Canonical ensemble

We now consider a situation where the system is allowed to exchange only energy with the surrounding.

So we consider our system together with the environment as an isolated system with a total energy lying between E_{tot} & $E_{tot} + \Delta E$.

Now, we can write the following

$$P(\text{System has energy } E) = P(\text{Reservoir has energy } E_T - E)$$

Probability system has energy E

$$\rho(E) \propto \Gamma_e(E_T - E), \quad \text{no of states available to the environment}$$

The environment is much bigger than the system and hence the energy of the environment $E_e \simeq E_T$ and $E \ll E_T$. Consequently, the E dependence can be expanded in Taylor series.

$$\rho(E) \propto \Gamma_e(E_T - E) \simeq \Gamma_e(E_e - E).$$

$$\simeq \Gamma_e(E_e) + E \frac{\partial \Gamma_e}{\partial E} + \mathcal{O}(E^2)$$

$$\simeq \Gamma_e(E_e) - E \frac{\partial \Gamma_e}{\partial E_e} + \mathcal{O}(E^2)$$

$$\simeq \Gamma_e(E_e)\left[1 - E \frac{\partial \ln \Gamma_e}{\partial E_e} + \mathcal{O}(E^2)\right]$$

$$\ln g(E) = \ln \Gamma_e(E_e) + \ln\left[1 - E\frac{\partial \ln \Gamma_e}{\partial E_e} + \mathcal{O}(E^2)\right]$$

$$= \ln \Gamma_e(E_e) - E\frac{\partial \ln \Gamma_e}{\partial E_e} + \mathcal{O}(E^2)$$

$$= \ln \Gamma_e(E_e) - \frac{E}{u_B}\frac{\partial S_e}{\partial E_e} + \mathcal{O}(E^2)$$

$$\left.\frac{\partial S_e}{\partial E_e}\right)_N = \frac{1}{T}$$

$$\Rightarrow \quad \ln g(E) = \ln \Gamma_e(E_e) - \frac{E}{u_B T} + \mathcal{O}(E^2)$$

$$g(E) = e^{\Gamma_e(E_e)}\, e^{-E/u_B T} = A\, e^{-E/u_B T}$$

Now, the distribution should be normalized to unity.

$$\Rightarrow \quad A = \left(\sum_{\text{all microstates}} e^{-E/u_B T}\right)^{-1} = Z^{-1}$$

with

$$Z = \sum_{\text{all microstate}} e^{-E/u_B T} \quad \rightarrow \quad \text{partition function.}$$

$$\longleftarrow \quad = \sum_E g(E)\, e^{-E/u_B T} \quad \text{where } g(E) \text{ no. of states of energy } E.$$

Connection with thermodynamics:

The Cannonical partition function involves a summation over the lowed energies. On the other hand, thermodynamic state is characterised by definite energy, while the statistical description envisages a distribution of energies.

Consequently, a definite number can be obtained if we consider the mean of the distribution. Now, this is only meaningful if the fluctuations around the mean are small. This is where the contact with macroscopic description must lie.

$$\langle E \rangle = \frac{1}{Z} \sum E \, e^{-E/k_B T}$$

$$\frac{\partial \langle E \rangle}{\partial T} = \frac{1}{Z} \sum \frac{E^2}{k_B T^2} e^{-E/k_B T} - \frac{1}{Z^2} \frac{dZ}{dT} \sum E \, e^{-E/k_B T}$$

$$Z = \sum_{States} e^{-E/k_B T}$$

$$\frac{dZ}{dT} = \sum e^{-E/k_B T} \frac{E}{(k_B T)^2}$$

$$\frac{\partial \langle E \rangle}{\partial T} = \frac{1}{Z} \sum \frac{E^2}{k_B T^2} e^{-E/k_B T} - \frac{1}{Z^2} \left(\frac{1}{k_B T^2} \sum E \, e^{-E/k_B T} \right) \sum E \, e^{-E/k_B T}$$

