Canonical Ensemble

The microcanonical ensemble is not very convenient for calculations since the computation of the available isoenergetic configurations in the phase space is possible only in very few cases (for example quadratic Hamiltonians). Another possible ensemble is the so-called canonical ensemble and it describes a close but not isolated system with fixed temperature T, fixed N and V. The canonical distribution function $\rho_c(\mathbf{x})$ can be derived starting from the microcanonical one as follows: let us consider an isolated system at equilibrium with fixed energy, as in the microcanonical ensemble, and divide it in two systems, A (the system we are interested in) and B (a reservoir) by a fixed-volume shell which prevents interchange of particles but allows interchange of heat. Moreover, let us assume that $N_A \ll N_B$ as well as all the extensive quantities $V_A \ll V_B$ and $E_A \ll E_B$. Of course $N = N_1 + N_2$, $V = V_1 + V_2$ and $E = E_1 + E_2$. The system A is the one we want to describe using the canonical ensemble. The Hamiltonian of the whole system is

$$H(\mathbf{x}_A, \mathbf{x}_B) = H_A(\mathbf{x}_A) + H_B(\mathbf{x}_B) + H_I(\mathbf{x}_A, \mathbf{x}_B),$$

where H_A and H_B are the Hamiltonians of the two systems A and B (so they are defined in the respective phase spaces), while H_I describes the interactions between particles of two systems. The microcanonical pdf of the entire system is

$$\rho_{mc}(\mathbf{x})\, D\mathbf{x} = \rho_{mc}(\mathbf{x}_A, \mathbf{x}_B)\, D\mathbf{x}_A D\mathbf{x}_B = \frac{\delta(H_A(\mathbf{x}_A) + H_B(\mathbf{x}_B) + H_I(\mathbf{x}_A, \mathbf{x}_B) - E)}{\omega(E)} D\mathbf{x}_A D\mathbf{x}_B.$$

The canonical pdf of system A is the marginal of $\rho_{mc}(\mathbf{x})$ so it is computed integrating over the degrees of freedom of B

$$\rho_c(\mathbf{x}_A) = \int_B D\mathbf{x}_B\, \rho_{mc}(\mathbf{x}) = \frac{\int_B D\mathbf{x}_B\, \delta(H_A(\mathbf{x}_A) + H_B(\mathbf{x}_B) + H_I(\mathbf{x}_A, \mathbf{x}_B) - E)}{\omega(E)}.$$

Assuming that the interactions between particles are short-range, we expect the the interaction term does not influence very much the total energy, so we can write

$$\rho_c(\mathbf{x}_A) \simeq \frac{\int_B D\mathbf{x}_B\, \delta(H_A(\mathbf{x}_A) + H_B(\mathbf{x}_B) - E)}{\omega(E)}.$$

Remembering that

$$\omega(E) = \int D\mathbf{x}\, \delta(H(\mathbf{x}) - E) \propto e^{\frac{S(E)}{k_B}},$$

$$\rho_c(\mathbf{x}_A) \simeq \frac{e^{\frac{S_B(E - H_A(\mathbf{x}_A))}{k_B}}}{e^{\frac{S(E)}{k_B}}}, \tag{1}$$

having adopted the compact notation

$$S_B(E - H_A(\mathbf{x}_A)) = S(E - H_A(\mathbf{x}_A), V_B, N_B).$$

Even if the energy of the entire system is constant, the energies of B and A fluctuate so the internal energies of the two systems are

$$U_A = \langle H_A \rangle,$$
$$U_B = \langle H_B \rangle,$$

and (neglecting the interaction term)

$$U = E \simeq U_A + U_B.$$

Since $E \gg H_A$, the function

$$S_B\left(E - H_A\right) \simeq S_B\left(U_B + U_A - H_A\right),$$

can be expanded around U_B

$$S_B\left(E - H_A\right) \simeq S_B\left(U_B\right) + \left.\frac{\partial S_B}{\partial E_B}\right|_{U=U_B}\left(U_A - H_A\right) = S_B\left(U_B\right) + \frac{1}{T}\left(U_A - H_A\right).$$

