Equilibrium statistical mechanics

A macroscopic system is a system composed by a huge number ($10^{22} - 10^{23}$, i.e. the order of the Avogadro number N_A) of elementary objects. With "elementary object" we mean objects that do not have internal degrees of freedom (or whose internal degrees of freedom are negligible) so that can be treated as material points. So, depending on the coarse graining of the description, elementary objects could be grains, proteins, simple molecules, atoms, electrons, etc.

Thermodynamics studies these systems from a macroscopic point of view, associating to every system a "macroscopic state" characterized by few macroscopic variables (thermodynamical coordinate) such as pressure, temperature, volume, internal energy, entropy, density etcetera. All these quantities describe some global property given by some average behavior of all the components of the system. The possibility to associate a precise macroscopic state to a system implies two hypotheses:

- the system has reached an equilibrium configuration
- the relative fluctuations are negligible and do not affect the macroscopic state

Of course many microscopical configurations can give rise to the same macroscopic state. The scope of the statistical mechanics is to explain the macroscopic properties of a system by statistical description of the microscopic behavior of a many-particle system.

The microscopic state of the system composed by N "particles" is completely determined once the generalized positions and conjugate momenta of each component are given. So one can associate each microscopic state to a vector in the phase space $\mathbf{x} \in \Omega$

$$\mathbf{x} = \begin{pmatrix} \mathbf{q} \\ \mathbf{p} \end{pmatrix} = \begin{pmatrix} q_{1x} \\ q_{1y} \\ \vdots \\ q_{Nz} \\ p_{1x} \\ p_{1y} \\ \vdots \\ p_{Nz} \end{pmatrix}.$$

The dynamics of the system is given by its Hamiltonian, for instance a monoatomic gas of identical atoms o mass m will be described by

$$H(\mathbf{x}) = \sum_{j=1}^{N} \frac{\vec{p}_j}{2m} + V(\vec{q}_j) + \sum_{i,j} V_I(\vec{q}_i - \vec{q}_j),$$

where the first term is the kinetic energy of each atom, the second one is the potential energy of external forces and the last one is the interaction energy. The time evolution is given by the Hamilton equation of motion

$$\dot{q}_j = \frac{\partial H}{\partial p_j},$$

$$\dot{p}_j = -\frac{\partial H}{\partial q_j},$$

whose solutions describes a trajectory in the phase space.

Due to the uncertainty in the initial conditions, at each time the system will occupy a point in the phase space with a certain pdf $\rho(\mathbf{x}, t)$. The following assumptions are done:

- if the system is at equilibrium, the pdf $\rho(\mathbf{x})$ is stationary (does not change in time)
- the system is assumed to be ergodic, so the temporal averages are equivalent to ensemble averages.

The pdf of equilibrium should satisfy the normalization condition [1]

$$\int D\mathbf{x}\, \rho(\mathbf{x}) = 1.$$

Given a quantity $A(\mathbf{x})$ its ensemble average is

$$\langle A(\mathbf{x}) \rangle = \int D\mathbf{x}\, \rho(\mathbf{x})\, A(\mathbf{x}).$$

Example 0.0.1. Internal energy. A first example is given by the internal energy which is the average of the Hamiltonian function

$$U = \langle E \rangle = \langle H(\mathbf{x}) \rangle.$$

If the system is noninteracting, then

$$H = \sum_{j=1}^{N} H_j,$$

and if all the particles are equivalent then the single particle mean energy is the same

$$\langle H_j \rangle = \epsilon, \ \forall j = 0, \dots, N,$$

so, as expected, the total energy is an extensive quantity

$$U = \langle H \rangle = N\epsilon.$$

[1] Being $\mathbf{x}$ a dimensional quantity, in order to have an dimensionless probability, the volume of the phase space has to be divided by a constant $\mathcal{A}$ of the same dimensions of $d\mathbf{x}$. The symbol $D\mathbf{x}$ is a compact notation meaning the infinitesimal volume divided by the suitable dimensional factor

$$d\mathbf{x} \to D\mathbf{x} = \frac{d\mathbf{x}}{\mathcal{A}}.$$

A natural choice for this rescaling comes from the quantum mechanics and it is the Planck constant $h \simeq 6 \cdot 10^{-34}$ Js is used. It has the dimensions of an action

$$[h] = \left[m\ell^2 t^{-1}\right] = [q\, p],$$

so, for a $3D$ system of Nparticles $\mathcal{A} \propto h^{3N}$. Moreover, if the system is composed by indistinguishable particles Gibbs shown that one has also to take into account the fact all the different particle-index permutations correspond to the same microscopic state so empirically he added a factor $N!$. This factor derives from quantum mechanics, and it is an approximation which is correct for high temperatures. So for a $3D$ system of indistinguishable particles we can write

$$d\mathbf{x} \to D\mathbf{x} = \frac{d\mathbf{x}}{\mathcal{A}N!} = \frac{d\mathbf{x}}{h^{3N}N!}.$$

