energies is accessible.

  total energy $E = \sum_i \varepsilon_i m_i$ $\to$ number of particles in state i

- However, the spacing of the levels ε_i is so small that one can consider ε as a continuous variable.

- There are also other quantities that are less obviously related to the mechanical quantities, such as.

4) Temperature, T.

5) Pressure, P

6) Entropy, S

- All these macroscopic quantities define microscopic state (macrostate) of the system. That is what we truely care about.

- one can intuitively understand how there can be many microscopic configurations (microstates) that give the same values of $N, V, E, \ldots$ i.e. the same microstate.

- Moreover, the microstate of the system is always evolving. The spacing between energy levels is so small that even the tiniest external perturbation induces transitions.

- Nevertheless, even if the microstates depends on time, the macrostate can be independent of time. In this case, the system is said to be in <u>equilibrium</u>..

  - A Typical Example: A Box full of gass. Even if the molecules keep moving, E, V and N stay basically constant.

- <u>Statistical Physics</u> tells us the macroscopic state of the system. once we know some of the laws that govern its microscopic dynamics but <u>ignoring the microscopic state of the system.</u>

- Given the generality of this definition, statistical physics is not only useful for describing boxes full of gas, but also - For instance - the universe as a hole....

- The next question is, given that a microstate is described by a huge amount of parameters (e.g. in the classical limit 3N coordinates and 3N momenta) while the macroscopic states are defined by a handful of parameters;

  How do we get rid of redundant information?

- The answer is: <u>By Averaging</u>.

- operatively averaging is performed over time,

$$\langle f \rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t f(t) \, dt .$$

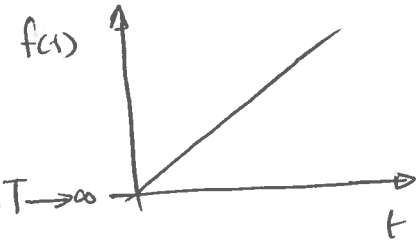
  - of course, this does not help us, since use of this definition of averaging needs the knowledge of the evolution of the system, i.e. of the microstate.

  - So, we introduce the idea of ensembles:

  - Instead of following the evolution of one microstate as a function of time, consider the set of all possible microstates at a given time. This set is called <u>Ensemble</u>.

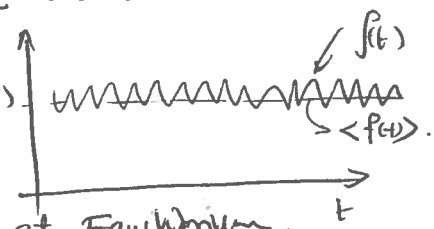
  - Eventually, we will want to identify the time average with the average on the ensemble, <u>with some appropriate weight</u>.

- Note that in general the limit, $\lim_{t\to\infty} \frac{1}{t}\int_0^t f(t)\,dt$, does not need to exist. eg. $f(t) = t$



then, the limit diverges as $T \to \infty$

- The cases we will consider are cases where the limit exists and ideally we will expect $f(t)$ to have a form like:

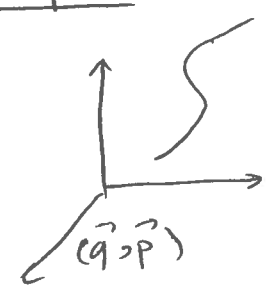


- systems where such averages exist, will be said to be at Equilibrium.

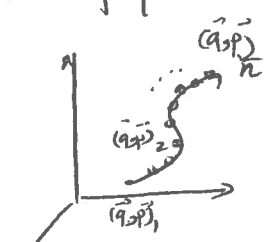
- Up to now, we have not improved the situation significantly, since we are still unable to compute $f(t)$, so we cannot compute $\langle f \rangle$.

- To proceed, let's consider the trajectory of system in the <u>phase space</u>.

$(\vec{q}(t), \vec{p}(t)) \longrightarrow$ This is a $6\underline{N}$ dimensional space.



and let's discretize it, taking a discrete but very large number of points on the trajectory:



- Now, we associate to each of these points, a "mental copy" of the system.. The set of these N mental copies is the so called "Ensemble".

$(\vec{q}, \vec{p})$

- The integral that gives $\langle f \rangle$ is now replaced by a discrete sum:

$$\langle f \rangle_{ens} = \sum_{i=1}^{\bar{N}} \frac{1}{\bar{N}} f((\vec{p},\vec{q})_i) .$$

- We then assume that there are many points $(\vec{p},\vec{q})_i$ and that they are very densly populated, so that we can define a density function:

$$\rho(\vec{p},\vec{q},t)$$

such that at the time t, in a volume $d^{3N}q \cdot d^{3N}p$ around the point $(\vec{p},\vec{q})$, there are $\rho(\vec{p},\vec{q},t) \cdot d^{3N}q \, d^{3N}p$ copies of the system.

- So, we can write.

$$\bar{N} = \int \rho(\vec{p},\vec{q},t) \, d^{3N}p \cdot d^{3N}q .$$

and replace the sum by an integral.

$$\boxed{\langle f \rangle_{ens} = \frac{1}{\int \rho(\vec{p},\vec{q},t) \cdot d^{3N}p \, d^{3N}q} \int \rho(\vec{p},\vec{q},t) f(\vec{q},\vec{p}) \cdot d^{3N}p \, d^{3N}q .}$$

- Note that in principle $\rho(\vec{p},\vec{q},t)$ can be completely arbitrary.

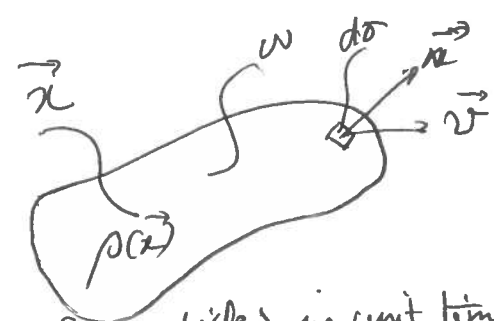
- How can we decide which form of $\rho(\vec{p},\vec{q},t)$ can describe the macroscopic system of interest and which ones do not?