Moreover, because of the additivity of S shown in **??**

$$S\left(E\right) \simeq S_A\left(U_A\right) + S_B\left(U_B\right).$$

Substituting in (1)

$$\rho_c\left(\mathbf{x}_A\right) = \frac{e^{\frac{S_B\left(U_B\right)}{k_B}} e^{\frac{U_A - H_A}{k_B T}}}{e^{\frac{S_A\left(U_A\right)}{k_B}} e^{\frac{S_B\left(U_B\right)}{k_B}}} = e^{\frac{U_A - TS_A\left(U_A\right)}{k_B T}} e^{-\frac{H_A}{k_B T}},$$

where one can recognize the Helmotz free energy

$$F_A\left(T, V_A, N_A\right) = U_A - TS_A\left(U_A\right).$$

So the pdf of A is

$$\rho_c\left(\mathbf{x}_A\right) = \frac{e^{-\beta H_A}}{e^{-\beta F_A}},$$

with $\beta = \frac{1}{k_B T}$. Now that the pdf has been found, we can forget the reservoir and consider only the system A. We drop the index A, which is no more necessary, since we refer to any closed system at thermal equilibrium with an external larger system. So we rewrite the canonical pdf as

$$\boxed{\rho_c\left(\mathbf{x}\right) = \frac{e^{-\beta H(\mathbf{x})}}{Z}},$$

which is the **Boltzman distribution**. Here we defined the canonical **partition function**

$$\boxed{Z = \int D\mathbf{x}\, e^{-\beta H(\mathbf{x})} = e^{-\beta F(T)}},$$

and

$$\boxed{F\left(T, V, N\right) = -\frac{1}{\beta}\ln Z}.$$

From the partition function one can calculate all the thermodynamic quantities:

- The internal energy

$$\boxed{U = \langle H \rangle = -\frac{\partial}{\partial \beta}\ln Z},$$

- Variance of the energy

$$\boxed{\sigma_E^2 = \frac{\partial^2}{\partial \beta^2}\ln Z = \frac{\partial}{\partial \beta}\left[\frac{1}{Z}\frac{\partial}{\partial \beta}Z\right] = \frac{1}{Z}\frac{\partial^2}{\partial \beta^2}Z - \left(\frac{1}{Z}\frac{\partial}{\partial \beta}Z\right)^2 = \left\langle H^2\right\rangle - \langle H\rangle^2}.$$

  To estimate the fluctuations we expand

$$\boxed{\sigma_E^2 = -\frac{\partial E}{\partial \beta} = -\left(\frac{\partial E}{\partial T}\right)_{V,N}\frac{\partial T}{\partial \beta} = C_V k_B T^2},$$

  so the relative fluctuations scale as expected

$$\frac{\sigma_E}{E} \sim \frac{1}{\sqrt{N}}$$

- All the momentsof the energies can be derived by

$$\boxed{\langle H^n \rangle = \frac{(-1)^n}{Z} \frac{\partial^n}{\partial \beta^n} Z},$$

- Entropy

$$\boxed{\frac{\partial F}{\partial T} = -S},$$

- Pressure

$$\boxed{\frac{\partial F}{\partial V} = -p}.$$

Equivalence with the microcanonical ensemble

In the thermodynamic limit we expect the canonical and microcanonical ensemble to provide an equivalent description. An isolated system at equilibrium with fixed number N of particles, volume V and energy $E = U$ has a microcanonical entropy $S_{micro}(E, V, N)$. If the same system (with the same V and N) was in thermal contact with a reservoir, one can describe it in the canonical ensemble fixing the temperature T such that $U(T) = \langle H \rangle = E$. Within these assumptions we expect that the canonical ensemble would provide the same value of the entropy