$$= \frac{1}{k_B T^2} \left[\frac{1}{Z} \sum E^2 e^{-E/k_B T} - \left(\frac{1}{Z} \sum E \, e^{-E/k_B T} \right)^2 \right]$$

$$= \frac{1}{k_B T^2} \left[\langle E^2 \rangle - \langle E \rangle^2 \right] = \frac{\langle \Delta E^2 \rangle}{k_B T^2}$$

$$\Rightarrow \langle \Delta E^2 \rangle = k_B T^2 C$$

The relative fluctuation $\dfrac{\langle \Delta E^2 \rangle^{1/2}}{\langle E \rangle} = \dfrac{\sqrt{k_B C T}}{\langle E \rangle}$

Since $C \sim \mathcal{O}(N)$

and $\langle E \rangle \sim \mathcal{O}(N)$

$$\Rightarrow \quad \frac{\langle \Delta E^2 \rangle^{1/2}}{\langle E \rangle} \sim \mathcal{O}\left(\frac{1}{\sqrt{N}}\right)$$

Thus, the fluctuations decreases in the thermodynamic limit of $N \to \infty$.

We now make the connection between statistical mechanics and thermodynamics even more transparent. We write the Cannonical distribution functions as

$$z = \sum_{States} e^{-E/k_B T}$$

$$= \int \Gamma(E) \, e^{-E/k_B T} \, dE$$

Where $\Gamma(E) \, dE$ is the number of microstates between E & $E + dE$.

$$\Rightarrow \quad z = \int e^{-(E - TS)/k_B T} \, dE$$

Now, $E - TS$ is $\mathcal{O}(N)$ and as before, the integrand is dominated by the minimum of $E - TS$. The minimum is obtained at $E = \bar{E}$, where

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

Which is the thermodynamic relation between entropy and

temperature, and $\bar{E}$ is the thermodynamic energy that one is familiar with. We expand $E - TS$ about $\bar{E}$ to obtain

$$E - TS = \bar{E} + E - \bar{E} - TS(\bar{E}) - T\left(\frac{\partial S}{\partial E}\right)_{\bar{E}} \Delta E$$

$$- \frac{T}{2}\left(\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}} \Delta E^2 + \mathcal{O}(\Delta E^3)$$

$$= \bar{E} + \Delta E\left(1 - T\left(\frac{\partial S}{\partial E}\right)_{\bar{E}}\right) - \frac{T}{2}\left(\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}} (\Delta E)^2 - TS(\bar{E})$$

$$= \bar{E} - TS(\bar{E}) - \frac{T}{2}\left(\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}} (\Delta E)^2$$

$$= \bar{F} - \frac{T}{2}\frac{\partial}{\partial E}\left(\frac{1}{T}\right)(\Delta E)^2$$

$$= \bar{F} + \frac{T}{2T^2}\left(\frac{\partial E}{\partial T}\right)^{-1}(\Delta E)^2$$

$$= \bar{F} + \frac{(\Delta E)^2}{2TC}$$

Where $\bar{F}$ is the thermodynamic Helmholtz free energy and is the minimum of the $E - TS$ provided $C > 0$.

$$Z = e^{-\bar{F}/\kappa T}\int e^{-(\Delta E)^2/2\kappa T^2 C}\, d\bar{E}$$

Clearly, if $C < 0$, then the integrand is exponentially diverging meaning fluctuations do not decrease.

Further, the canonical distribution function corresponds to a Gaussian fluctuation about the mean energy. Clearly, the integrand in $\mathcal{O}(C^{1/2})$ and hence $\mathcal{O}(N^{1/2})$

$$\Rightarrow \quad \ln Z = -\frac{F}{k_B T} + \ln\left[\mathcal{O}(N^{1/2})\right]$$

The first term is $\mathcal{O}(N)$ and hence dominates in the thermodynamic limit and therefore

$$F = -k_B T \ln Z.$$

This is the desired connection between the statistical mechanical quantity Z and the thermodynamic quantity F.