- <u>Answer</u> : since for a system at equilibrium, we want $\langle f(t)\rangle = \text{const}$, we will require that ρ does not depend explicitly on time. In other words : $\partial\rho/\partial t = 0$

- The requirement $\partial\rho/\partial t = 0$, has important implications, as we will describe below :

  - $\rho(\vec{q},\vec{p},t)$ can be generally thought of as the density of a fluid in phase space.

  - let's consider in general a fluid with density $\rho(\vec{x},t)$ and let's analyze the case of a small volume ω surrounded by a closed surface σ



  - the total change of the number of particles in unit time in the volume ω is

$$\frac{\partial}{\partial t}\int_{\omega} \rho \, d^3x$$

• If particles are not created or destroyed, the change has to be equal to the flux across the surface σ of W.

$$-\int_{\sigma} \rho \vec{v} \cdot \vec{n} \, d\sigma$$

Using divergence theorem, becomes.

$$-\int_{W} \vec{\nabla} \cdot (\rho \vec{v}) \, d^3x = -\int_{W} \mathrm{div}(\rho \vec{v}) \cdot d^3x.$$

• let us apply this to our ensemble. Since ρ is associated to a given conserved number of copies of our system, it has to obey the continuity equation:

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0$$

where $\vec{v} = \left(\frac{dq_i}{dt}, \frac{dp_i}{dt} \right)$ is the velocity of representative points in the phase space.

- let's expand the divergence term:

$$\vec{\nabla}\cdot(\rho\vec{v}) = \sum_{i=1}^{3N}\left\{\frac{\partial\rho}{\partial q_i}\cdot\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i + \left(\rho\frac{\partial\dot{q}_i}{\partial q_i} + \rho\frac{\partial\dot{p}_i}{\partial p_i}\right)\right\}$$

- Using dynamical equations:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

where H is the Hamiltonian of the system. $\left(H = \underset{\text{kinetic}}{T} + \underset{\text{potential}}{V} = \frac{p^2}{2m} + V(q)\right)$.

Note that $f_i = \frac{-\partial V}{\partial q_i}$, which along with $\frac{dp_i}{dt} = f_i$ leads to the second identity.

- By inserting the above 2 identities in the equation on top of the page, we see:

$$0 = \frac{\partial\rho}{\partial t} + \vec{\nabla}\cdot(\rho\vec{v}) = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3}\left\{\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\cdot\dot{p}_i\right\}$$

$$= \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3}\left\{\frac{\partial\rho}{\partial q_i}\cdot\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\cdot\frac{\partial H}{\partial q_i}\right\}$$

$$= \frac{\partial\rho}{\partial t} + \underbrace{[\rho, H]}_{\text{Poisson Bracket.}} \xrightarrow[\text{equilibrium}]{\text{for}} \boxed{\frac{\partial\rho}{\partial t} = -[\rho, H] = 0}$$

a criterion to check if $\rho(\vec{p}^{3N}, \vec{q}_i^{3N})$ is at the equilibrium or not?

- let's focus now on the physics of these mathematical equations.

- We call a system <u>isolated</u> that does not exchange anything with the exterior space. More particularly, its energy E will be constant.

- We postulate that density function a closed system is

$$\rho(p,q) = \text{const} \times \underbrace{\delta}_{\text{dirac's delta.}}\left(H(p,q) - E\right)$$

- And the system only explores ~~the~~ a hypersurface manifold $(H(p,q)=E)$ in a closed system at the equilibrium.

- We call this ensemble <u>microcanonical</u> ensemble. In this ensemble

$$\langle f \rangle = \frac{\int_{\omega} f(\vec{p},\vec{q})\, d_p^{3N}\, d_q^{3N}}{\int_{\omega} d_p^{3N}\, d_q^{3N}}$$

where ω is the surface $H(p,q) = E$.

- The physical significance of the postulate are:

① All the microstates (compatible with conservation of energy) have <u>equal weight</u> in the determination of the macrostate.

(2) As the weight of each point in the ensemble is the measure of the probability that a specific microstate goes through that point this postulate is refered to as

"Postulate of Equal A Priori Probabilities"

- give that all the microstates have the same probability of being realized, what will determine the macrostate of the system?

- Well, the answer is the macrostate that corresponds to the largest number of microstates. This will give the equilibrium state of the system.

- So, we see that for the microcanonical ensemble the only thing that matters is the total number of states accessible to the system.

- Let us call this quantity Ω. We will have $\Omega = \Omega(N, V, E)$.

Does Ω have a macroscopic interpretation?

- To explain, consider two boxes of gas A_1, A_2 with (N_1, V_1, E_1) and (N_2, V_2, E_2). The system $A_1 + A_2$ is closed and let A_1 and A_2 be able to exchange energy, but neither matter nor volume.

A_1	A_2
(N_1, V_1, E_1)	(N_2, V_2, E_2)

- let the total energy be $E_0 = E_1 + E_2 = \text{constant}$. The total number of microstates of $A_0 = A_1 + A_2$ will be given by the product

$$\Omega_0 = \Omega_1(E_1) \cdot \Omega_2(E_2) = \Omega_1(E_1) \cdot \Omega_2(E_0 - E_1) = \Omega_0(E_1, E_0 - E_1)$$

- The equilibrium value of E_1 will be the one that maximizes Ω_0, i.e. the one that corresponds to the largest number of microstates.

- We compute this by deriving $\left.\frac{\partial \Omega_0}{\partial E_1}\right|_{\bar{E}_1} = 0$, which is equivalent to: $\Rightarrow$ Equilibrium.

$$\left.\frac{\partial \Omega_1}{\partial E_1}\right|_{\bar{E}_1} \Omega_2(E_2) + \Omega_1(\bar{E}_1) \cdot \left.\frac{\partial \Omega_2}{\partial E_2}\right|_{E_2} \frac{\partial E_2}{\partial E_1} = 0$$

Using $E_2 = E_0 - E_1$,

$$\beta_1 = \left.\frac{\partial \ln \Omega_1}{\partial E_1}\right|_{\bar{E}_1} = \left.\frac{\partial \ln \Omega_2}{\partial E_2}\right|_{\bar{E}_2} = \beta_2$$

- let's physically interpret this, starting with an arbitrary value E_1^i of E_1, there will be $\Omega(E_1^i, E_0 - E_1^i)$ microstates corresponding to this macrostate. But the system will spend the largest amount of time in the macrostate that corresponds to the maximum value of the # of microstates. This is the macrostates for which $E_1 = \bar{E}_1$.

