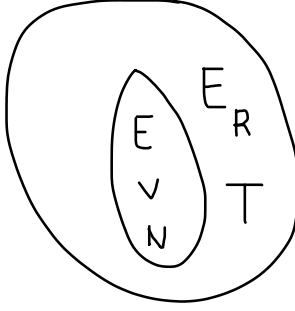# Canonical ensemble

Consider a system of interest in contact with a thermal reservoir – a system separated from reservoir by an impermeable wall which is thermally conducting. Let E be the energy of the system, and $E_T - E$ be the energy of the reservoir. Total energy E_T is fixed. Then,

$$\Omega_T(E_T) = \int \frac{dE}{\Delta} \, \Omega(E) \, \Omega_T(E_T - E)$$

Here, $\Omega(E)$ is the total number of microstates of the system and $\Omega_T(E - E)$ is the total number of microstates of the reservoir.

Note that $E_T = E_R + E$ is the total energy, i.e., system + reservoir.

Here, the integration is over all the available energy of the sub-system.

The probability that the system has energy E is therefore,

$$P(E) \propto \Omega(E) \, \Omega_R(E_T - E) = \Omega(E) \, e^{S_R(E_T - E)/k_B}$$

Where we have used that $S_R = k_B \ln \Omega_R(E_T - E)$. This implies $\Omega_R(E_T - E) = e^{S_R(E_T - E)/k_B}$. Since the reservoir is large $E \ll E_T$, we can expand $\Omega_R(E_T - E)$ (Taylor expansion)

$$\Omega_R(E_T - E) \approx \exp\left\{\frac{1}{k_B}\left[S_R(E_T) - \frac{\partial S_R}{\partial E_R} E + \cdots\right]\right\}$$

$$\Omega_R(E_T - E) \approx \exp\left\{\frac{1}{k_B}\left[S_R(E_T) - \frac{E}{T}\right]\right\} = Constant \, \exp\left\{-\frac{E}{k_B T}\right\}$$

So,

$$P(E) \propto \Omega(E) \, e^{-\frac{E}{k_B T}}$$

$$P(E) \propto e^{\frac{S(E)}{k_B}} \, e^{-\frac{E}{k_B T}} = e^{-\frac{(E - T S)}{k_B T}} = e^{-\frac{A}{k_B T}}$$

Where, we have used $S(E) = k_B \ln \Omega(E)$ and $A = E - T S$ is the Helmholtz free energy.

$$P(E) = \frac{\frac{\Omega(E)}{\Delta} e^{-\frac{E}{k_B T}}}{Z}$$

$$Z = \int \frac{dE}{\Delta} \, \Omega(E) \, e^{-\frac{E}{k_B T}}$$

It is the canonical partition function. Note that Z is the Laplace transformation of the partition function $\Omega(E)$.

Using the density of states,

$$g(E) = \int \frac{dq_i\, dp_i}{h^{3N}}\ \delta(H[q_i, p_i] - E)$$

$$\Omega(E) = g(E)\Delta$$

or

$$g(E) = \Omega(E)/\Delta$$

Then

$$Z = \int dE\ g(E)\ e^{-\frac{E}{k_B T}}$$

Probability in terms of g(E),

$$P(E) = \frac{g(E)\ e^{-\frac{E}{k_B T}}}{Z}$$

The partition function in terms of phase-space variables,

$$Z = \frac{1}{N!} \frac{1}{h^{3N}} \int dq_i\, dp_i\, e^{-\beta H[q_i, p_i]}$$

The density of states $g(E)$ has built into it all the information about a system as far as its thermodynamic behavior is concerned. Here, $\beta = 1/(k_B T)$. Note that here $N!$ term in the expression is needed in the case of indistinguishable particles. In the case of distinguishable particles, $N!$ term is not required.

The average energy of a canonical ensemble

In canonical ensemble, the energy of the system is not constant, as it constantly exchanges energy with the heat-bath. However, we can always calculate the average energy. Average energy, like the average of any quantity, can be written as

$$\langle E \rangle = \int dE\ E\ P(E)$$

$$\langle E \rangle = \frac{\int dE\ g(E)\ E\ e^{-\beta E}}{\int dE\ g(E)\ e^{-\beta E}} = \frac{\int dE\ g(E)\ E\ e^{-\beta E}}{Z}$$

$$\langle E \rangle = \frac{-\frac{\partial}{\partial \beta}\left[\int dE\ g(E)\ e^{-\beta E}\right]}{\int dE\ g(E)\ e^{-\beta E}} = -\frac{\partial}{\partial \beta} \ln\left[\int dE\ g(E)\ e^{-\beta E}\right] = -\frac{\partial}{\partial \beta} \ln Z$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

