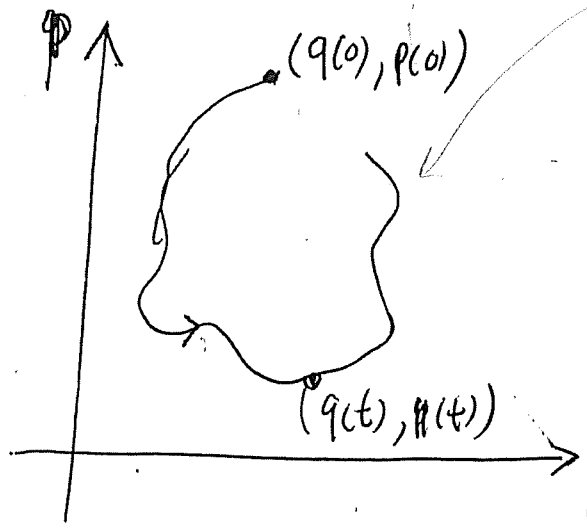
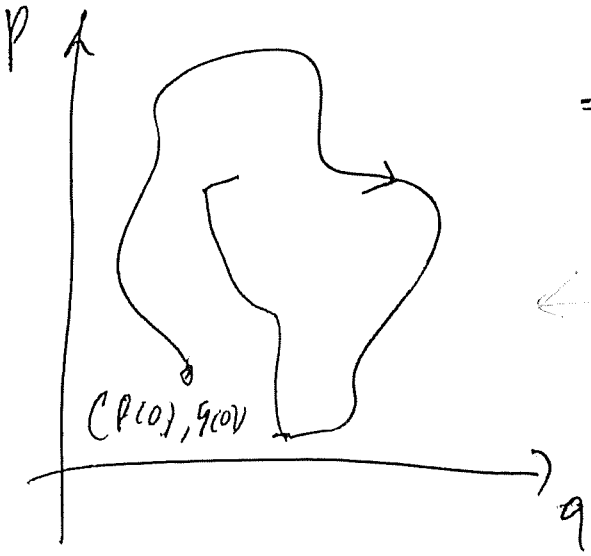
Classical Statistical physics

1) Concept of ensembles

~~We have seen that~~ We now revisit the a system of Classical gas again. We consider the state of a gas of N classical particles, given by $3N$ canonical coordinates $(q_1, q_2, \ldots, q_N) \equiv q$ and by $3N$ conjugate momentum $(p_1, p_2, \ldots, p_N) \equiv p$. These variables define a $6N$-dimensional space or phase space Γ, when each point on Γ represents a state of the microscopic system. (q, p).



The time evolution of the system can be represented as path, or trajectory, q through the phase space Γ of this system.



$\Rightarrow$ An observable G is an arbitrary function of (q, p): $G(p, q)$. The time-average value of starting at $t = 0$ with $(q(0), p(0))$ is depend (macroscopic equilibrium)

$$\langle \mathcal{O} \rangle_t(q_0, p_0) = \frac{1}{t} \int_0^t dt\, \mathcal{O}(p, q) \qquad (2)$$

which depends on the initial conditions (q_0, p_0)

$\Rightarrow$ As time passes, the trajectory of the system winds through the phase space. If the motion takes place in a bounded domain, one might expect that as $t \to \infty$ the average values of most observable settle down to some sort of <u>equilibrium</u> values (time-independent).

Q: What would the phase space trajectory look like if the system approached dynamical equilibrium?

A: One can say that the frequency with which different neighborhoods of the phase space are visited converges to a finite value $\rho(q, p)$ at each point in phase space.

ensemble.

For very large N, ~~the phase space~~ it is very difficult to ~~find~~ determine a particular position of each particle. However, what we are interested is the macroscopic quantities i.e., E, V and P which is a consequence of a large number of microstates. i.e., a large number of points in phase space.

: an ensemble of systems ~~which~~ is a set of all possible microstates.

Let the state of the ~~state~~ system be specified by a set (q, p) and postulate that the probability for the system to be in the neighborhood of the state (q, p) is

$$dp\,dq\,\rho(q,p) = \prod_{i=1}^{N} dp_i \prod_{i=1}^{N} dq_i\,\rho(q,p)$$

$dp\,dq\,\rho(q,p)$ ← the number of points contained in the small element volume.

$\prod_{i=1}^{N} dp_i \prod_{i=1}^{N} dq_i$ element volume of the phase space.

It gives the fraction of systems in the ensemble that are in the state (p, q).

Keeping with usual probabilistic notions, the probability measure has been normalized so that the integral of the probability measure for all possible states is unity

$$\int \frac{dp\,dq}{h^{3N} C}\,\rho(q,p) = 1$$

The ensemble average of the observable O is defined as

$$\langle O \rangle_\rho \equiv \int dp\,dq\,\rho(q,p)\,O(p,q)$$

$\Delta X \Delta p_x \geq \hbar$ with quantum correction

h is an arbitrary predetermined constant with units $q \times p$ time providing correct dimensions to ρ.

C is an overcounting correction factor (see below)

Birkhoff's theorem states that if the motion is restricted to a bounded domain, then for many initial conditions there exists an ensemble such that the time-average value of the observable equals an ensemble average

$$\lim_{t\to\infty} \langle \mathcal{O} \rangle_t (q_0, p_0) = \langle \mathcal{O} \rangle_\rho$$

which called the "ergodic hypothesis".

$\langle \mathcal{O} \rangle_t (q_0, p_0)$ becomes independent of initial conditions as $t \to \infty$. implies that the flow passes arbitrary close to any point q, p in phase space at some later time.

Liouville theorem

Suppose $\rho \equiv \rho(q, p, t)$, we find the total derivatives

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0$$

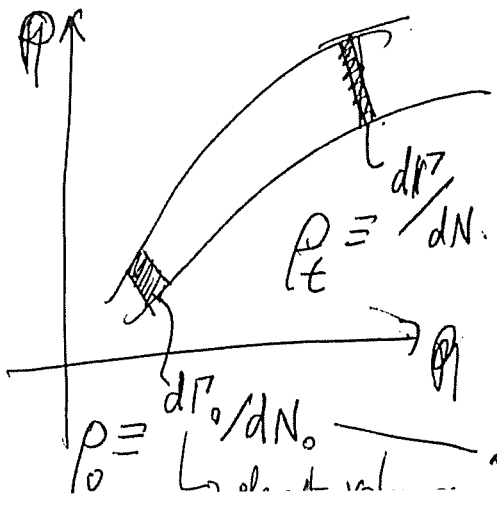
$$= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right)$$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{H, \rho\}$$

Liouville's theorem states that "The distribution function is constant along trajectory in phase space"

$$\Rightarrow \quad 0 = \frac{\partial \rho}{\partial t} + \{H, \rho\}$$

Then one can imagine the motion of the ensemble in phase space to be like the flow of a fluid.



$$\rho_t = \rho_0$$

$$\boxed{d\Gamma = d\Gamma_0}.$$

Equilibrium ensembles

At equilibrium we have a requirement that $\rho \equiv \rho(t)$.