The relation can alternatively derived from Boltzmann hypothesis $\quad \langle S \rangle = k_B \langle \ln \Gamma(E) \rangle$

The thermodynamic entropy

$$S \equiv \langle S \rangle = -k_B \langle \ln \mathcal{S}(E) \rangle$$

$$= -k_B \left\langle \ln\left(e^{-E/k_B T}/Z\right) \right\rangle$$

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

$$= k_B \ln Z + E/T$$

$$\Rightarrow \quad E - TS = -k_B T \ln Z$$

$$F = -k_B T \ln Z.$$

One particle partition function

For a non-interacting system, the calculation of the partition function is trivial. The Hamiltonian for such a system is given by

$$\mathcal{H} = \sum_i \mathcal{H}_i$$

Where $\mathcal{H}_i$ is the Hamiltonian for individual particles.

Then $\quad Z = \prod_i Q_i$

Where $\quad Q_i = \sum_{states} e^{-\beta \mathcal{H}_i}$

Since they are non-interacting particles, Q_i would be independent of i and therefore

$$Z = Q^N \quad \text{for} \quad N \text{ particles.}$$

For N indistinguishable particles

$$Z = \frac{Q^N}{N!}$$

Two level System. System can be in 0, or ϵ State

$$Q = \sum_i e^{-\beta \epsilon_i} = 1 + e^{-\beta \epsilon}$$

Then $\quad Z = Q^N$

$$\ln Z = N \ln Q$$

$$\ln Z = N \ln \left(1 + e^{-\beta \epsilon}\right)$$

$\beta = \frac{1}{k_B T}$

$\frac{\partial \beta}{\partial T} = -\frac{1}{k_B} \frac{1}{T^2}$

$$E = \langle E \rangle = \frac{1}{Z} \sum E \, e^{-\beta \epsilon}$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{V,N}$$

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

$$F = E - TS$$

$$S = F$$

$$F = k_B T^2 \frac{\partial \ln Z}{\partial T} - TS$$

$$\Rightarrow \quad TS = k_B T^2 \frac{\partial \ln Z}{\partial T} + k_B T \ln Z$$

$$S = k_B T \frac{\partial \ln Z}{\partial T} + k_B \ln Z$$

$$= k_B \frac{\partial}{\partial T} (T \ln Z)$$

$$\Rightarrow \quad S = k_B \frac{\partial}{\partial T} \left[TN \ln \left(1 + e^{-\beta \epsilon}\right) \right]$$

$$= k_B N \ln \left(1 + e^{-\beta \epsilon}\right) + \frac{N k_B T \epsilon \, e^{-\beta \epsilon}}{\left(1 + e^{-\beta \epsilon}\right)} \frac{\partial \beta}{\partial T}$$

$$S = Nk_B \ln\left(1 + e^{-\beta\epsilon}\right) + \frac{Nk_B T\epsilon \cdot e^{-\beta\epsilon}}{(1 + e^{-\beta\epsilon})} \frac{1}{k_B T^2}$$

$$= Nk_B \ln\left(1 + e^{-\beta\epsilon}\right) + \frac{N\epsilon/T}{(e^{\beta\epsilon} + 1)}$$

$$S = Nk_B \left[\ln\left(1 + e^{-\beta\epsilon}\right) + \frac{\beta\epsilon}{(e^{\beta\epsilon} + 1)} \right]$$

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} N \ln\left(1 + e^{-\beta\epsilon}\right)$$

$$E = \frac{+N\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \left(\frac{N\epsilon}{e^{\beta\epsilon} + 1}\right)$$