The factor $\mathcal{A}$ can be interpreted as the **fundamental volume** corresponding to a microstate. In classical mechanics this choice is arbitrary while it assumes a physical meaning in quantum mechanics.

The next step is to see how this quantity fluctuates. Denoting with σ^2 the energy's variance of a single particle, the variance of the internal energy is $\sigma_U^2 = N\sigma^2$ so the relative fluctuations decrease by increasing N as

$$\frac{\sigma_U}{U} \propto \frac{1}{\sqrt{N}}.$$

These properties remain valid also if there are short-range interactions as result of the central limit behavior.

To determine $\rho(\mathbf{x})$ one has to fix some constraints among the number of particles, the volume, the total energy, the temperature, the pressure etc. Every choice corresponds to a a different *ensemble* or, in other terms, a restriction on the available phase space. Hereafter we list some possible ensembles that can be chosen

1. Taking an isolated system in a given volume restricts the possible configurations to those with same energy, same N and same V: we talk about *microcanonical ensemble.* In this case variables such as the temperature or the pressure fluctuate.

2. Another ensemble can be obtained fixing N, V and T, this is called *canonical ensemble.* Here the energy fluctuates, while the temperature is fixed. This case corresponds to closed system which is in equilibrium with a thermal reservoir.

3. Fixing V, T and the chemical potential μ one obtains the *grand canonical ensemble* corresponding to an open system in equilibrium with a thermal reservoir where particles can move inside and outside.

4. Fixing T, p and N one obtains the *isobaric-isothermal ensemble* where the volume and the internal energy are fluctuating quantities.

All these ensembles equivalently describe the same system at equilibrium providing that the averaged quantities are the same for each ensemble, meaning that they provide the same results for the macroscopic quantities

$$\begin{aligned} U = E_{micro} = \langle H \rangle_{can} = \langle H \rangle_{grandcan} = \langle H \rangle_{isop}, \\ S = S_{micro} = \langle S \rangle_{can} = \langle S \rangle_{grandcan} = \langle S \rangle_{isop} \\ N = N_{micro} = N_{can} = \langle N \rangle_{grancan} = N_{isop}, \\ \dots \end{aligned}$$

Microcanonical ensemble

Assumptions:

- Isolated system (N and E is fixed).
- Fixed V
- Thermal equilibrium
- All the microscopic states corresponding to the same macroscopic state are equally likely

$$\rho_{mc}(\mathbf{x}) = \begin{cases} \text{cost} & H = E \\ 0 & H \neq E \end{cases} = C\delta(H(\mathbf{x}) - E).$$

The normalization coefficient must be

$$C = \frac{\Delta}{\Delta \int_\Omega \delta\left(H\left(\mathbf{x}\right) - E\right) D\mathbf{x}} = \frac{\Delta}{\Gamma},$$

and $\Gamma\left(N, V, E\right) = \Delta \int_\Omega \delta\left(H\left(\mathbf{x}\right) - E\right) D\mathbf{x}$ is called **microcanonical partition function**. The factor Δ is arbitrary and intensive, it has the dimensions of an energy, and it has been added to define the partition function as a dimensionless quantity. In this way it can be interpreted as the measure of the available microscopic states

- The partition function and the pdf are defined in term of delta functions, but in practice it could be more convenient and intuitive to consider a constant pdf for all the possible states having an energy E up to a very small tolerance (which can be sent to zero) $E - \Delta < \mathrm{H} < \mathrm{E}$.

$$\rho_{mc}\left(\mathbf{x}\right) \simeq \begin{cases} \frac{1}{\Gamma_\Delta} & E - \Delta < \mathrm{H} < \mathrm{E} \\ 0 & \text{otherwise} \end{cases}.$$

The volume in the phase space of this set of configuration is called $\Gamma_\Delta\left(N, V, E\right)$. All the thermodynamical properties will be almost independent on the size of Δ as long as it is chosen intensive.