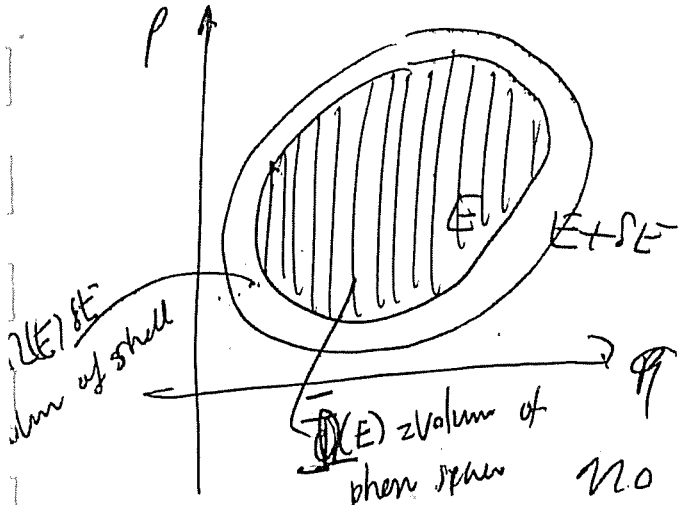
$$\Rightarrow \quad 0 = \{H, \rho\}$$

Since H is conserved, then ρ must be a function of conserved quantities, i.e., energy, number of particles.

$\Rightarrow$ The system changes its microscopic state continually even in equilibrium, but the distribution of microscopic states within the ensemble becomes time-independent.

As the evolution of (p, q) conserves the energy, this leads naturally to consider an ensemble of states of a fixed energy (internal energy) called microcanonical ensemble.

We now consider an isolated system with a fixed number of particles, fixed volume V and energy varying between E and $E+\delta E$ where δE is very small.



The region of phase space between hypersurface E and $E+\delta E$ is called the energy shell. At equilibrium no particular region of the energy shell should play a special role; i.e. all points in shell have the same statistical weight.

$$\sigma = \{H, \rho\}$$

The microcanonical distribution function ρ can be postulated to have the form

$$\rho(q,p) = \begin{cases} \dfrac{1}{\Omega(E)\,\delta E} & ; E < H(p,q) < E+\delta E \\ 0 & ; \text{otherwise} \end{cases}$$

Cont.

(Surface area of energy shell)

where the normalized constant $\Omega(E)$ depends only on E (only conserved quantity here). $\Omega(E)\,\delta E$ is the volume of the energy shell.

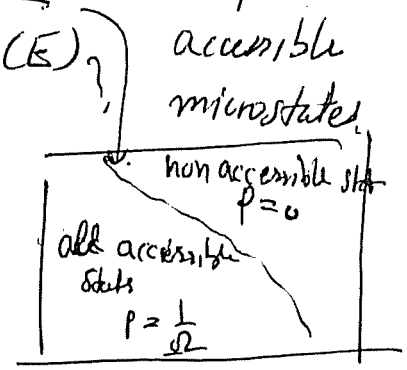
$$\bar{\Omega}(E+\delta E) - \bar{\Omega}(E) \simeq \frac{\partial \bar{\Omega}}{\partial E}\delta E \equiv \Omega(E)\,\delta E$$

In the limit $\delta E \to 0$, we have

$$\rho(q,p) = \frac{1}{\Omega(E)}\,\delta(E - H(q,p))$$

$\Omega(E) \to$ "partition function" $\equiv$ all possible accessible microstates

The normalisation determines $\Omega(E)$,



$$\int \frac{dp\,dq}{h^{3N} C}\,\rho = 1.$$

$C = N!$ called as "correct Boltzmann counting".

The classic example of this overcounting is a system of indistinguishable particles

$$E \equiv \frac{p_1^2}{2} + \frac{p_2^2}{2} \quad \text{or} \quad \frac{p_2^2}{2} + \frac{p_1^2}{2}$$

$2!$

$$E = \frac{p_1^2 + p_2^2 + p_3^2}{2} \quad \text{or} \quad \frac{p_1^2 + p_3^2 + p_2^2}{2}$$

$$\text{or} \quad \frac{p_3^2 + p_1^2 + p_2^2}{2} \quad \text{or} \quad \frac{p_3^2 + p_2^2 + p_1^2}{2}$$

$$\text{or} \quad \frac{p_2^2 + p_3^2 + p_1^2}{2} \quad \text{or} \quad \frac{p_2^2 + p_3^2 + p_1^2}{2}$$

$3! = 6$.

The mean value of observable O is given by

$$\langle O \rangle = \int \frac{dpdq}{h^{3N} N!} \rho O$$

and Normalisation condition gives

$$\Omega(E) = \int \frac{dpdq}{h^{3N} N!} \delta(E - H(p,q))$$

$$= \frac{d}{dE} \int \frac{dpdq}{h^{3N} N!} \theta(E - H(p,q))$$

$$= \frac{d}{dE} \bar{\Omega}(E)$$

The Classical Ideal gas.

Now we will demonstrate how to compute $\Omega(E)$. We consider a classical system of N atoms with no internal interaction.

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

$$\Rightarrow \Omega(E) = \frac{1}{h^{3N} N!} \int_V d^3x_1 \dots \int_V d^3x_N \int d^3p_1 \dots \int d^3p_N \, \delta\left(E - \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)$$

and

$$\bar{\Omega}(E) = \frac{1}{h^{3N} N!} \int d^3x_1 \cdots \int d^3x_N \int d^3p_1 \cdots \int d^3p_N \, \Theta\left(E - \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)$$

Consider the d-dimensional Gaussian integral

$$I = \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_d \, e^{-(p_1^2 + \cdots p_d^2)} = \left(\sqrt{\pi}\right)^d$$

in spherical polar coordinates:

$$I = \int_0^\infty dp \, p^{d-1} \int d\Omega_d \, e^{-p^2}$$

($d\Omega_d$: an element area on the d-dimensional unit sphere.)

$$= \frac{1}{2} \int_0^\infty dt \, t^{\frac{d}{2}-1} e^{-t} \int d\Omega_d$$

$$= \frac{1}{2} \Gamma\left(\frac{d}{2}\right) \int d\Omega_d$$

$$\Rightarrow \int d\Omega_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$$

Then we introduce the surface area of the d-dimensional unit sphere

$$(2\pi)^d K_d \equiv \int d\Omega_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$$

Then

$$\bar{\Omega}(E) = \frac{1}{h^{3N} N!} \underbrace{\int_V d^3x_1 \cdots \int_V d^3x_N}_{V \cdots V} \int d^3p_1 \cdots \int d^3p_N \, \theta(\ldots)$$

V^N

$$E - \sum_{i=1}^{3N} \frac{p_i^2}{2m} = 0.$$

$$p = \sum_{i=1}^{3N} p_i^2 = 2mE$$

$$p = \sqrt{2mE}$$

$$= \frac{V^N}{h^{3N} N!} \int_0^{\sqrt{2mE}} dp \, p^{3N-1} \int d\Omega_{3N}.$$

$$= \frac{V^N 2(\pi mE)^{3N/2}}{h^{3N} N! \, \Gamma(3N/2) \, 2N}; \quad \Gamma(3N/2) = \left(\frac{3N}{2} - 1\right)!$$

$$\int_0^{\sqrt{2mE}} p^{3N-1} = \frac{(2mE)^{3N/2}}{3N} = \frac{V^N (2\pi mE)^{3N/2}}{h^{3N} N! (3N/2)!}$$

For very large N

$\Rightarrow N! \sim N^N e^{-N} (2\pi N)^{1/2}$ Stirling formula.

$$\bar{\Omega}(E) \simeq \left(\frac{V}{N}\right)^N \left(\frac{4\pi mE}{3h^2E}\right)^{3N/2} e^{3N/2}$$