Classical Ideal gas

We consider a classical ideal gas in D-dimension with the Hamiltonian
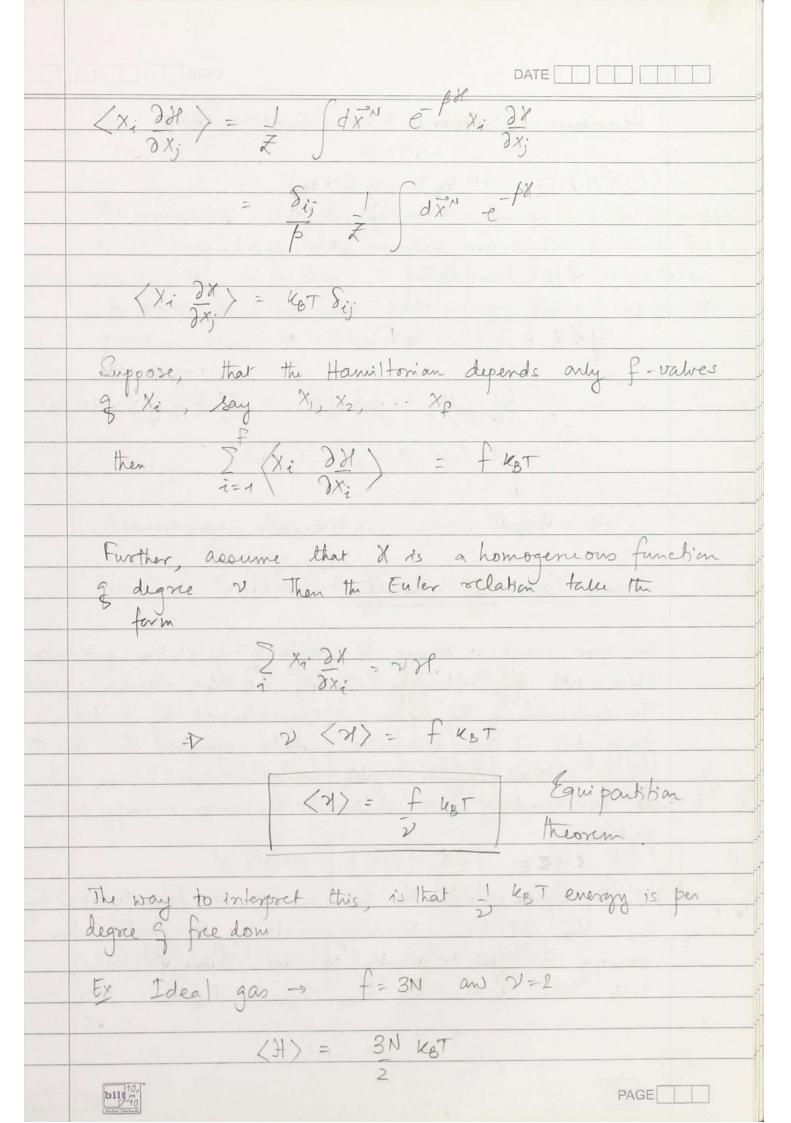
$$\mathcal{H} = K \sum_{i=1}^{N} p_i^{\nu}$$

where $p = |\vec{p}|$. In other words, the Hamiltonian is a homogeneous function of degree ν. The one particle partition function is given by

$$Q = \frac{1}{(2\pi\hbar)^D} \int d^D q \int d^D p \; e^{-\beta K p^{\nu}}$$

Obviously, $K > 0$ and $\nu > 0$ for the integral to

converge. The two cases that is interesting to us are

$$\nu = 2 \quad \text{and} \quad \kappa = \tfrac{1}{2m} \quad \rightarrow \quad \text{corresponds to the energy of non relativistic gas.}$$

and the other case

$$\nu = 1 \qquad \text{and} \quad \kappa = c$$

which is the case for ultra-relativistic gas or gas of a massless particles.

$$Q = \frac{1}{(2\pi\hbar)^D} \int d^D q \int d^D p \; e^{-\beta\kappa p^\nu} \qquad \qquad 1-\nu+D-1$$

$$= \frac{V}{(2\pi\hbar)^D} \frac{2\pi^{D/2}}{\Gamma(D/2)} \int_0^\infty dp \; p^{D-1} \, e^{-\beta\kappa p^\nu}$$