- So, there will be a transition during which energy flows between the two systems and E_1 goes from $E_1^{(1)}$ to $\bar{E}_1$.

- This transition process ends with $\beta_1 = \beta_2$.

- This is the same phenomenon that happens when the temperature of two systems equilibriates, so it makes sense to think that β is a function of the temperature.

- Now, we recall the thermodynamic relation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

and compare it with.

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

to give thate $\partial S \propto \partial \ln \Omega + \text{const}$.

- Indeed, it turns out that : $\boxed{S = k_B \ln \Omega}$

k_B : Boltzmann Constant : $[k_B]$ = Energy / Temperature

note : $\beta = \frac{1}{k_B T}$. $k_B = 8.62 \times 10^{-5}$ eV/°K

- Let's try to understand the interpretation of other quantities.
- Suppose now the total volume $V_0 = V_1 + V_2$ of A stays constant but the wall between A_1 and A_2 can move, so V_1 and V_2 can change.
- As before, we conclude that the equilibrium values of $\bar{V}_1$ and $\bar{V}_2$ of V_1 and V_2 will be determined by imposing:

$$\eta_1 = \left(\frac{\partial \ln \Omega_1}{\partial V_1}\right)_{N_1, E_1} \quad \text{and} \quad \eta_2 = \left(\frac{\partial \ln \Omega_2}{\partial V_2}\right)_{N_2, E_2}$$

are equal.

- Finally, suppose A_1 and A_2 can exchange particles such that $N_0 = N_1 + N_2$ is conserved. A_1 and A_2 will be in equilibrium when $\zeta_1 = \zeta_2$, where:

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

- Compare $\eta = \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N, E}$, $\zeta = \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V, E}$ to

$$dE = TdS - PdV + \mu dN$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N, V}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N, E}, \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{V, E}$$

- So two systems that can exchange energy, volume and particles will be in equilibrium when:

$$\begin{cases} T_1 = T_2 & : \text{Temperatures} \\ P_1 = P_2 & : \text{pressure} \\ \mu_1 = \mu_2 & : \text{chemical potentials.} \end{cases}$$

- OK! We are now ready to study our first system: "The ideal gas".
- Let's consider a system of non-interacting particles:
- The number of states available to each particle will be proportional to the volume of the system, so that the total # of states of the system will be proportional to $(\text{volume})^N$.

$$\Omega(N,V,E) = V^N \Omega_1(N,E)$$

where Ω_1 has still to be determined.

- That is already a powerful result!
- Indeed, we have seen

$$\frac{P}{T} = k \frac{\partial}{\partial V} \ln \Omega = k \frac{N}{V}.$$

- This is just the ideal gas law:

$$PV = NRT.$$

- Once we define the gas constant $R = kN_A$, where N_A is the avogadro's number, and

$$n = \frac{N}{N_A}$$

is the number of moles of gas.

- Let us go ahead and compare Ω for a <u>nonrelativistic ideal gas</u>:

- We compute the total number of states of a quantized <u>free nonrelativistic</u> particle in a cubic box of side L,

- By requiring that the wave functions vanish at the edge of the box, one finds that the state of the particle is defined by three quantum numbers n_x^i, n_y^i and n_z^i; $n_i = 1, 2, 3, \ldots$

and the energy of the i-th particle is:

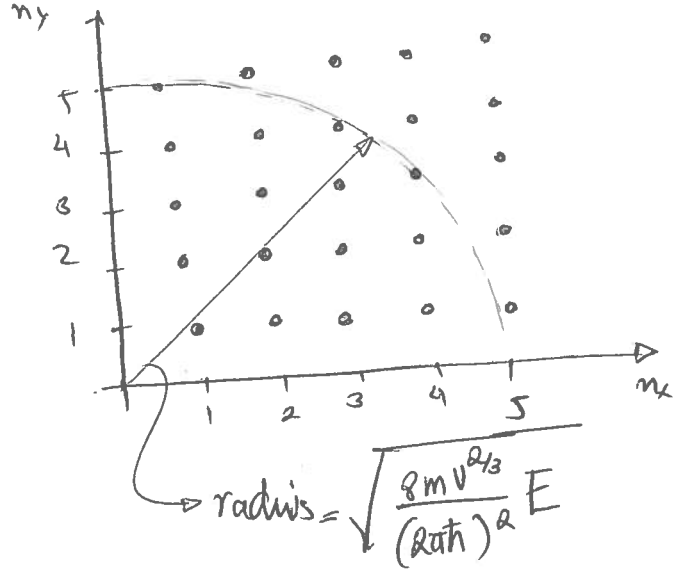
$$\varepsilon_i\left(n_x^i, n_y^i, n_z^i\right) = \frac{(2\pi\hbar)^2}{8mL^2}\left(n_x^{i\,2} + n_y^{i\,2} + n_z^{i\,2}\right)$$

- Now, we sum this relation for all of the particles:

$$\sum_{r=1}^{3N} n_r^2 = \frac{8mL^2}{(2\pi\hbar)^2} \sum \varepsilon_i = \frac{8mV^{2/3}}{(2\pi\hbar)^2} E .$$

- So in principle, we should find how many 3N-uples of Non-negative integers $(N_1, N_2, \ldots N_{3N})$ satisfy the above equation.