Similarly, we find

$$\Omega(E) = \frac{V^N \, 2\pi m \, (2\pi mE)^{\frac{3N}{2}-1}}{h^{3N} N! \left(\frac{3N}{2}-1\right)!}$$

$N \to \infty$

$$\Omega(E) \cong \left(\frac{V}{N}\right)^N \left(\frac{4\pi mE}{3h^2N}\right)^{\frac{3N}{2}} e^{\frac{5N}{2}} \frac{1}{E} \frac{3N}{2}$$

$$= \bar{\Omega}(E) \frac{3N}{2} \frac{1}{E}$$

The entropy is

$$S = -k_B \, \mathrm{Tr}(\rho \log \rho)$$

trace operation Tr is an integration over phase space.

$$= -k_B \, \mathrm{Tr}\left(\rho \log\left(\frac{1}{\Omega(E)\delta E}\right)\right)$$

$$= -k_B \log\left(\frac{1}{\Omega(E)\delta E}\right) \mathrm{Tr}\,\rho \qquad \int \frac{dpdq}{h^{3N} N!} \rho = 1$$

$$= k_B \log\left(\Omega(E)\,\delta E\right)$$

Thus the entropy is proportional to the logarithm of the accessible phase space volume.

We find that for large N

$$\log(\Omega(E)\delta E) = \log(\bar{\Omega}(E)) + \mathcal{O}\left(\log \frac{E}{N\delta E}\right)$$

or

$$\log(\Omega(E)\delta E) \cong \log(\bar{\Omega}(E))$$

Then the entropy

$$S = k_B \log(\bar{\Omega}(E)) \quad \text{(Boltzmann entropy)!!}$$

$$= N k_B \log\left[\frac{V}{N}\left(\frac{4\pi m E}{3h^2 N}\right)^{3/2}\right] + \frac{5}{2} k_B N.$$

for classical ideal gas.

We now can solve for $E = U$.

$$U = E = \frac{3N^{5/3}h}{4\pi m V^{2/3}} e^{\frac{2S}{3Nk_B} - \frac{5}{3}}$$

Then we can find

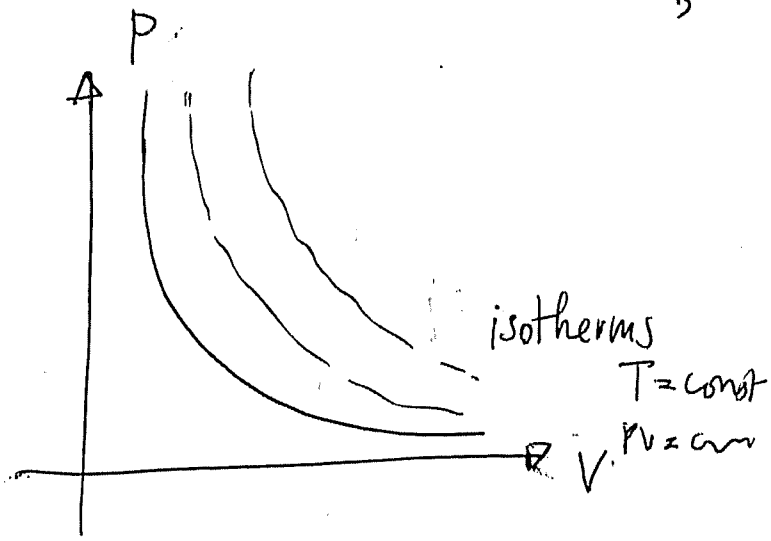
$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{2U}{3Nk_B} \Rightarrow U = \frac{3}{2} N k_B T \quad \text{!!}$$

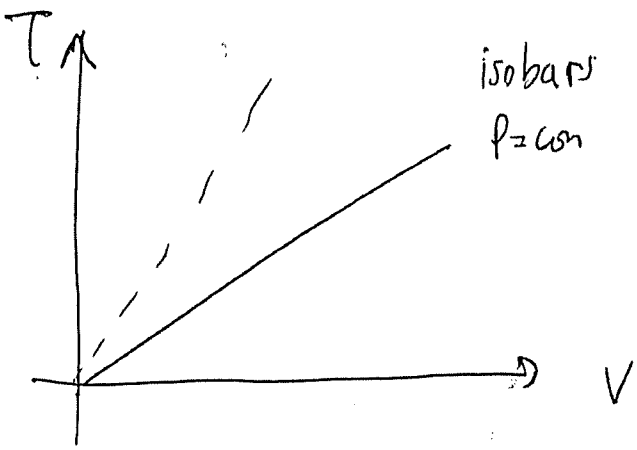
$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \frac{2U}{3V} = \frac{N k_B T}{V}$$

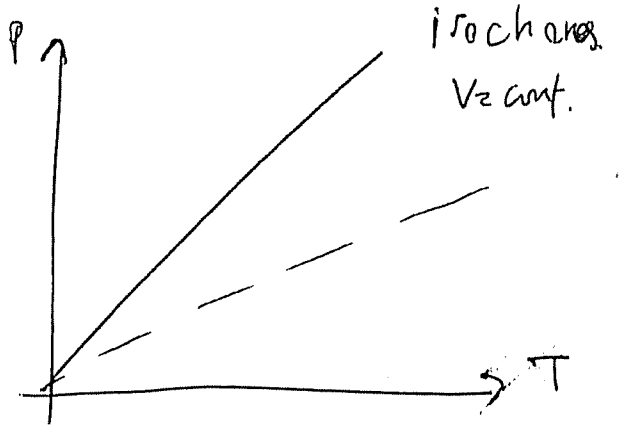
$$\Rightarrow \quad pV = N k_B T \quad !!$$

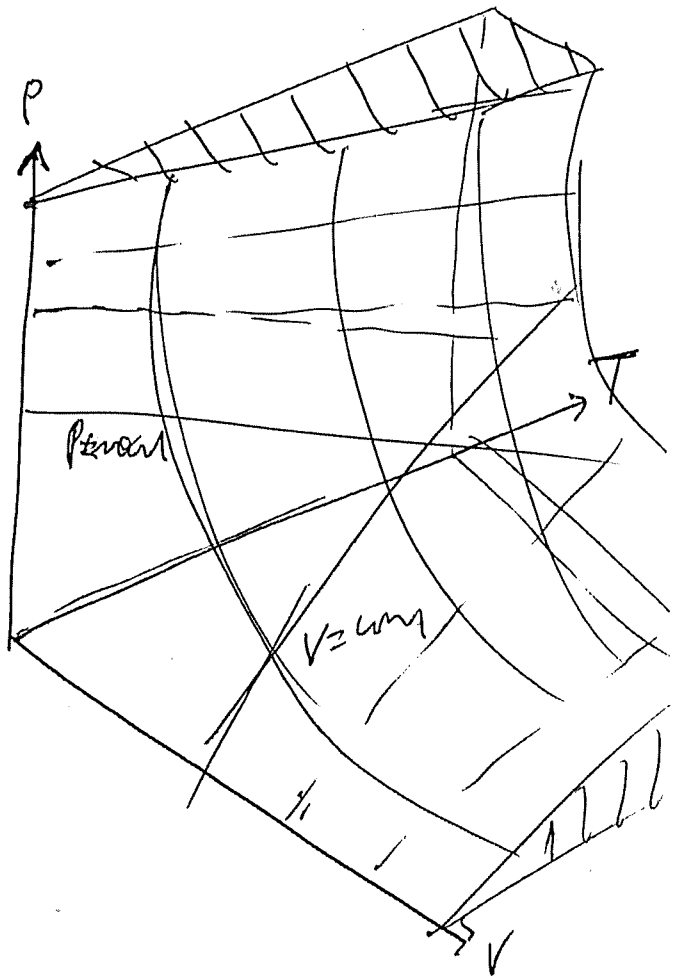
$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,N} = \frac{U}{N}\left(\frac{5}{3} - \frac{2}{3}\frac{S}{N k_B}\right)$$