Energy fluctuations

Since energy of a system is not constant in canonical ensemble, apart from calculating its average, we will also be interested in knowing how much the energy deviates from its average value. A good measure of it is the energy fluctuation, defined as

$$\Delta E = \sqrt{\langle (E - \langle E \rangle)^2 \rangle}$$

where the angular brackets denote thermal average or ensemble average. This expression can be simplified as follows

$$\Delta E = \sqrt{\langle (E^2 - 2\,E\langle E \rangle + \langle E \rangle^2) \rangle}$$

$$\Delta E = \sqrt{\langle E^2 \rangle - 2\langle E \rangle\langle E \rangle + \langle E \rangle^2}$$

$$\Delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2}$$

Square of energy fluctuation can be written, for canonical ensemble, as

$$\Delta E^2 = \langle E^2 \rangle - \langle E \rangle^2$$

$$\Delta E^2 = \frac{\int dE\ g(E)\ E^2\ e^{-\beta E}}{\int dE\ g(E)\ e^{-\beta E}} - \left(-\frac{\partial \ln Z}{\partial \beta} \right)^2$$

$$\Delta E^2 = \frac{\int dE\ g(E)\ \frac{\partial^2}{\partial \beta^2} e^{-\beta E}}{\int dE\ g(E)\ e^{-\beta E}} - \left(\frac{\partial \ln Z}{\partial \beta} \right)^2$$

$$\Delta E^2 = \frac{\frac{\partial^2}{\partial \beta^2} \int dE\ g(E)\ e^{-\beta E}}{\int dE\ g(E)\ e^{-\beta E}} - \left(\frac{\partial \ln Z}{\partial \beta} \right)^2$$

$$\Delta E^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{\partial \ln Z}{\partial \beta} \right)^2$$

$$\Delta E^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

The last step can be verified by working backwards and obtaining the last but one step. Energy fluctuation also depends quite simply on the partition function. The above result can be manipulated to obtain some useful relations

$$\Delta E^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial}{\partial \beta}\left(-\frac{\partial \ln Z}{\partial \beta} \right)$$

$$\Delta E^2 = -\frac{\partial}{\partial \beta}\langle E \rangle$$

$$\Delta E^2 = -\frac{\partial T}{\partial \beta}\frac{\partial}{\partial T}\langle E \rangle$$

$$\Delta E^2 = -\frac{\partial T}{\partial \beta} C_v = \frac{1}{k \beta^2} C_v$$

$$\Delta E^2 = k T^2 C_v$$

In the above expression, $\frac{\partial \langle E \rangle}{\partial T}$ is the specific heat (at constant volume) of the system. Thus, we see that energy fluctuations are intimately related to the specific heat of the system.

Relation between canonical and microcanonical ensembles

Microcanonical and canonical ensemble describe physically different scenarios. One with energy fixed, and the other with energy constantly exchanged with a heat-bath. One might wonder how different the results obtained from the two would be. Also, one would like to understand how crucial is the choice of the ensemble, to study the properties of a system, because for a given system, it may not always be possible to estimate if considering the system to isolated is a good approximation or not.

We know that the average energy of a gas is proportional to the number of particles, $\langle E \rangle \propto N$. So should be the specific heat, because specific heat is just $\frac{\partial \langle E \rangle}{\partial T}$. So, $C_v \propto N$. Thus, energy fluctuations should be proportional to $\sqrt{N}$

$$\Delta E \propto \sqrt{C_v}$$

$$\Delta E \propto \sqrt{N}$$

Magnitude of fluctuation can be correctly estimated by the quantity $\Delta E / \langle E \rangle$

$$\frac{\Delta E}{\langle E \rangle} \propto \frac{\sqrt{C_v}}{\langle E \rangle}$$

$$\frac{\Delta E}{\langle E \rangle} \propto \frac{\sqrt{N}}{N}$$

$$\frac{\Delta E}{\langle E \rangle} \propto \frac{1}{\sqrt{N}}$$

It is clear than in the thermodynamic limit, the fluctuation would become zero

$$\lim_{N \to \infty} \frac{\Delta E}{\langle E \rangle} \propto \lim_{N \to \infty} \frac{1}{\sqrt{N}} = 0$$

So, in the limit of number of particles being very large, the fluctuations are negligible, and the energy remains practically constant. If the energy is (almost) constant, one can also safely use microcanonical ensemble to describe the system. So, we conclude that the in the thermodynamic limit ($N \to \infty$), canonical and microcanonical ensembles should give similar results.