Graphically:



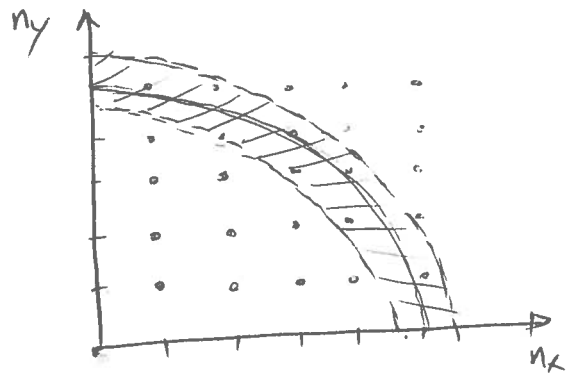
- This is a kind of diophantine equation (equation for which only integer solutions are sought for). A problem that is known to be very difficult.
- Also, the number of states will be an extremely irregular function of E!
- Something that is much easier to compute is the number of states between

$$E - \frac{1}{2}\Delta \text{ and } E + \frac{1}{2}\Delta \quad ; \quad \Delta \ll E.$$

- we expect this to be a much regular function.

- This is also a much more realistic situation, as we said that E will never be exactly constant and that external perturbations will change E by an amount much smaller than E, But much larger than the typical energy spacing.

- Define $\Gamma(N, V, E; A)$ as the number of states with energy between $E - A/2$ and $E + A/2$:



- If we define $\Sigma(N, V, E)$ as the total # of states with energy smaller than E; then

$$\Gamma(N, V, E; A) = A \frac{\partial}{\partial E} \Sigma(N, V, E)$$

- But it is easy to compute Σ! It will be just the volume of the positive "octant" of 3N-dimensional sphere with radius $\sqrt{8mE}\, L / 2\pi\hbar$.

- How do we compute the volume of a sphere of Radius $\underline{R}$ in N dimensions? It is given by:

$$V_N = \int_{\sum_{i=1}^{n} x_i^2 < R^2} dx_1\, dx_2 \cdots dx_n = \int_0^R r^{n-1} dr \int d\Omega_{n-1} = \frac{R^n}{n} \int d\Omega_{n-1}$$

where we have gone to spherical coordinates. we have now to compute $\int d\Omega_{n-1}$. we use:

$$\left(\sqrt{\pi}\right)^n = \int_{-\infty}^{+\infty} e^{-x_1^2} dx_1 \int_{-\infty}^{+\infty} e^{-x_2^2} dx_2 \cdots \int_{-\infty}^{+\infty} e^{-x_n^2} dx_n$$

$$= \int_0^{+\infty} r^{n-1} dr\, e^{-r^2} \int d\Omega_{n-1} = \frac{1}{2}\Gamma\left(\frac{n}{2}\right) \int d\Omega_{n-1}$$

$$\text{So, } V_n = \frac{R^n}{n} \cdot \pi^{\frac{n}{2}} \frac{2}{\Gamma\left(\frac{n}{2}\right)} = \frac{R^n \pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2}+1\right)} = \boxed{\frac{R^n \pi^{n/2}}{\left(\frac{n}{2}\right)!}}$$

- In our case, we are interested in the volume of an octant. This gives an extra factor of $(1/2)^n$. So our final results:

$$\Sigma(N,V,E) = \left(\frac{\sqrt{8mE}\, L}{2\pi\hbar}\right)^{3N} \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} \cdot \left(\frac{1}{2}\right)^{3N}.$$

- Using Stirling's formula: $\Gamma(n+1) \simeq n^n \cdot e^{-n}$; $n \gg 1$

- Thus we get:

$$\Sigma(N,V,E) = V^N \left[\left(\frac{4\pi e m E}{3N} \right)^{\frac{3}{2}} \frac{1}{(2\pi\hbar)^3} \right]^N.$$

- from this it follows that:

$$\ln \Gamma(N,V,E,A) \approx N \ln \left(\frac{V}{(2\pi\hbar)^3} \left(\frac{4\pi m E}{3N} \right)^{\frac{3}{2}} \right) + \frac{3}{2} N$$

$$+ \left\{ \ln\left(\frac{3N}{2}\right) + \ln\left(\frac{A}{E}\right) \right\}$$

where we neglect $\ln\left(\frac{3N}{2}\right)$ and $\ln\left(\frac{A}{E}\right)$.

- Notice that $\ln\left(\frac{A}{E}\right) \to -\infty$ as $A \to 0$, but for any reasonable value of A, $\left|\ln\left(\frac{A}{E}\right)\right| \ll N$. is negligible.

- No, we identify Ω with Γ. (notice that the dependence on A has disappeared) and start studying the thermodynamics of ideal gas.

- let's start from the entropy, noting that $\Gamma(N,V,E,A) = \Omega(N,V,E)$ defined before:

$$S = k_B \ln \Omega = N k_B \ln \left[\frac{V}{(2\pi\hbar)^3} \left(\frac{4\pi m E}{3N} \right)^{\frac{3}{2}} \right] + \frac{3}{2} N k_B$$

- Using $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$ to get:

$$E = \frac{3}{2} N k_B T = \frac{3}{2} nRT \rightarrow (R = k_B R)$$

- Specific heat specifies how much heat we must give to the system to increase its temperature by $1^\circ k$.
- The specific heat at constant volume C_V and at constant pressure C_P.

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \left(\frac{\partial E}{\partial T}\right)_{N,V} \; ; \; C_P = T\left(\frac{\partial S}{\partial T}\right)_{N,P}.$$

so that

$$C_V = \frac{3}{2} N k_B$$

- To get C_P, we have to consider S as a function of (T, P, N)
- But from $dE = TdS - PdV + \mu dN$, we have S as a function of (E, V, N): To change the variable we re-write:

$$dE = TdS - d(PV) + VdP + \mu dN.$$

so that: $T\,(dS)_{P,N} = d(E + PV)_{P,N}$ and

enthalpy

$H = E + PV$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} = \left[\frac{\partial (E+PV)}{\partial T}\right]_{P,N} = \left(\frac{\partial H}{\partial T}\right)_{P,N}.$$