$$= -k_B T \ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right)$$



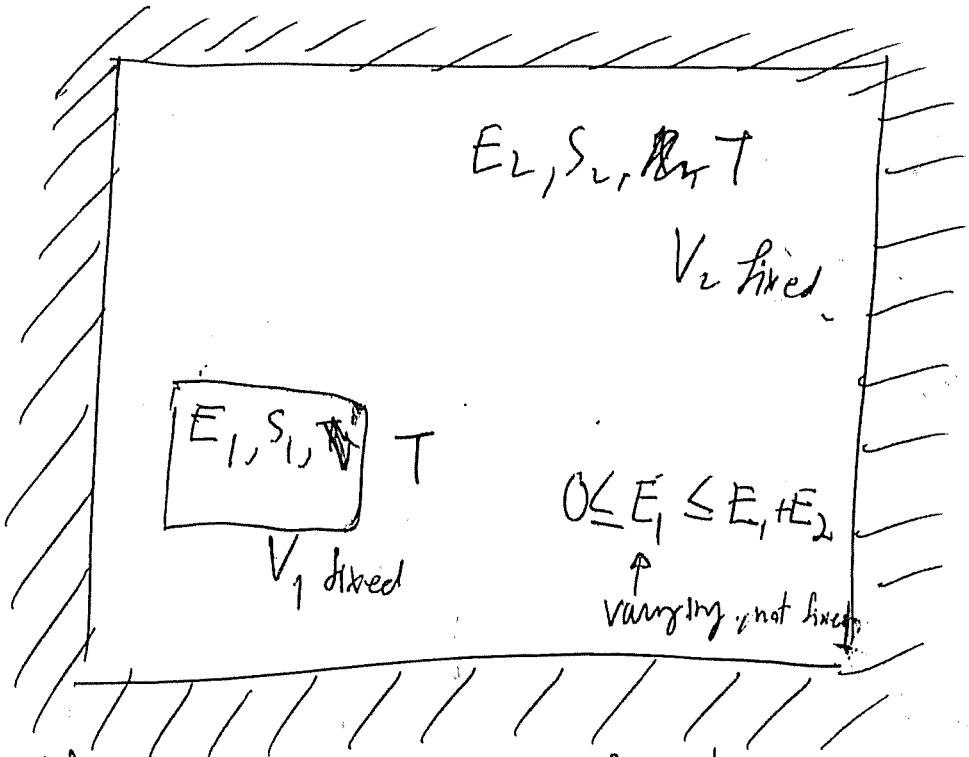






The canonical ensemble

We consider the system ① embbedded in the reservoir (system ②) and we consider the system as a whole.



The Hamiltonian is

$$H = H_1 + H_2 + W$$

interaction ≈ small

Then we find the micro canonical density matrix

$$\rho = \frac{1}{\Omega_{1,2}(E)} \delta(E - H_1 - H_2)$$

$$H_1 + H_2 - E$$

and let $w(E_1)$ be the prob density for subsystem ① to have the energy E_1 given by

$$w(E_1) = \langle \delta(H_1 - E_1) \rangle$$

$$= \int \frac{dp_1 dq_1}{h^{3N} N_1!} \int \frac{dp_2 dq_2}{h^{3N} N_2!} \cdot \rho \, \delta(H_1 - E_1)$$

$$= \int d\Gamma_1 \int d\Gamma_2 \, \frac{\delta(H_1 + H_2 - E)\,\delta(H_1 - E_1)}{\Omega_{1,2}(E)}$$

$$= \frac{\Omega_2(E - E_1)\,\Omega_1(E_1)}{\Omega_{1,2}(E)} \quad \text{— (a)}$$

where $\Omega_1(E_1) = \int d\Gamma_1 \, \delta(H_1 - E_1)$

$$\Omega_2(E - E_1) = \int d\Gamma_2 \, \delta(H_2 - \underbrace{E + E_1}_{E_2}) \quad \text{— (b)}$$

The most probable value of E_1 denoted by E_1^* can be found by: $\frac{d\,\omega(E_1)}{dE_1} = 0$

$$\Rightarrow -\frac{d}{dE_1}\Omega_2(E - E_1)\,\Omega_1(E_1)\Big|_{E_1^*} + \Omega_2(E - E_1)\frac{d}{dE_1}\Omega_1(E_1)\Big|_{E_1^*} = 0$$

Using $S = k_B \log(\Omega(E)\delta E)$

$$\frac{dS}{\partial E} = \frac{k_B}{\Omega(E)}\,\frac{\partial \Omega(E)}{\partial E}\,\delta E$$

$E = E_1 + E_2$

$0 = dE_1 + dE_2$

Thus

$$\frac{1}{\Omega_2(E_2)} \frac{d}{dE_1} \Omega_2(E - E_1)\Big|_{E_1^*} = \frac{1}{\Omega_1(E_1)} \frac{d}{dE_1} \Omega_1(E_1)\Big|_{E_1^*}$$

$$-\frac{1}{\Omega_2(E_2)} \frac{d}{dE_2} \Omega_2(E_2)\Big|_{E - E_1^*} = \frac{1}{\Omega_1(E_1)} \frac{d}{dE_1} \Omega_1(E_1)\Big|_{E_1^*}$$

$$-\frac{1}{k} \frac{\partial}{\partial E_2} S_2(E_2)\Big|_{E - E_1^*} = \frac{1}{k} \frac{\partial}{\partial E_1} S_1(E_1)\Big|_{E_1^*}$$

Using the definition of temperature

$$\Rightarrow \quad T_1 = T_2 \qquad \text{\#!!}$$

The most probable configuration, the temperatures of the two subsystems are equal.

Once we know the total energy [8.

$$E = E_1 + E_2$$

Then the microcanonical ensemble of the total system is

$$\Omega_{1,2}(E) = \sum_{0 \le E_1 \le E} \Omega_1(E_1)\,\Omega_2(E - E_1)$$

(from (9) page 16)

$$\omega(E_1)\,\Omega_{1,2}(E) = \Omega_1(E_1)\,\Omega_2(E - E_1)$$

$$\Rightarrow \underbrace{\sum_{E_1} \omega(E_1)}_{1}\,\Omega_{1,2}(E) = \sum_{E_1} \Omega_1(E_1)\,\Omega_2(E - E_1)$$

$$\Omega_{1,2}(E) = \sum_{0 \le E_1 \le E} \Omega_1(E_1)\,\Omega_2(E - E_1)$$

What we want to compute next is the ρ_1 for ~~each~~ sub system (1). We start ~~we~~ to write

$$\langle A \rangle_1 = \int d\Gamma_1 \int d\Gamma_2\, A(p_1, q_1)\, \rho(q, p)$$

$$= \int d\Gamma_1\, \rho_1(p_1, q_1)\, A(p_1, q_1)$$

When we define

$$\rho_1(q_1, p_1) \equiv \int d\Gamma_2 \, \rho(q, p)$$

$$= \int d\Gamma_2 \frac{\delta(H_1 + H_2 - E)}{\Omega_{1,2}(E)}$$

Using (b) page 16.