Substitute $y = \beta\kappa p^\nu$ you get the final form

$$dy = \nu\beta\kappa \, p^{\nu-1} \, dp.$$

$$Q = \frac{V}{(2\pi\hbar)^D} \frac{2\pi^{D/2}}{\Gamma(D/2)} \int_0^\infty \frac{dy}{\nu\beta\kappa} \; p^{(1-\nu)} \, p^{(D-1)} \, e^{-\beta\kappa p^\nu}$$

$$= \frac{V}{\nu(2\pi\hbar)^D} \frac{(2\pi)^{D/2}}{\Gamma(D/2)} \frac{1}{\beta\kappa} \int dy \; p^{(D/\nu - 1)\nu} \, e^{-y}$$

$$= \frac{V}{\nu(2\pi\hbar)^D} \frac{(2\pi)^{D/2}}{\Gamma(D/2)} \frac{1}{\beta\kappa} \int dy \; \left(\frac{y}{\beta\kappa}\right)^{\left(\frac{D}{\nu}-1\right)} \, e^{-y}$$

$$= \frac{V}{\nu(2\pi\hbar)^D} \frac{(2\pi)^{D/2}}{\Gamma(D/2)} \frac{1}{(\beta\kappa)^{D/\nu}}$$

$$Q = \frac{V}{(2\pi\hbar)^D} \frac{2\pi^{D/2}}{\Gamma(D/2)} \frac{1}{(\beta k)^{D/\nu}} \Gamma(D/\nu)$$

$$Q = \frac{V}{\Lambda_T}$$

$$\Lambda_T = \frac{1}{C_{D,\nu}(\kappa_B T)^{D/\nu}}$$

$$C_{D,\nu} = \frac{1}{\nu(2\pi\hbar)^D} \frac{2\pi^{D/2}}{\Gamma(D/2)} \frac{\Gamma(D/\nu)}{k^{D/\nu}}$$

$$Z = \frac{Q^N}{N!} = \frac{1}{N!} \frac{V^N}{\Lambda_T^N}$$

$$\ln Z = N \ln\left(\frac{V}{\Lambda_T}\right) - \ln N!$$

$$= N \ln\left(\frac{V}{\Lambda_T}\right) - N \ln N + N$$

$$\ln Z = N\left[\ln\left(\frac{V}{N\Lambda_T}\right) + 1\right]$$

$$F = -\kappa_B T \ln Z = -N\kappa_B T\left[\ln\frac{V}{N\Lambda_T} + 1\right]$$

Non relativistic gas in 3D

$$\Lambda_T = \left[C_{3,2}(\kappa_B T)^{3/2}\right]^{-1}$$

$$C_{3,2} = \frac{1}{2} \frac{1}{(2\pi\hbar)^{3/2}} \frac{2\pi^{3/2}}{\Gamma(3/2)} \frac{\Gamma(3/2)}{K^{3/2}}$$

$$= \frac{\pi^{3/2}}{(2\pi\hbar)^3} \frac{1}{K^{3/2}}$$

$$\Lambda_T = \left[\frac{\pi^{3/2}}{(2\pi\hbar)^3} \frac{1}{K^{3/2}} (u_B T)^{3/2} \right]^{-1}$$

$$= \left[\frac{(2\pi K_B T m)^{3/2}}{(2\pi\hbar)^3} \right]^{-1} = \left[\frac{2\pi K_B T m}{(2\pi\hbar)^2} \right]^{-3/2}$$

$$= \left(\frac{m k_B T}{2\pi\hbar^2} \right)^{-3/2} = \left(\frac{2\pi\hbar^2}{m k_B T} \right)^{3/2}$$

Relativistic Gas

$$\Lambda_T = \frac{1}{C_{3,1} (u_B T)^3}$$

$$C_{3,1} = \frac{1}{(2\pi\hbar)^3} \frac{2\pi^{3/2}}{\Gamma(3/2)} \frac{\Gamma(3)}{K^3}$$

$$\Lambda_T = \frac{(2\pi\hbar)^3 \Gamma(3/2) K^3}{2\pi^{3/2} \Gamma(3) (u_B T)^3} = \pi^2 \left(\frac{c\hbar}{K_B T} \right)^3$$