$$S_{micro}(E, V, N) = S_{can}(T(E), V, N).$$

The partition function

$$\begin{aligned} Z &= \int D\mathbf{x}\, e^{-\beta H(\mathbf{x})} = \int d\epsilon\, \omega(\epsilon)\, e^{-\beta\epsilon} \propto \int d\epsilon\, e^{\beta E + \frac{S_{micro}(\epsilon,V,N)}{k_B}} = \\ &= \int d\epsilon\, e^{-\beta(TS_{micro}(\epsilon,V,N)-\epsilon)}, \end{aligned}$$

can be evaluated by the saddle point method expanding up to the second order $f(\epsilon) = TS_{micro}(\epsilon, V, N) - \epsilon$ around its maximum $\bar{\epsilon}$

$$\begin{aligned} f(\epsilon) &\simeq TS_{micro}(\bar{\epsilon}, V, N) - \bar{\epsilon} + \left(T \left. \frac{\partial S_{micro}(\epsilon, V, N)}{\partial \epsilon} \right|_{\epsilon=\bar{\epsilon}} - 1 \right) (\epsilon - \bar{\epsilon}) + \frac{T}{2} \left. \frac{\partial^2 S_{micro}(\epsilon, V, N)}{\partial \epsilon^2} \right|_{\epsilon=\bar{\epsilon}} (\epsilon - \bar{\epsilon})^2 = \\ &= TS_{micro}(\bar{\epsilon}, V, N) - \bar{\epsilon} + \frac{T}{2} \left. \frac{\partial^2 S_{micro}(\epsilon, V, N)}{\partial \epsilon^2} \right|_{\epsilon=\bar{\epsilon}} (\epsilon - \bar{\epsilon})^2, \end{aligned}$$

the first order term is zero if

$$\left. \frac{\partial S_{micro}(\epsilon, V, N)}{\partial \epsilon} \right|_{\epsilon=\bar{\epsilon}} = \frac{1}{T},$$

so one can chose T such that $\bar{\epsilon}$ is the energy in the microcanonical enesemble $\bar{\epsilon} = E$. With this choice

$$\left. \frac{\partial^2 S_{micro}(\epsilon, V, N)}{\partial \epsilon^2} \right|_{\epsilon=\bar{\epsilon}} = -\frac{1}{T^2 C_V},$$

$$Z \propto e^{\beta(TS_{micro}(E,V,N)-E)} \sqrt{2\pi k_B T^2 C_V},$$

$$F = -\frac{1}{\beta} \ln Z = (E - TS_{micro}(E, V, N)) - \frac{k_B T}{2} \ln C_V + \text{intensive terms}.$$

Thus, one can compute the entropy which, up to subextensive terms, coincides with the microcanonical one

$$S_{can}(T(E), V, N) = -\frac{\partial F}{\partial T} = S_{micro}(E, V, N) - \frac{k_B}{2} \ln C_V \simeq S_{micro}(E, V, N).$$

Central limit theorem and large deviations

The Boltzmann distribution is related to the central limit theorem. To see it, let us first derive the pdf of the energy

$$\begin{aligned}\rho_E(E) &= \int D\mathbf{x}\,\rho_c(\mathbf{x})\,\delta(E-H(\mathbf{x})) = \int D\mathbf{x}\,\frac{e^{-\beta H(\mathbf{x})}}{Z}\delta(E-H(\mathbf{x})) = \\ &= \frac{e^{-\beta E}}{Z}\int D\mathbf{x}\,\delta(E-H(\mathbf{x})) = \frac{e^{-\beta E}}{Z}\omega(E),\end{aligned}$$

so, in exponential form

$$\rho_E(E) = \frac{e^{-\beta(E-TS(E))}}{Z\epsilon_0}.$$

Remembering that both the energy and the entropy are extensive variables, we can write $E = N\epsilon$, $S(E) = NS(\epsilon)$, $F = Nf$ where ϵ is the arithmetic mean energy per particle