$$\rho_1(q_1, p_1) = \frac{\Omega_2(E - H_1)}{\Omega_{1,2}(E)}$$

and using the fact that $E \simeq E_2 \gg E_1$, then we may expand $\Omega_2(E - H_1)$ in terms of H_1.

$$\Rightarrow k_B \log \Omega_2(E - H_1) = S_2(E - H_1)$$

$$= S_2(E) - H_1 \frac{\partial S_2}{\partial E_2}\Big|_{E_2 = E} + \dots$$

$$= S_2(E) - \frac{H_1}{T} + \dots$$

Here we use $\left(\frac{1}{T}\right) = k_B \frac{\partial}{\partial E_2} \log \Omega_2(E - H_1)$ (both temperature / both system).

$$= k_B \frac{\partial}{\partial E} \log \Omega_2(E - H_1)$$

$$\Rightarrow \quad \Omega_2(E-H_1) = e^{S_2(E)/k_B} \cdot e^{-H_1/k_BT} \cdot \frac{1}{\Omega_2(E)}$$

$$\log \Omega_2(E-H_1) = \log \Omega_2(E)$$

$$+ \; -H_1 \frac{\partial}{\partial E_2} : - \; .$$

$$\Rightarrow \quad \frac{\Omega_2(E-H_1)}{\Omega_2(E)} = e^{-H_1/k_BT}$$

$$\Rightarrow \quad \rho_1(p_1, q_1) = \frac{\Omega_2(E)\, e^{-H_1/k_BT}}{\Omega_{1,2}(E)}$$

Canonical density: $\rho_C \equiv \rho_1$

$$= \frac{e^{-H_1/k_BT}}{Z}$$

Z → normalisation factor !!

$$Z \equiv \frac{\Omega_2(E)\, \Omega_{1,2}(E)}{\Omega_2(E)}$$

$$= \frac{\Omega_{1,2}(E)}{\Omega_2(E_1+E_2)} \equiv \frac{\Omega_{1,2}(E)}{\Omega_2(E_2)\, e^{E_1/k_BT}}$$

$$= \frac{\Omega_{1,2}(E)}{\Omega_{1,2}(E)}\, e^{-E_1/k_BT}$$

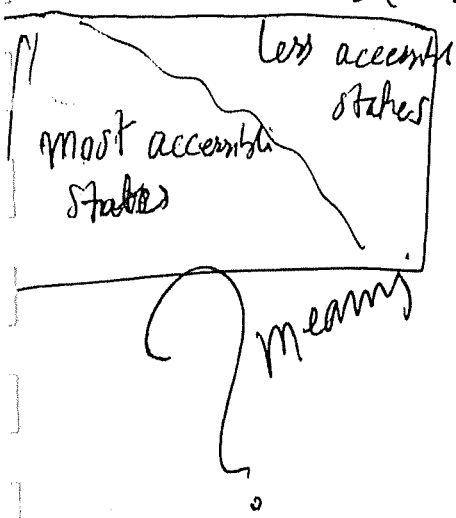
Z is called the "partition function"

Using definition

$$\Omega_1(E) = \int \frac{dp\,dq}{h^{3N} N!}\,\delta(H - E)$$

$$\Rightarrow \frac{\Omega_{1,2}(E)}{\Omega_2(E_2)} = \frac{\int dp\,dq\,\delta(H-E)}{\int dp_2\,dq_2\,\delta(H_2 - E_2)}$$

$$\frac{\Omega_{1,2}(E)}{\Omega_2(E_2)} = \sum_{E_1} \frac{\Omega_1(E_1)\,\Omega_2(E_2)}{\Omega_2(E_2)}$$



$$= \sum_{E_1} \Omega_1(E_1)$$

$$= \int dE_1 \int \frac{dp_1\,dq_1}{h^{3N} N!}\,\delta(H_1 - E_1)$$

$$\Rightarrow Z = \int dE_1 \int \frac{dp_1\,dq_1}{h^{3N} N!}\,\delta(H_1 - E_1)\, e^{-E_1/k_B T}$$

$$= \int \frac{dp_1\,dq_1}{h^{3N} N!}\, e^{-H_1/k_B T}$$

Entropy of canonical ensemble

$$= -k_B \langle \log \rho_C \rangle$$

$$S_C = -k_B \, Tr(\rho \log \rho_C)$$

($\log_e = \ln$)

$$= -k_B \, Tr \, \rho \log \left(\frac{e^{-\beta H_1}}{Z} \right) \quad ; \beta = \frac{1}{k_B T}$$

$$= -k_B \left[-\beta \langle H_1 \rangle - \ln Z \right]$$

$$S_C = \frac{\langle H_1 \rangle}{T} + k_B \ln Z$$

$$\Rightarrow -k_B T \ln Z = U - TS \quad ; U = \langle H_1 \rangle$$

$$F = U - TS$$ (Helmholtz free energy)

$$\boxed{Z = e^{-\beta F}}$$

$$\boxed{F = -k_B T \ln Z}$$

Fixed V, fixed N?

$\ln$

$\frac{\partial Z}{\partial \beta} = -F e^{-\beta F} \Rightarrow$

$$U = \langle H_1 \rangle = \int d\Gamma_1 \, H_1 \rho_C$$

$$= \int d\Gamma_1 \, H_1 \frac{e^{-\beta H_1}}{Z}$$

$$= \frac{1}{Z} \int d\Gamma_1 \, H_1 e^{-\beta H_1}$$

$$\boxed{U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}}$$ — defining Z.

Equipartition Theorem

Consider the quantity $y_i \frac{\partial H}{\partial y_i}$; $y = \beta q$.

$$\left\langle y_i \frac{\partial H}{\partial y_j} \right\rangle = \frac{1}{Z} \int d\Gamma \, y_i \frac{\partial H}{\partial y_j} e^{-\beta H}$$

$$= \frac{1}{Z} \int d\Gamma \, y_i \frac{\partial e^{-\beta H}}{\partial y_j} \beta \left(\frac{1}{\beta}\right)$$

$$= \frac{1}{Z} \beta \left[\int d\Gamma \, e^{-\beta H} y_i - \int d\Gamma \, e^{-\beta H} \frac{\partial y_i}{\partial y_j} \right]$$

drops off rapidly as $y \to \infty$

$$= \beta \delta_{ij}$$

$$H = T(p) + V(q)$$

Ex $$V(q) = \sum_i V_i = \sum_i \frac{m\omega^2 q_i^2}{2}$$

$$\left\langle q_i \frac{\partial V_i}{\partial q_j} \right\rangle = m\omega^2 q_i^2 = m\frac{\omega^2 q_i^2}{2}$$

$$= 2\langle V_i \rangle$$

$$\frac{k_B T}{2} = \langle V_i \rangle$$

↓ average value of potential of each degree of freedom.

$$\langle V \rangle = 3N \frac{k_B T}{2} \quad \#$$

$$\left\langle p_i \frac{\partial T}{\partial p_j} \right\rangle = 2\langle T_i \rangle \Rightarrow \langle T_i \rangle = \frac{k_B T}{2}$$

$$\Rightarrow \langle T \rangle = 3N \frac{k_B T}{2}$$

$$\langle H \rangle = \langle T \rangle + \langle V \rangle = 3N k_B T \quad \#.$$