Equipartition Theorem

Contains both coordinate & momenta

Let's denote the phase space variables by X_i where i goes from 1 to $2N$ for a system with N degrees of freedom. We want to calculate the average of the quantity $X_i \frac{\partial H}{\partial x_j}$. If the Hamiltonian is independent of x_j then this is zero.

$$\left\langle X_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{Z} \int d\bar{x}^N e^{-\beta H} X_i \frac{\partial H}{\partial x_j}$$

Where γ is the differential measure in the phase space. No, consider the integration over the variable x_j.

$$e^{-\beta H} \frac{\partial H}{\partial x_j} = -\frac{1}{\beta} \frac{\partial}{\partial x_j} \left(e^{-\beta H} \right)$$

$$\int dx_j \, e^{-\beta H} X_i \frac{\partial H}{\partial x_j} = -\frac{1}{\beta} \int dx_j \, X_i \frac{\partial}{\partial x_j} e^{-\beta H}$$

$$= -\frac{1}{\beta} \int dx_j \, X_i \frac{\partial}{\partial x_j} e^{-\beta H}$$

$$= -\frac{1}{\beta} \left[-X_i e^{-\beta H} \Big| + \int dx_j \, e^{-\beta H} \frac{\partial X_i}{\partial x_j} \right]$$

The first term is zero at boundaries. Therefore,

$$\int dx_j \, e^{-\beta H} X_i \frac{\partial H}{\partial x_j} = +\frac{1}{\beta} \int dx_j \, e^{-\beta H} \frac{\partial X_i}{\partial x_j}$$

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \frac{1}{Z} \int d\vec{x}^N \; e^{-\beta \mathcal{H}} \; x_i \frac{\partial \mathcal{H}}{\partial x_j}$$

$$= \frac{\delta_{ij}}{\beta} \frac{1}{Z} \int d\vec{x}^N \; e^{-\beta \mathcal{H}}$$

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = k_B T \, \delta_{ij}$$

Suppose, that the Hamiltonian depends only f-values of x_i, say $x_1, x_2, \ldots x_f$

then
$$\sum_{i=1}^{F} \left\langle x_i \frac{\partial \mathcal{H}}{\partial x_i} \right\rangle = f \, k_B T$$

Further, assume that $\mathcal{H}$ is a homogeneous function of degree ν. Then the Euler relation take the form

$$\sum_i x_i \frac{\partial \mathcal{H}}{\partial x_i} = \nu \mathcal{H}.$$

$$\Rightarrow \qquad \nu \langle \mathcal{H} \rangle = f \, k_B T$$

$$\boxed{\langle \mathcal{H} \rangle = \frac{f}{\nu} k_B T}$$
Equipartition theorem.

The way to interpret this, is that $\frac{1}{2} k_B T$ energy is per degree of freedom.

Ex Ideal gas $\rightarrow$ $f = 3N$ and $\nu = 2$

$$\langle \mathcal{H} \rangle = \frac{3N \, k_B T}{2}$$

Harmonic Oscillators $\rightarrow f = 6N, \quad \nu = 2$

$$\langle \mathcal{H} \rangle = \frac{6N}{2} k_B T = 3N k_B T$$

$$\langle p_r \dot{q}_r \rangle = k_B T$$

$$\langle q_r \dot{p}_r \rangle = -k_B T$$

$$\sum_r \langle q_r \dot{p}_r \rangle = -3N k_B T \qquad \sum_r \langle p_r \dot{q}_r \rangle = 3N k_B T$$

$\downarrow$

Virial.

Grand Canonical Ensemble

we now want to discuss the probability distribution of a system which not only exchanges energy but also number of particles. The equilibrium of the system is characterized by a definite temperature T and a definite particle number N. - this is made possible by the system being in equilibrium with the surrounding with which it exchanges energy and particles.

Let the system S and the environment be characterized by E_{tot}, N_{tot} and V_{tot}. At any instant the system has energy E, particle number N and volume V (fixed) such that $E, N, V \ll E_{tot}, N_{tot}$ and V_{tot}.