$$\epsilon = \frac{1}{N}\sum_{j=1}^{N}\epsilon_j,$$

so the central limit theorem should apply. The pdf can be written as

$$\rho_\epsilon(\epsilon) = N\frac{e^{-\beta N(\epsilon-TS(\epsilon))}}{Z\epsilon_0} = \frac{N}{\epsilon_0}e^{-\beta N(\epsilon-TS(\epsilon)-f(T))} = \frac{N}{\epsilon_0}e^{-NI(\epsilon)},$$

and the exponent is the Cramer's function that we introduced in the study of the large deviations. To recover the central limit theorem, I(ϵ) can be expanded around the minimum $\epsilon = u$

$$\frac{\partial}{\partial\epsilon}(\epsilon - TS(\epsilon) - f(T)) = 1 - T\frac{\partial}{\partial\epsilon}S(\epsilon) = 0,$$

which is the energy that in the microcanonical should correspond to the temperature T[1][2]

$$\left(\frac{\partial}{\partial\epsilon}S(\epsilon)\right)_{\epsilon=u} = \frac{1}{T}.$$

[1]Notice that in the microcanonical

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

[2]which is a function of E. In the canonical ensemble T is fixed and corresponds to a mean energy U

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

The relation between T and S is given by

$$\frac{\partial}{\partial T}F(T) = -S(T).$$

Moreover, we know from the first principle of the thermodynamics that

$$dE = Nc_V dT \Longrightarrow \left(\frac{\partial E}{\partial T}\right)_{V,N} = Nc_V,$$

hence

$$\left(\frac{\partial^2}{\partial E^2}S(E)\right)_{V,N} = \left(\frac{\partial}{\partial E}\frac{1}{T(E)}\right)_{V,N} = -\frac{1}{Nc_V(E)}\frac{1}{T^2(E)}.$$

Going back to the canonical ensemble, the same equation apply and, if E is set equal to U after the derivation, one obtains

$$\left(\frac{\partial^2}{\partial E^2}S(E)\right)_{V,N,E=U} = -\frac{1}{Nc_V}\frac{1}{T^2}.$$

For this value $u = \langle e \rangle$

$$I'(u) = 0,$$

and the gaussian approximation near the mean value is

$$I(\epsilon) \simeq \frac{1}{2} I''(u) (\epsilon - u)^2 .$$

The energy fluctuations are

$$\mathrm{Var}[\epsilon] = \left\langle (\epsilon - u)^2 \right\rangle = \frac{1}{N I''(u)} = \frac{c_V T}{N\beta} = \frac{k_B T^2}{N} c_V,$$

the concavity of the Cramer's function has to be positive because it is related to the specific heat at fixed volume.

Ideal gas in the canonical ensemble

The thermodynamics of an ideal gas can be recovered in the canonical ensemble. Starting from the Hamiltonian

$$H = \sum_j \frac{\vec{p}_j^2}{2m},$$

one can compute the partition function

$$z = \frac{V}{h^3} \left(\int dp\, e^{-\frac{p^2}{2m}\beta} \right)^3 = \frac{V}{h^3} (2m\pi)^{\frac{3}{2}} \beta^{-\frac{3}{2}} = \frac{V}{\lambda^3},$$

where λ is the thermal wave length

$$\lambda = \frac{h}{\sqrt{2\pi m k_B}} T^{-\frac{1}{2}} = \frac{h}{\sqrt{2\pi m}} \beta^{\frac{1}{2}},$$

$$Z = \frac{z^N}{N!} = \frac{V^N}{N! \lambda^{3N}}.$$

Then the internal energy is given by

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta} \ln Z = -\frac{1}{Z} \frac{\partial\lambda}{\partial\beta} \frac{\partial}{\partial\lambda} Z = -\frac{\lambda}{2Z\beta} \frac{\partial}{\partial\lambda} Z = \\ &= \frac{\lambda}{2Z\beta} 3NZ\lambda^{-1} = \frac{3}{2} N k_B T. \end{aligned}$$