Ideal gas

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m}.$$

$$Z = \int d\Gamma\, e^{-\beta H} = \frac{1}{h^{3N} N!} \int d^3q_1 \cdots \int d^3q_N \int d^3p_1 \cdots \int d^3p_N$$

$$e^{p^2/2mk_BT}.$$

where $p^2 = p_1^2 + p_2^2 + p_3^2 + \cdots p_N^2$

$$= \frac{1}{h^{3N} N!} \left(\int d^3q \int d^3p\, e^{p^2/2mk_BT} \right)^N$$

$$= \frac{V^N}{h^{3N} N!} \left(\int d^3p\, e^{p^2/2mk_BT} \right)^N$$

$$Z = \frac{V^N}{h^{3N} N!} \left(2\pi m k_B T \right)^{3N/2} \longrightarrow N \text{ very large.}$$

$$N! \sim N^N e^{-N} (2\pi N)^{1/2}$$

$$F = -k_B T \ln Z = -N k_B T \ln \left(\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right)$$

$$-N k_B T$$

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{3N}{2} k_B T$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -\left(-k_B T \frac{\partial \ln Z}{\partial T}\right)$$

$$= N k_B \ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) + \frac{5N}{2} k_B$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(-k_B T \frac{\partial \ln Z}{\partial V}\right)$$

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

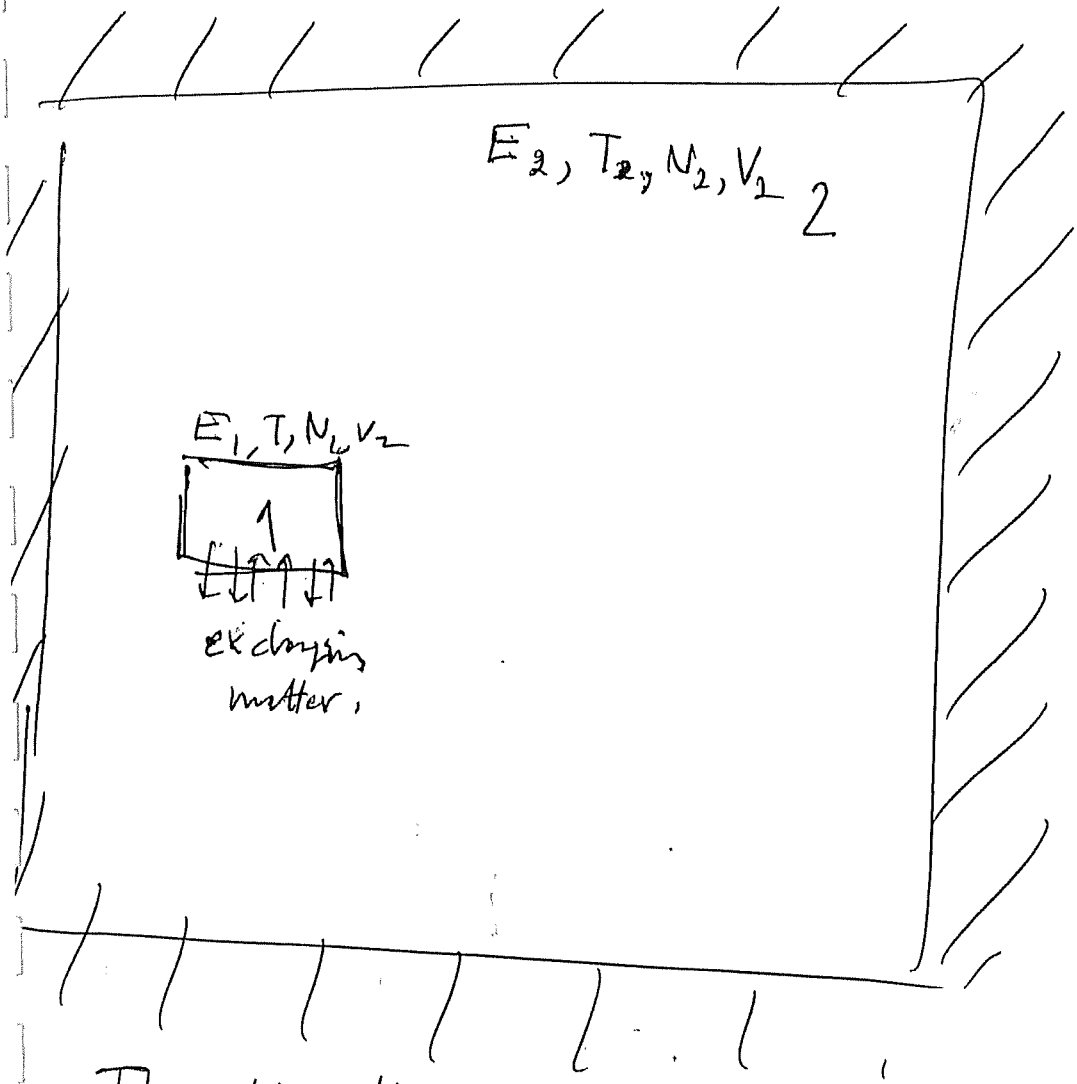
$$PV = N k_B T$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right)$$

We have seen that we can compute the internal quantity through the partition function!! Z.

Later we will see ~~that it turns out.~~ the partition function turns out to be the most important quantity in Statistical Mechanics.

Grand canonical ensemble



A whole system is isolated

$N = N_1 + N_2$

$V = V_1 + V_2$

$N_1 \ll N_2$

$V_1 \ll V_2$

fixed.

The Hamiltonian is

$$H(q, p, N) = H(p_1, q_1, N_1) + H(p_2, q_2, N_2)$$

The partion fun for a whole system at given temperature T

$$Z_N(V, T) = \frac{1}{h^{3N} N!} \int dp\, dq\, e^{-\beta H(p, q, N)}$$

We are actually interested in subsystem (1)

$$Z_N(V, T) = \frac{1}{h^{3N} N!} \sum_{N_1=0}^{N} \frac{N!}{N_1!(N-N_1)!} \int dp_1\, dp_2 \int_{V_1} dq_1 \int_{V_2} dq_2$$

$$e^{-\beta (H(p_1, q_1, N_1) + H(p_2, q_2, N-N_1))}$$

When the factor $\frac{N!}{N_1!(N-N_1)!} = \frac{N!}{N_1!\,N_2!}$

accounts for the number of configurations with fixed N_1 and N_2 by permuting the particles in each subsystem.

$$Z_N = \sum_{N_1=0}^{N} \frac{1}{h^{3N_1} N_1!} \int_{V_1} dq_1 dp_1 \, e^{-\beta H(p_1, q_1, N_1)} \cdot \frac{1}{h^{3N_2} N_2!} \int_{V_2} dq_2 dp_2 \, e^{-\beta H(q_2, p_2, N_2)}$$

We now introduce the pro density for subsystem 1 to have the Energy E_1, number of particles N_1 and volume V_1

$$\omega(E_1, N_1, V_1) = \frac{\Omega_1(E_1, N_1, V_1)\, \Omega_2(E - E_1, N - N_1, V - V_1)}{\Omega_{1,2}(E, N, V)}$$

$$\Rightarrow \frac{d\omega}{dE_1} = 0 \Rightarrow T_1 = T_2$$

$$\Rightarrow \frac{\partial \omega}{\partial N_1} = 0 \Rightarrow \mu_1 = \mu_2$$

$$\mu = -k_B T \frac{\partial}{\partial N} \log \Omega(E, N)$$

$$\frac{d\Omega_1}{dN_1}\,\Omega_2\Big|_{N_1^*} = \Omega_1\frac{d\Omega_2}{dN_1}\Big|_{N_1^*} = 0$$

$$\frac{1}{\Omega_1}\frac{d\Omega_1}{dN_1}\Big|_{N_1^*} = -\frac{1}{\Omega_2}\frac{d\Omega_2}{dN_2}\Big|_{N-N_1^*}$$

$$\frac{1}{\Omega_1(E_1,N_1)}\frac{d\Omega_1(E_1,N_1)}{dN_1}\Big|_{N_1^*} = -\frac{1}{\Omega_2(E_2,N_2)}\frac{d\Omega_2(E_2,N_2)}{dN_2}\Big|_{N_2^*}$$

$$\frac{1}{\delta E_1}\frac{d\Omega_1}{dN_1}\Big|_{N_1^*} = -\frac{1}{\delta E_2}\frac{d\Omega_2}{dN_2}\Big|_{N_2^*}$$

$$+\frac{1}{\delta E_1}$$

$$\boxed{\mu_1 = \mu_2}$$

We obtain a condition for the maximum probability the equalization of temperature and chemical potential.