Helmholtz free energy

We know that the Helmholtz free energy is given by

$$A = E - TS \implies E = A + TS$$

$$E = A - T\left(\frac{\partial A}{\partial T}\right)_{V,N} = -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{V,N}$$

$$E = -k_B T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{k_B T}\right)\right]_{V,N}$$

$$E = -k_B T^2\left[\frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta}(\beta A)\right]_{V,N}$$

Note that $\beta = k_B T$, and $\frac{\partial \beta}{\partial T} = \frac{-1}{k_B T^2}$. It implies,

$$E = \left[\frac{\partial}{\partial \beta}(\beta A)\right]_{V,N}$$

Here E is indeed the total internal energy of the system. However, we have

$$\langle E \rangle = -\frac{\partial}{\partial \beta}\ln Z$$

By comparing the above two expressions, we get the expression for the Helmholtz free energy in terms of the canonical partition function.

$$A = -\frac{1}{\beta}\ln Z$$

$$A = -k_B T \ln Z$$

In other words,

$$-\frac{A}{T} = S - \frac{E}{T}$$

Is the Legendre transformation of S. As mentioned earlier, the canonical partition function

$$Z = \int \frac{dE}{\Delta}\,\Omega(E)\,e^{-\frac{E}{k_B T}}$$

Which is the Laplace transformation of the partition function $\Omega(E)$.

By looking at the above two equations, we can make a general statement: If one takes the Laplace transformation of a partition function, the corresponding thermodynamic potential of the new partition function is just the Legendre transformation of the original thermodynamic potential.

Classical Ideal Gas in Canonical Ensemble

Let us study our simplest problem of a classical ideal gas, which we studied using micro- canonical ensemble earlier, now using canonical ensemble. Energy of the gas is given by

$$E = \sum_{i=1}^{N} \left(\frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right)$$

Where the sum over i goes all over N particles. The partition function thus can be written as

$$Z = \frac{1}{h^{3N}} \int e^{-\beta E} \prod_{i=1}^{N} dp_{xi}\, dp_{yi} dp_{zi} dx_i dy_i dz_i$$

$$Z = \frac{1}{h^{3N}} \int exp\left[-\beta \sum_{i=1}^{N} \left(\frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right) \right] \prod_{i=1}^{N} dp_{xi}\, dp_{yi} dp_{zi}\ dx_i dy_i dz_i$$

$$Z = \frac{1}{h^{3N}} \int \prod_{i=1}^{N} exp\left[-\beta \left(\frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right) \right] dp_{xi} dp_{yi} dp_{zi}\ dx_i dy_i dz_i$$

$$Z = \frac{1}{h^{3N}} \prod_{i=1}^{N} \int exp\left[-\beta \left(\frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right) \right] dp_{xi} dp_{yi} dp_{zi}\ dx_i dy_i dz_i$$

Since the particles are non-interacting and identical, these N integrals will also be identical. Integral over space will just give the volume of the box enclosing the gas, and momenta will vary from $-\infty$ to $-\infty$. Partition function thus looks like

$$Z = \frac{1}{h^{3N}} \prod_{i=1}^{N} V \int_{-\infty}^{\infty} exp\left[-\beta \frac{p_{xi}^2}{2m} \right] dp_{xi} \int_{-\infty}^{\infty} exp\left[-\beta \frac{p_{yi}^2}{2m} \right] dp_{yi} \int_{-\infty}^{\infty} exp\left[-\beta \frac{p_{zi}^2}{2m} \right] dp_{zi}$$

Using the properties of Gaussian integrals, this above equation simplifies to

$$Z = \frac{1}{h^{3N}} \prod_{i=1}^{N} \int_{-\infty}^{\infty} V \left(\frac{2\,m\,\pi}{\beta} \right)^{3/2}$$

$$Z = \frac{V^N}{h^{3N}} \left(\frac{2\,m\,\pi}{\beta} \right)^{3N/2}$$

Average energy is now given by

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln \left[\frac{V^N}{h^{3N}} \left(\frac{2\,m\,\pi}{\beta} \right)^{3N/2} \right]$$

The above equation can be simplified, and it gives the well-known result.

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

Entropy of the ideal gas can now be calculated by using the relation

$$S = \beta k_B \langle E \rangle + k_B \ln(Z)$$

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

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

We know that $\langle E \rangle = \frac{3}{2} N k_B T$. We have now the entropy for the canonical ensemble.

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

This result is identical to the one obtained using microcanonical ensemble, if one identifies the average energy $\langle E \rangle$ with the fixed energy E in microcanonical ensemble.

For indistinguishable particles, one should have an additional factor of $1/N!$ in the partition function. Thus, canonical and microcanonical ensemble yield identical results for the classical ideal gas, as they should.

For indistinguishable particles, using the Stirling's formula $\ln[N!] = N \ln[N] - N$ (for large N), we can recover the **Sackur-Tetrode equation**

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