As we said, the energy is not fixed ad its fluctuation can be computed from

$$\mathrm{Var}[E] = \frac{\partial^2}{\partial\beta^2} \ln Z = \frac{3}{2} N k_B^2 T^2 = N c_V k_B T^2.$$

As expected, the relative fluctuations become smaller and smaller in the thermodynamical limit

$$\frac{\sigma_E}{U} = \sqrt{\frac{2}{3N}}.$$

The free energy is

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

from which one can obtain the equation of state

$$p = -\frac{\partial F}{\partial V} = k_B T \frac{N}{V} \Longrightarrow pV = N k_B T,$$

and the entropy,

$$S = -\frac{\partial F}{\partial T} = N k_B \left[\ln \frac{v}{\lambda^3} + \frac{5}{2} \right].$$

As expected, the result is the same obtained in the microcanonical ensemble.

Exercise 0.0.1. We consider a model for the atmosphere consisting in a cylinder of section A containing a mixture of O_2 and N_2. We assume that the gas has the same temperature for every altitude. At the level of the sea, the mixture is composed by 20% of O_2 and 80% of N_2. Assuming that the total number N of molecules in the cylinder is constant, compute the densities $n_{O_2}(z)$ and $n_{N_2}(z)$ of the of the two species as a function of the height z.

Maxwell distribution of velocity

The pdf of the velocity of a single particle in an ideal gas, can be obtained from the canonical pdf noticing della it can be factorized as

$$\rho = \frac{1}{Z} \prod_j e^{-\frac{\vec{p}_j^2}{2mk_BT}},$$

and each term represents the marginal distribution of $\vec{p}$ of each particle. Hence one obtains the Maxwell distribution

$$\rho(\vec{p}) = \frac{e^{-\frac{\vec{p}^2}{2mk_BT}}}{(2m\pi k_B T)^{\frac{3}{2}}} \Rightarrow \rho(\vec{v}) = \frac{e^{-\frac{m\vec{v}^2}{2k_BT}}}{\left(\frac{2\pi k_B T}{m}\right)^{\frac{3}{2}}}. \tag{2}$$

For each component

$$\rho(p_i) = \frac{e^{-\frac{p_i^2}{2mk_BT}}}{(2m\pi k_B T)^{\frac{1}{2}}} \Rightarrow \boxed{\rho(v_i) = \frac{e^{-\frac{mv_i^2}{2k_BT}}}{\left(\frac{2\pi k_B T}{m}\right)^{\frac{1}{2}}}}.$$

The mean velocity is

$$\langle v_i \rangle = 0,$$

and its variance is proportional to the temperature

$$\langle v_i^2 \rangle = \frac{k_B T}{m},$$

as expected from the kinetic theory.

Exercise 0.0.2. Using the Maxwell distribution prove that the pdf of $|\vec{p}|$ is

$$\boxed{\rho(|\vec{p}|) = \sqrt{\frac{2}{\pi}} \frac{|\vec{p}|^2 e^{-\frac{\vec{p}^2}{2mk_BT}}}{(mk_BT)^{\frac{3}{2}}}},$$

and the pdf of the energy per particle ϵ is

$$\boxed{\rho(\epsilon) = \sqrt{\frac{4}{\pi}} \beta^{\frac{3}{2}} \sqrt{\epsilon} e^{-\epsilon\beta}}.$$

Equipartition theorem

Consider a **quadratic Hamiltonian**

$$H = \sum_{j=1}^{M} a_j x_j^2,$$

then it is easy to see that

$$\boxed{\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = 2\delta_{ij} a_j \left\langle x_j^2 \right\rangle = \delta_{ij} k_B T}.$$