Then the microcanonical ensemble for a whole system is

$$\Omega_{1,2}(E,N) = \sum_{\substack{0 \le E_1 \le E \\ 0 \le N_1 \le N}} \Omega_1(E_1,N_1)\,\Omega_2(E-E_1,N-N_1)$$

Then we find the density matrix for subsystem ①

$$\rho_1(q_1,p_1) = \frac{\Omega_2(E-H_1,N-N_1)}{\Omega_{1,2}(E,N)}$$

Again, we expand Ω_2 with respect to H_1 and N_1 $\quad N \simeq N_2 \gg N_1$, $E \simeq E_2 \gg E_1 \simeq H_1$

$$\Rightarrow k_B \log \Omega_2(E-H_1,N-N_1) = S_2(E-H_1,N-N_1)$$

$$= S_2(E,N) - H_1 \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2=E} + \cdots$$

$$- N_1 \left.\frac{\partial S_2}{\partial N_2}\right|_{N_2=N} + \cdots$$

Using $\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)$

$$= S_2(E,N) - \frac{H_1}{T} + \frac{\mu N_1}{T}$$

~~$\log \Omega_2(E,N) = \log \Omega$~~

$$\log \Omega_2(E-E_1, N-N_1) \approx \log \Omega_2(E,N) - \frac{H_1}{k_B T} + \frac{\mu N_1}{k_B T}$$

$$\frac{\Omega_2(E-E_1, N-N_1)}{\Omega_2(E,N)} = e^{-(H_1 - \mu N_1)/k_B T}$$

$$\Rightarrow \rho_1(q_1, p_1) = \frac{e^{-(H_1 - \mu N_1)/k_B T} \, \Omega_2(E,N)}{\Omega_{1,2}(E,N)}$$

$$\| \quad \rho_G$$

$$= \frac{e^{-(H_1 - \mu N_1)/k_B T}}{Z_G}$$

Z_G) normalisation factor

$$Z_G = \frac{\Omega_{1,2}(E,N)}{\Omega_2(E,N)}$$

$$= \frac{\Omega_{1,2}(E,N)}{\Omega_2(E_1+E_2, N_1+N_2)} = \frac{\Omega_{1,2}(E,N)}{\Omega_2(E_2,N_2)\, e^{E_1/k_B T} e^{\mu N_1/k_B T}}$$

$$Z_G = \frac{\Omega_{1,2}(E,N)}{\Omega_2(E_2,N_2)} e^{-(E_1 - \mu N_1)/k_B T}$$

Using $\Omega_{1,2}(E,N) = \sum_{\substack{0 \le E_1 \le E \\ 0 \le N_1 \le N}} \Omega_1(E_1,N_1)\Omega_2(E-E_1,N-N_1)$

$$\Rightarrow Z_G = \sum_{E_1,N_1} \Omega_1(E_1) e^{-(E_1 - \mu N_1)/k_B T}$$

$$= \sum_{N_1} \int d\Gamma_1 \int dE_1 \, \delta(H_1 - E_1) e^{-(E_1 - \mu N_1)/k_B T}$$

$$\boxed{Z_G = \sum_{N_1} \int \frac{dp_1 dq_1}{h^{3N_1} N_1!} e^{-(H_1 - \mu N_1)/k_B T}}$$

The average value of an operator O in the grand canonical ensemble is

$$\langle O \rangle = \mathrm{Tr}(\rho_G O)$$

Entropy of grand canonical ensemble

$$S_G = -k_B \, Tr(\rho_G \log \rho_G)$$

$$= -k_B \, Tr \, \rho_G \left(\frac{e^{-\beta H_1 + \mu N_1 \beta}}{Z_G} \right)$$

$$= -k_B \left[-\beta \langle H_1 \rangle + \mu\beta \langle N_1 \rangle \right\} - \ln Z_G \Big]$$

$$S_G = \frac{1}{T} \left(\langle H_1 \rangle - \mu \langle N_1 \rangle \right) + k_B \ln Z_G \quad \text{**}$$

Rearranging

$$-k_B T \ln Z_G = \frac{\langle H_1 \rangle - \mu \langle N_1 \rangle - TS_G}{T}$$

$$= F - \mu \langle N_1 \rangle \equiv \Phi \quad \text{grand potential}$$

$$Z_G = e^{-\beta \Phi}$$

$$d\Phi = \left(\frac{\partial \Phi}{\partial T} \right)_{N,\mu} dT + \left(\frac{\partial \Phi}{\partial V} \right)_{T,\mu} dV + \left(\frac{\partial \Phi}{\partial \mu} \right)_{V,T} d\mu$$

$$= -S \, dT - p \, dV - N \, d\mu$$

The internal energy

$$\langle H_1 \rangle = U = -\frac{1}{Z_G}\frac{\partial Z_G}{\partial \beta}$$

$$\Rightarrow \quad C_V = \left(\frac{\partial U}{\partial T}\right)_{V,\mu}$$

Compute

$$\langle N_1 \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = +k_B T \frac{\partial}{\partial \mu} \ln Z_G$$

$$= \frac{k_B T}{Z_G}\frac{\partial}{\partial \mu} Z_G$$

$$= \sum_{N_1} \int \frac{dp_1 dq_1}{h^{3N_1} N_1!} N_1 e^{-(H_1 - \mu N_1)/k_B T}$$

$$\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = -k_B \ln Z_G = -S_G.$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} = \frac{5}{2} k_B \frac{V}{\lambda^3} + k_B T \left(-\frac{\mu}{k_B T^2}\right) \frac{V}{\lambda^3}$$

$$= \left(\frac{5}{2} k_B N - k_B \frac{\mu}{T} \frac{V}{\lambda^3}\right) N$$

$$= \frac{5}{2} k_B N - \frac{\mu N}{T}$$

对 W 求导

$$E = \Phi + TS + \mu N$$

$$= -k_B T N + T\left(\frac{5}{2} k_B N - \frac{\mu N}{T}\right) + \mu N$$

$$= \frac{3}{2} N k_B T \quad //$$

$$E = -\left(\frac{\partial \ln Z}{\partial \beta}\right) = \frac{3V}{\lambda^3} \frac{\partial \lambda}{\partial \beta} = \frac{3N}{\lambda} \frac{\partial \lambda}{\partial \beta}$$

$$\frac{\partial \lambda}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{h}{\sqrt{2\pi m \beta}} = -\frac{1}{2} h \sqrt{2\pi m \beta^3} (2\pi m)$$

$$= -\frac{1}{2} 2\pi m h \sqrt{2\pi m \beta}$$

$$\frac{3}{\lambda} N \frac{\partial}{\partial \beta} \ln \lambda$$

$$\frac{\partial}{\partial \beta} \ln \frac{h}{\sqrt{2\pi m \beta}} = \frac{1}{2} \frac{\partial}{\partial \beta} \ln (2\pi m \beta)$$

$$= -\frac{1}{2} \frac{1}{2\pi m \beta} (2\pi m)$$

Ideal gas

$$Z_G = \sum_{N} \frac{1}{N!\,h^{3N}} \int dq_1 \cdots dq_N \int dp_1 \cdots dp_N \, e^{-\beta \sum_{i=1}^{3N} p_i^2/2m}$$

$$= \sum_{N}^{\infty} \frac{1}{N!} e^{\beta\mu N} \left[\frac{V}{\lambda^3} \right]^N ; \lambda = \frac{h}{\sqrt{2\pi m k T}}$$