- So, that is straightforward to get:

$$C_p = \frac{5}{2} N k_B = \frac{5}{2} nR$$

- Finally, for a reversible adiabatic process (S = const., N = const.),

we see immediately that

$$V \cdot E^{3/2} = \text{const.} \longrightarrow V^{5/2} P = \text{constant.}$$

- Is there any problem in what we did so far? (The Gibbs Paradox).
- consider two boxes of ideal gas, with volumes V_1 and V_2 of particles N_1, N_2 and mass of m_1 and m_2 at the same temperature T:
- for each of them:

$$S_i = N_i k_B \ln V_i + \frac{3}{2} N_i k_B \cdot \left\{ 1 + \ln\left(\frac{2\pi m_i k_B T}{(2\pi\hbar)^2} \right) \right\}$$

- So the total entropy is $S_1 + S_2$.
- Now, let's mix the gasses.
- The total entropy after mixing will be: ($V = V_1 + V_2$)

$$S_T = \sum_i \left[N_i k_B \ln V + \frac{3}{2} N_i k_B \left\{ 1 + \ln\left(\frac{2\pi m_i k_B T}{(2\pi\hbar)^2} \right) \right\} \right]$$

- The change in entropy is:

$$\Delta S = S_T - (S_1 + S_2) = (N_1 + N_2) k_B \ln(V_1 + V_2) - N_1 k_B \ln V_1 - N_2 k_B \ln V_2$$

$$= N_1 k_B \ln\left(\frac{V_1+V_2}{V_1}\right) + N_2 k_B \ln\left(\frac{V_1+V_2}{V_2}\right).$$

- Notice that ΔS is positive, and is associated with the so-called entropy of mixing:
- In general, mixing two gases leads to an increase in entropy (it is an irreversible process).
- So far, everything looks ok. However, mixing of gases of identical species with identical temperature and density should be a <u>reversible</u> process. identical density means $\frac{N_1}{V_1} = \frac{N_2}{V_2}$ but in our case:

$$\Delta S = N_1 k_B \ln\left(\frac{N_1+N_2}{N_1}\right) + N_2 k_B \ln\left(\frac{N_1+N_2}{N_2}\right)$$

which is still positive. Something's wrong. This is the so called Gibbs paradox.). How can we fix this?

- We can rewrite the excess of entropy mixing as:

$$(\Delta S)^{excess} = k_B \left[\ln((N_1+N_2)!) - \ln((N_1)!) - \ln((N_2)!)\right]$$

- so that if we substract $k\ln(N)!$ to our definition of entropy, things seem to work. Is such subtraction physically motivated? (Yes, of course)

- Indeed, our calculations did not take into account the fact that our ideal gas is made of <u>indistinguishable</u> particles.

- This means that a microstate with particle $\underline{1}$ in state a and particle $\underline{2}$ in state b is the same as the microstate with particle $\underline{1}$ in state b and particle $\underline{2}$ in state a.

- These two states should be counted as one.

- This implies that we have overcounted the number of states with n_1 particles in state $\underline{1}$, n_2 particles in state $\underline{2}$, ..., n_k in state k by a factor:

$$\frac{N!}{n_1!\, n_2! \cdots n_k! \cdots}$$

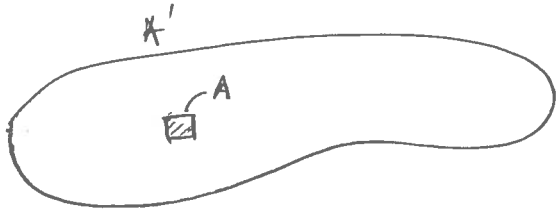
- So in computing Ω we should take this factor into account.

- For general $n_1, n_2, \ldots, n_k, \ldots$ this is very complicated but for sufficiently high Temperature Temperature, or dilute gas, $n_1, n_2, \ldots, n_k \ldots$ is either ϕ or 1!

- So in this case, the overcounting factor is just $N!$.
- Taking this factor into account, we get the Sakur Tetrode equation for the entropy:

$$S = N k_B \ln\left(\frac{V}{N}\right) + \frac{3}{2} N k_B \left[\frac{5}{3} + \ln\left(\frac{2\pi m k_B T}{(2\pi\hbar)^2}\right)\right]$$

- The canonical ensemble:
- Due to the difficulties in implementing the condition $E = \text{const}$, it is difficult to study (both theoretically and experimentally) the microcanonical ensemble.
- We call a system <u>closed</u> that can exchange work and energy — but not matter — with the rest of the world.
- such systems are described by the <u>canonical ensemble</u>.
- To study the canonical ensemble, consider a "small" system $\underline{A}$ that can exchange energy with a reservoir (<u>a much bigger</u> system) A'.



- Let E_0 be the total energy of $A'+A$. What is the probability that A has total energy E_r.

- If $A+A'$ forms an isolated system, the total # of microstates will be :

$$\Omega^{Tot} = \Omega_{A'}(E_0 - E_r)\,\Omega_A(E_r)$$

- And the probability that $\underline{A}$ has energy E_r will be just

$$P_r \propto \Omega_{A'}(E_0 - E_r)\,\Omega_A(E_r)$$

or

$$\ln P_r \propto \ln \Omega'_A(E_0 - E_r) + \cancel{\ln \Omega_A(E_r)}$$

negligible for small A system.

$$= \ln \Omega_{A'}(E_0) - \beta E_r$$

use taylor expansion & consider $\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V}$

- so that our closed system will obey the canonical distribution :

$$P_r \propto \exp(-\beta E_r) = e^{-\frac{E_r}{k_B T}}.$$

the so-called Boltzmann factor.

- In the microcanonical ensemble, only states with energy E are allowed, and all have the same probability.

- In the canonical ensemble, states of all energies are allowed but with different probability. the larger the energy the smaller the probability.

- Normalizing the probability of a state with energy E_r to be realized is given by the canonical distribution

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}.$$

- While in microcanonical ensemble, the total energy is kept fixed, in the canonical ensemble the total temperature is fixed.

- In the microcanonical ensemble the total # of states of the system played an important role.

- For the canonical ensemble, the most important quantity is the partition function

$$Q_N(V,T) = \sum_r \exp\left(-E_r/k_B T\right)$$

- Does it correspond to some thermodynamic quantity? Yes.

- Start from $dU = dE = TdS - PdV + \mu dN = -SdT + d(TS)$

  and define the so-called helmholtz free energy : $A = U - TS$.