Proof. Using the Canonical Ensemble

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle &= 2a_j \int D\mathbf{x} \frac{e^{-\beta H}}{Z} x_i x_j = 2\delta_{ij} a_j \left\langle x_j^2 \right\rangle = \\ &= \frac{2\delta_{ij} a_j}{Z} \int D\mathbf{x} x_j^2 e^{-\beta H} = 2\delta_{ij} a_j \frac{1}{2a_j \beta} = \delta_{ij} k_B T. \end{aligned}$$

□

A very direct consequence is that for a system with quadratic Hamiltonians, every quadratic term gives a contribution to the mean energy which is is

$$E_j = a_j \left\langle x_j^2 \right\rangle = \frac{k_B T}{2}.$$

Example 0.0.3. Monoatomic ideal gas

$$H = \sum_{j=1}^{N} \frac{\vec{p}_j^2}{2m},$$

$$U = \frac{3N}{2} k_B T.$$

Example 0.0.4. Diatomic ideal gas

$$H = \sum_{j=1}^{N} \left[\frac{\vec{p}_j^2}{2m} + \frac{L_\theta^2}{2I_\theta} + \frac{L_\phi^2}{2I_\phi} \right],$$

$$U = \frac{5N}{2} k_B T.$$

Example 0.0.5. Independent harmonic oscillators (good approximations for solids at high temperature)

$$H = \sum_{j=1}^{N} \left(\frac{\vec{p}_j^2}{2m} + \frac{m\omega^2 \vec{q}_j^2}{2} \right),$$

$$U = 3N k_B T.$$

This is the **Dulong-Petit** law.

Even if we derived it for a particular Hamiltonians, the **equipartion theorem**

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

is more general and extends to a very large class of models, but we will not discuss it here.

Example 0.0.6. Ultrarelativistic gas

$$H = c\sum_{j=1}^{N} |\vec{p}_j| = c\sum_{j=1}^{N} \sqrt{p_{xj}^2 + p_{yj}^2 + p_{zj}^2},$$

$\alpha = x, y, z$

$$\left\langle p_{\alpha j} \frac{\partial H}{\partial p_{\alpha j}} \right\rangle = c \left\langle \frac{p_{\alpha j}^2}{|\vec{p}_j|} \right\rangle = k_B T \implies c \left\langle \frac{p_{xj}^2 + p_{yj}^2 + p_{zj}^2}{|\vec{p}_j|} \right\rangle = c \langle |\vec{p}_j| \rangle = 3k_B T,$$

$$U = c\sum_{j=1}^{N} \langle |\vec{p}_j| \rangle = 3Nk_B T.$$

Virial theorem

From the equipartition theorem and for two positions $q_{\alpha j}$ and $q_{\beta l}$, one has

$$\left\langle q_{\alpha j} \frac{\partial H}{\partial q_{\beta l}} \right\rangle = k_B T \delta_{j,l} \delta_{\alpha,\beta},$$

and, in terms of forces,

$$\langle q_{\alpha j} F_{\beta l} \rangle = -k_B T \delta_{j,l} \delta_{\alpha,\beta}.$$

Summing one gets

$$\frac{1}{2}\sum_j \left\langle \vec{q_j} \cdot \vec{F_j} \right\rangle = -\frac{3}{2} N k_B T = \langle E_K \rangle ,$$

where the quantity $\frac{1}{2}\sum_j \left\langle \vec{q_j} \cdot \vec{F_j} \right\rangle$ is called **virial**. For each particle the total force acting on it can be decomposed in two contributions: the internal one, given by the interactions with other particles, and the confinement (external) forces from the walls

$$\vec{F_j} = \vec{F}_j^{int} + \vec{F}_j^{ext}.$$

In a perfect gas we know that only the external forces contribute

$$\sum_j \left\langle \vec{q_j} \cdot \vec{F}_j^{ext} \right\rangle = -3Nk_B T = -3pV,$$

so we obtain the **Virial theorem**

$$\boxed{pV = Nk_B T + \frac{1}{3}\sum_j \left\langle \vec{q_j} \cdot \vec{F}_j^{int} \right\rangle}.$$