↑ thermal wavelength

$$= e^{z V/\lambda^3}$$

where $z = e^{\beta\mu}$ is the fugacity.

$$\Phi = -k_B T \log Z_G = -k_B T \, z V/\lambda^3$$

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = z V/\lambda^3$$

$$PV = -V \left(\frac{\partial \Phi}{\partial V}\right)_{T,V} = -\Phi$$

$$= N k_B T \quad !!$$

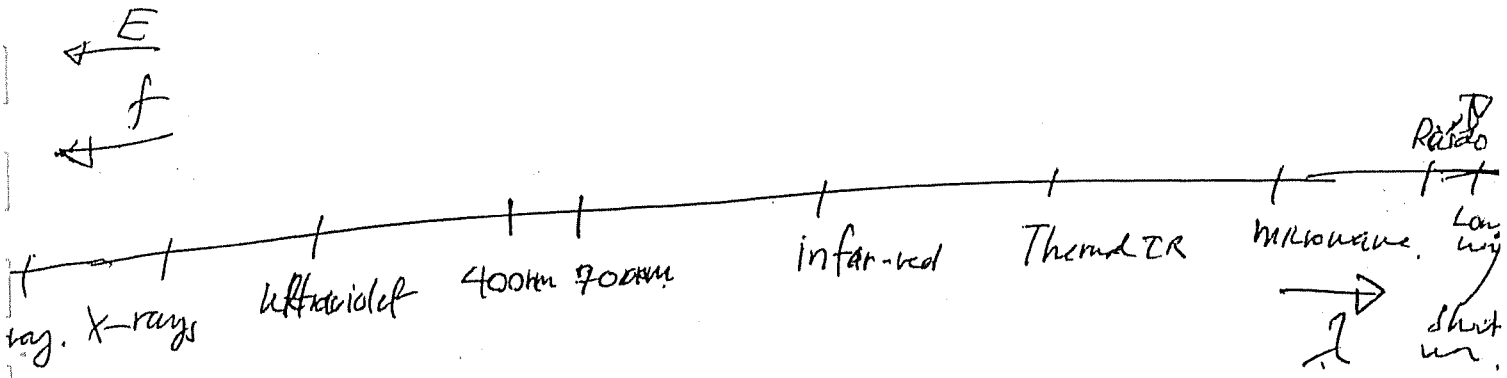
$$\log z = \beta\mu$$

$$\mu = \frac{1}{\beta} \log z = \frac{1}{\beta} \log \left(\frac{V/N}{\lambda^3} \right) = -k_B T \log \left(\frac{k_B T}{P \lambda^3} \right)$$

$$= k_B T \log P - k_B T \log k_B T$$

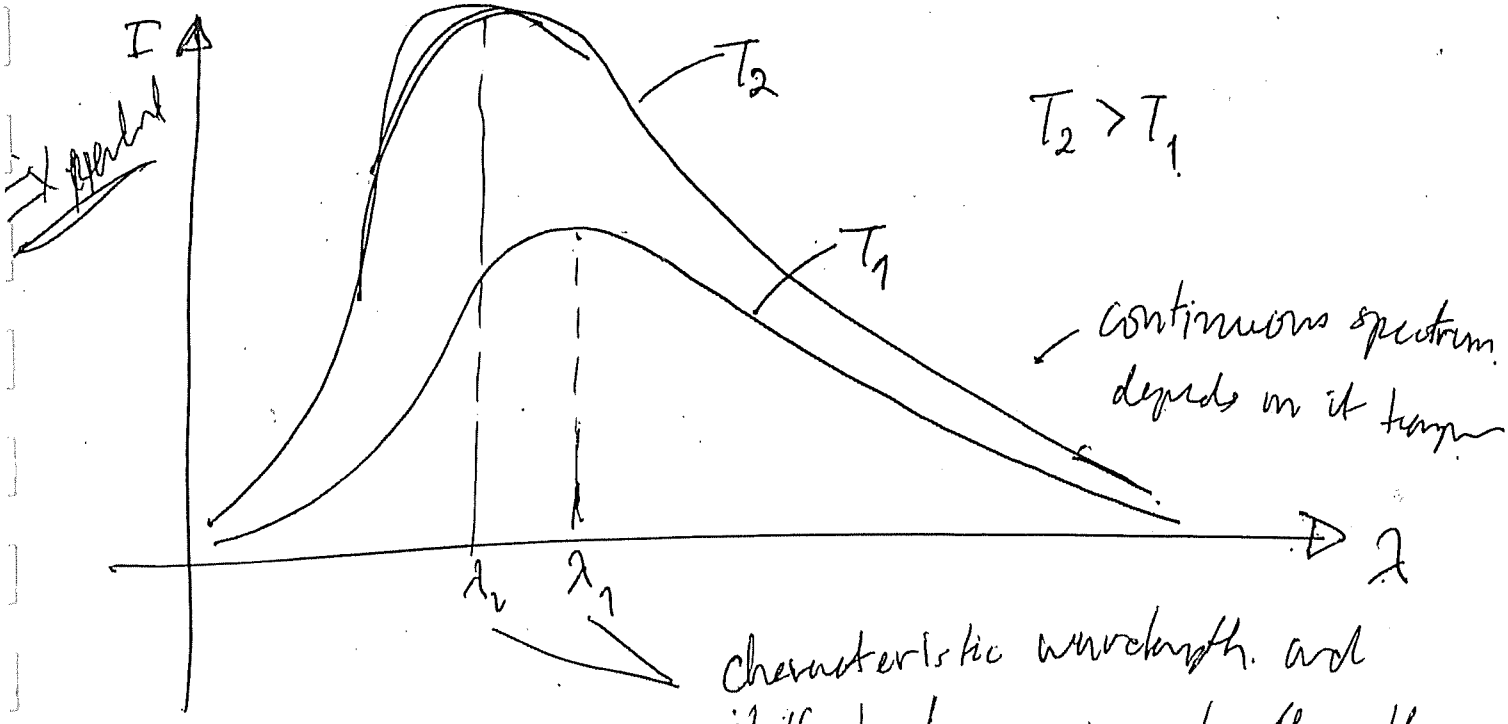
Spectrum.

C



→ Thermal radiation – a type of EM radiation emitted by an object at particular temperature.

Metal → deep red → more yellow.



characteristic wavelength and shifts to lower wavelength with increasing T.

~~At room temperature, most~~ emission in infared range (cannot see).