- For which: $S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$, $P = \left(-\frac{\partial A}{\partial V}\right)_{N,T}$, $\mu = \left(\frac{\partial A}{\partial N}\right)_{V,}$

- Therefore:

$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_{N,V} = \left(\frac{\partial (A/k_BT)}{\partial (1/k_BT)}\right)_{N,V}$$

- let's compare this with the average energy in the canonical ensemble:

$$U = \frac{\sum E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \left(-\frac{\partial}{\partial \beta} \ln Q_N(T,V)\right)_{N,V}$$

- This yields the identity:

$$\boxed{A(N,V,T) = -k_BT \cdot \ln Q_N(V,T)}$$

- From this expression, the full thermodynamics of the system is determined.

- For instance,

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V}.$$

- The expression of the entropy is especially interesting in this context:
- the probability for the system to be in a state with energy

E_r is:

$$P_r = \frac{1}{Q_N(T,V)} \cdot e^{-E_r/k_BT}.$$

- That gives $\langle \ln P_r \rangle = \sum P_r \ln P_r =$

$$= -\sum P_r \ln Q_N(T,V) - \sum P_r E_r \frac{1}{k_BT}.$$

$$= -\ln Q_N(T,V) - \frac{U}{k_BT} = \frac{A}{k_BT} - \frac{U}{k_BT} = -S/k_B$$

Therefore:

$$\boxed{S = -k_B \sum P_r \cdot \ln P_r}$$

- Consequence I : For $T = 0^\circ k$, $P_r = 1$ for $E_r = 0$

  under the hypothesis that the ground state is not degenerate.

  $P_r = 0$ for $E > 0$

$\longrightarrow$ $S = 0$ at $0^\circ k$ (Nernst heat theorem / 3rd law of thermodynamics)

- Consequence II : The definition : $S = -k_B \sum P_r \ln P_r$ is a starting point in information theory and one can use it as a fundamental definition of entropy.

- Consequence III : This definition also applies for the microcanonical ensemble, in that case $P_r = 1/\Omega$ For all r, then

$$\Rightarrow S = -k_B \sum_r \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = -k_B \ln \Omega$$

- Degeneracy :

- A quantum system can have degenerate energy levels different states with the same level of energy.

- The extension of the definition of partition function to this case is straightforward:

- If g_i is the degeneracy of the ith level, then

$$Q_N(T,V) = \sum_i g_i \, e^{-E_i/k_BT} .$$

and all the g_i states with equal energy E_i are equally likely to be realized.

- Also, as the energy level are very thinly spaced (WRT to k_BT), it is convenient to go to a continuum description...

- In this description, the probability of the system to be in a microstate with energy between E and E+dE is:

$$P(E).dE = e^{-\beta E} g(E).dE$$

where $g(E)$ is the density of states.

- There are $g(E).dE$ states with energy between E and E+dE.

Note: $\begin{cases} [g(E)] = [E^{-1}] \\ [g_i] = [1] \end{cases}$

- Let's consider classical systems:

- In the canonical ensemble, the expectation value for the quantity f is

$$\langle f \rangle = \sum f_i P_i = \frac{\sum f_i g_i e^{-\beta E_i}}{\sum g_i e^{-\beta E_i}}.$$

- In the classical limit, and going back to the density functions, we have:

$$\langle f \rangle = \frac{\int_{\vec{p},\vec{q}} f(\vec{p},\vec{q})\, e^{-\beta H(p,q)}\, d^{3N}q \cdot d^{3N}p}{\int e^{-\beta H(p,q)}\, d^{3N}q \cdot d^{3N}p}.$$

So that we have:

$$Q(T,V) \propto \int e^{-\beta H(p,q)}\, d^{3N}p \cdot d^{3N}q$$

- Now, notice that we have to put some probability constant.

- Indeed, as the helmholtz free energy is ln of $Q_N(T,V)$, Q_N has to be dimensionless...

- since the dimension of $dq\,dp$ is the dimension of an action, we redefine:

$$Q_N(T,V) = \frac{1}{N!\,h^{3N}} \int e^{-\beta H(p,q)}\, d^3q \cdot d^3p .$$

where h has to be a fundamental constant with dimension of an action.

- we have also introduced a factor $N!$ to avoid the Gibbs paradox.
- let us now compute $Q_N(T,V)$ for a classical non-interacting gas:
- in such case : $H(p,q) = \sum_i \frac{1}{2m} p_i^2$

$$Q_N(T,V) = \frac{1}{N!\,h^{3N}} \int d^{3N}q \int d^{3N}p\; e^{-\sum_{i=1}^{N} \frac{p_i^2}{2mk_BT}} .$$

$$= \frac{V^N}{N!\,h^{3N}} \left[\int_0^\infty 4\pi p^2 dp\, e^{-\frac{p^2}{2mk_BT}} \right]^N \quad \left(x = \frac{p}{\sqrt{2mk_BT}} \right)$$

$$= \frac{V^N}{N!\,h^{3N}} \left[4\pi (2mk_BT)^{\frac{3}{2}} \int_0^{+\infty} x^2 e^{-x^2} \cdot dx \right]^N$$

with $\int_0^{+\infty} x^2 e^{-x^2} dx = \frac{1}{2}\Gamma\left(\frac{3}{2}\right) = \frac{1}{4}\sqrt{\pi}$.

$$Q_N(T,V) = \frac{V^N}{N!\,h^{3N}} \left[(2\pi m k_B T)^{\frac{3}{2}} \right]^N$$

- So that using $N! \cong N^N e^{-N}$.

$$A(N,T,V) = N k_B T \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{3}{2}} \right\} - 1 \right]$$

- And all the thermodynamics $\left(PV = N k_B T, \; U = \frac{3}{2} N k_B T, \ldots \right)$

- In particular, the entropy follows:

$$S = \left(- \frac{\partial A}{\partial T} \right)_{N,V} = N k_B \left[\ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \right\} + \frac{5}{2} \right]$$

- Comparing with the microcanonical entropy, we see that indeed

$$h = 2\pi\hbar.$$

- So that we see that indeed one quantum mechanical state corresponds to a cell of volume $\Delta p . \Delta q = 2\pi\hbar$ in the phase space, in agreement with Heisenberg Uncertainty. $\left(\frac{dp . dq}{h} = \underset{\text{unit volume in phase space}}{1} \longrightarrow dp . dq = h = 2\pi\hbar \right)$

- Notice, that I could have written for the ideal gas,

$$Q_N(T,V) = \frac{1}{N!} \left[Q_1(T,V) \right]^N$$

$$Q_1(T,V) = \frac{1}{h^3}\int d^3p\, d^3q\, e^{-\beta H_1(p,q)} = \dots = \frac{V}{h^3}\int_0^{+\infty} 4\pi p^2\, dp\, e^{-\frac{p^2}{2m}\beta}$$

(defining the energy of a single particle $\varepsilon = p^2/2m$).

$$= \int_0^{+\infty} d\varepsilon \left[\frac{V}{h^3} 2\pi (2m)^{\frac{3}{2}} \varepsilon^{1/2} \right] e^{-\beta\varepsilon}$$

that I compare with $Q \sim \int d\varepsilon\, g(\varepsilon)\, e^{-\beta\varepsilon}$.

- To find the single particle density of states:

$$g_1(\varepsilon) = \frac{V}{h^3} 2\pi (2m)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}}.$$

a monotonically increasing function of ε.

- Another system of interest is a system of independent harmonic oscillators:

- Consider a system of N degree of freedom, each with a harmonic oscillator hamiltonian:

$$H = \sum_{i=1}^{N} \frac{1}{2} m\omega^2 q_i^2 + \frac{1}{2m} p_i^2$$

- The partition function of a harmonic oscillator is:

$$Q_1(\beta) = \int \frac{dq\,dp}{2\pi\hbar} \exp\left\{ -\beta\left(\frac{1}{2}m\omega^2 q^2 + \frac{1}{2m}p^2\right)\right\}$$

$$\hookrightarrow \int_{-\infty}^{+\infty} \exp(-ax^2) = \sqrt{\frac{\pi}{a}}$$

$$= \frac{1}{\beta\hbar\omega}$$

- So, the total partition function is $Q_N(\beta) = (\beta\hbar\omega)^{-N}$

- Treat the oscillator as distinguishable $\rightarrow$ no $\frac{1}{N!}$ factor.

- The Helmholtz free energy is:

$$A = N k_B T \ln\left(\frac{\hbar\omega}{k_B T}\right).$$

So that

$$\begin{cases} \mu = k_B T \ln\left(\frac{\hbar\omega}{k_B T}\right), \quad P = 0 \\ S = N k_B \left[\ln\left(\frac{k_B T}{\hbar\omega}\right) + 1\right] \end{cases}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V}$$

$$U = N k_B T, \quad C_P = C_V - N k_B.$$

$\downarrow$

- "Equipartition theorem": energy $\frac{1}{2}k_B T$ for each quadratic term in the lagrangian

- Notice that the entropy here does not go to zero as $T \to 0$.

This is an <u>artifact of classical approximation</u>.

- To do things correctly, let's see what happens at the quantum leve

- In this case, the levels are: (energy levels of harmonic oscillator)

note that $\frac{1}{2}\hbar\omega$ cannot be explained classically

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2, \ldots$$

so that:

$$Q_1(\beta) = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$= \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)}$$

- For N oscillators: $Q_N(\beta) = \left[Q_1(\beta)\right]^N$

so that:

$$A = N\left[\frac{1}{2}\hbar\omega + k_B T \ln\left(1 - e^{-\beta\hbar\omega}\right)\right]$$

- So, we see that what is the classical limit in this case: it corresponds to $\beta\hbar\omega \ll 1 \to T \gg \frac{\hbar\omega}{k}$.

- Indeed in this limit,

$$Q_1(\beta) = \frac{1}{2 \cdot \frac{1}{2}\beta\hbar\omega} = \frac{1}{\beta\hbar\omega}.$$

- Thermodynamics quantities:

$$\mu = \frac{A}{N}, \quad P = 0$$

$$S = N k_B \left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln\left\{ 1 - e^{-\beta\hbar\omega} \right\} \right]$$

Notice that <u>S correctly goes to ϕ</u> as $\beta\hbar\omega \to \infty$.

$U = A + TS \longrightarrow$: $U = N\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right)$ that goes to $\frac{N}{2}\hbar\omega$ for $T \to \infty$

- Notice that equipartition theorem does not hold here.)

- Equipartition theorem can be proved as follows:

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = \frac{\int d^{3N}p \, d^{3N}q \, e^{-\beta H} p_i \frac{\partial H}{\partial p_i}}{\int d^{3N}p \, d^{3N}q \, e^{-\beta H}}.$$

integrating by parts : $e^{-\beta H} \frac{\partial H}{\partial p_i} = \frac{d}{dp_i}\left(e^{-\beta H}\right) \cdot \left(-\frac{1}{\beta}\right)$.

- we have : $\int d^{3N}p \cdot d^{3N}q \; e^{-\beta H} p_i \frac{\partial H}{\partial p_i}$

$$= \int \underbrace{\left\{ d^{3N}p \cdot d^{3N}q \cdot dp_i \right\}}_{\substack{\text{integrating on all } d^{3N}p \, d^{3N}q \\ \text{except } dp_i}} \left[p_i \, e^{-\beta H} \left(-\frac{1}{\beta}\right) \right]_{p_i=-\infty}^{p_i=+\infty} + \frac{1}{\beta} \int d^{3N}p \, d^{3N}q \; e^{-\beta H}$$

- As $H(p_i \to \pm\infty) \to \infty$, the first term vanishes, so we get:

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = k_B T.$$

- Analogous calculations give

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = k_B T$$

- So, that if H is of the form:

$$H = \sum_{j=1}^{M} A_j p_j^2 + \sum_{j=1}^{M'} B_j q_j^2 \text{ , then we will have:}$$

$$2H = \sum_{j=1}^{M'} q_j \frac{\partial H}{\partial q_j} + \sum_{j=1}^{M} p_i \frac{\partial H}{\partial p_i}$$

- And so we get $\langle 2H \rangle = \left\langle \sum_{j=1}^{M'} q_j \frac{\partial H}{\partial q_j} + \sum_{j=1}^{M} p_j \frac{\partial H}{\partial p_j} \right\rangle$

$$= (M + M') k_B T.$$

$$U = \frac{1}{2}(M+M')k_BT \xrightarrow{M+M'=3N} U = \frac{3N}{2}k_BT$$

- which is the equipartition theorem:

- Notice also that

$$\sum_i \langle q_i \frac{\partial H}{\partial q_i} \rangle = -\sum_i \langle q_i \dot{p}_i \rangle = -\mathcal{V}$$

where $\mathcal{V}$ is the so-called virial of the system.

- if our system has 3N degrees of freedom, then we get immediately:

$$\mathcal{V} = -3Nk_BT.$$

- Now, consider an ideal gas: In this case, the only forces acting on the molecules are the ones of the container of the gas. So, the force is $-P\,ds\,\hat{n}$, where P is pressure, ds is the surface element of the walls of the container and $\hat{n}$ is the outward normal.

- Being $\dot{p}_i = f_i$ the ith component of the force, we get.

$$\mathcal{V} = \sum_i q_i F_i = -P\oint_S \vec{r}\cdot\vec{n}\,ds \xrightarrow[\text{theorem}]{\text{divergence}} -P\int_{Vol}(\vec{\nabla}\cdot\vec{r})\,dV = -3PV$$

- so that we obtain for an ideal gas:

$$PV = Nk_BT$$

- <u>Grand Canonical Ensemble</u> is used to describe systems that can exchange energy and matter with a reservoir (open system).

- An analysis analogus to the one made to derive the canonical distribution tells us that the probability to find the system in a state with energy E and number of particles N is:

$$P(E,N) \propto \exp\left[-\alpha N - \beta E\right]$$

where $\alpha = \dfrac{-\mu}{k_BT}$ and $\beta = \dfrac{1}{k_BT}$.

- It makes sense to define the grand canonical partition function as:

$$\mathcal{Q}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{Q_N(V,T)}_{\text{This is just a } N \text{ particle partition function.}}.$$

- $e^{\beta\mu}$ is the so-called fugaty.

- let's see which thermodynamic potential this is related to ...

$$dU = TdS - PdV + \mu dN$$

$$d(U - TS - \mu N) = d(A - \mu N) = -SdT - PdV + Nd\mu$$

- Up to now nothing is new, but now notice:

$$\left(\frac{\partial(U - TS - \mu N)}{\partial V}\right)_{T,\mu} = -P$$

- But now: $U - TS - \mu N$ depends only on μ, T, and V. μ and T are intensive variables, while V is an extensive variable.
- Since P is intensive, the differential above can be integrated, giving

a function that does not depend on (P, V)

$$U - TS - \mu N = -PV + \Delta(\mu, T).$$

where $P = P(\mu, T)$.

- Notice that, as U, TS, μN and PV are extensive quantities, Δ should also be extensive. But, as it depends only on intensive variables, it has to vanish. So, we find:

$$\left(\frac{\partial(PV)}{\partial V}\right)_{T,\mu} = P \quad (\text{obvious})$$

$$\left(\frac{\partial (PV)}{\partial T}\right)_{V,\mu} = S \quad ; \quad \left(\frac{\partial (PV)}{\partial \mu}\right)_{T,V} = N$$

Compare this with:

$$\frac{1}{Q}\frac{\partial Q}{\partial \mu} \cdots$$

$$\left(\frac{\partial \ln Q}{\partial \mu}\right)_{V,T} = \beta \langle N \rangle .$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{\mu,T} = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{Q} \frac{\partial Q_N(T,V)}{\partial V} = \frac{P}{k_B T} .$$

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{\mu,V} = -\frac{1}{k_B T^2}\left(\frac{\partial \ln Q}{\partial \beta}\right)_{\mu,V} =$$

$$= \frac{-1}{k_B T^2}\left[\mu\langle N\rangle + \frac{1}{Q}\sum_{N=0}^{\infty} e^{\beta\mu N}\frac{\partial Q_N}{\partial \beta}\right] .$$

$$= -\frac{1}{k_B T^2}\left[\mu\langle N\rangle - U\right] .$$

$$S = -k_B \langle \ln P_N(V,T)\rangle$$

probability: see page 29/41

$$= \sum \frac{1}{Q} e^{+\beta\mu N - \beta H}\{-\ln Q - \beta H + \beta\mu N\} \rightarrow$$

$$S = k_B \ln Q + k_B \beta U - k_B \beta \langle N\rangle$$

grand canonical potential.

$$\Phi = k_B T \ln Q(\mu, T, V) .$$

$$\Phi = U - TS - \mu\langle N\rangle$$

- In many cases, grand canonical partition function, is more easy to compute than the canonical one. As the constraint may be difficult to realize.

- A side note: interpretation of μ:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

- So μ is how the energy of the system changes, when I add a particle to it while keeping S and U constant.

- For example, consider a system of harmonic oscillators:

$$\mu = \frac{1}{2}\hbar\omega + k_B T \ln\left(1 - e^{-\hbar\omega/k_B T}\right)$$

- For $k_B T \to 0 \Rightarrow \mu = \frac{1}{2}\hbar\omega$: if we add a particle at 0 temperature, it goes to the ground state, and energy increases by $\frac{\hbar\omega}{2}$

For $k_B T \gg \hbar\omega$, $\mu \approx -k_B T \ln\left(\frac{k_B T}{\hbar\omega}\right) < 0$

- How come this value is negative?

- Because of constraint S constant: adding a particle with energy $\sim k_B T$ increases the energy by $k_B T$, but this also increases the entropy by $\sim k_B \ln\left(\frac{k_B T}{\hbar\omega}\right)$ (This is because $S \sim N \ln N$)

- So that to keep S constant, I need to actually reduce the energy of the whole system.