The available phase space is a thin shell around the iso-energy surface whose volume is

$$\Gamma_\Delta\left(E\right) = \int_{E-\Delta<\mathrm{H}<\mathrm{E}} D\mathbf{x},$$

this is tends to the microcanonical partition function. The number of microscopic states of the region of the phase space for which $H\left(\mathbf{x}\right) < E$ is

$$\Sigma\left(E\right) = \int_{\mathrm{H}<\mathrm{E}} D\mathbf{x} = \int_\Omega \theta\left(E - H\left(\mathbf{x}\right)\right) D\mathbf{x},$$

and so

$$\Gamma_\Delta\left(E\right) = \Sigma\left(E\right) - \Sigma\left(E - \Delta\right) \simeq \frac{\partial \Sigma\left(E\right)}{\partial E}\Delta = \omega\left(E\right)\Delta,$$

where we have defined the **density of states**

$$\boxed{\omega\left(E\right) = \frac{\partial \Sigma\left(E\right)}{\partial E} = \int_\Omega \frac{\partial}{\partial E}\theta\left(E - H\left(\mathbf{x}\right)\right) D\mathbf{x} = \int_\Omega \delta\left(H\left(\mathbf{x}\right) - E\right) D\mathbf{x}}.$$

Hence, we can write the pdf in the microcanomical ensemble as

$$\boxed{\rho_{mc}\left(\mathbf{x}\right) = \frac{\delta\left(H\left(\mathbf{x}\right) - E\right)}{\omega\left(E\right)}}.$$

In the microcanonical ensemble the natural potential is the internal energy $E = U$ which is fixed, so the variable which is most suitable to be evaluated is the entropy, being a function of U, V and N (all fixed).

Boltzmann's entropy If W is number of available states in a discrete space, then the Entropy is

$$\boxed{S = k_B \ln W}.$$

For a continuous system, in the microcanonical ensemble the Boltzmann equation becomes

$$S(U,V,N) = k_B \ln \Gamma(U).$$

To compute it one can consider $\Gamma_\Delta(U)$ instead, observing that, for $N \to \infty$, the volume in the phase space accumulates close to its boundary [2] so in this limit the following equivalent expressions can be used to compute the entropy

$$\boxed{S(U,V,N) = k_B \ln \Gamma_\Delta(U) \simeq k_B \ln \Sigma(U) \simeq k_B \ln [\omega(U)\Delta]}.$$

Notice that:

- The density of states can be written as
$$\omega(U) \propto e^{\frac{S(U,V,N)}{k_B}}.$$
- The natural variables on which the entropy depends are U, V, N. Fixing N, from the first principle of the thermodynamics for a reversible transformation
$$dQ_{rev} = dU + pdV,$$
dividing by T one obtains
$$dS = \frac{1}{T}dU + \frac{p}{T}dV,$$
hence from S one can derive the temperature and the pressure as
$$\boxed{\frac{\partial S}{\partial U} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{p}{T}}.$$

Exercise 0.0.2. Consider an ideal gas at thermal equilibrium, which is described by N free particles

$$H = \sum_i \frac{\vec{p}_i^2}{2m}.$$

1. Remembering the formula of the volume of an hypersphere, show that
$$\Sigma(U) = \int_{H<E} \frac{d\mathbf{x}}{h^{3N} N!} = \left(\frac{2\pi m}{h^2}\right)^{\frac{3N}{2}} \frac{1}{N!\Gamma\left(\frac{3N}{2}+1\right)} V^N U^{\frac{3N}{2}}.$$
2. Using the Stirling approximation for the factorial of large numbers
$$\ln N! \simeq N \ln N - N,$$
show that the entropy is given by the **Sackur-Tetrode formula**:
$$\boxed{S(U,V,N) = k_B \left(N \ln \frac{V}{N} \left(\frac{4\pi m U}{3Nh^2}\right)^{\frac{3}{2}} + \frac{5N}{2} \right)}, \tag{1}$$

[2] In a d-dimensional space consider an interval characterized by a typical length r. Its volume has the form

$$\Sigma(r) = \phi r^d,$$

where ϕ is a dimensionless form factor which characterizes its shape. We consider a thin shell close to the boundary of tickness $r\epsilon$ with $\epsilon \ll 1$. The volume of the shell is the difference of the volumes of the two resulting intervals which are similar

$$\Gamma_\epsilon(r) = \Sigma(r) - \Sigma(r - r\epsilon) = \phi r^d \left(1 - (1-\epsilon)^d\right).$$

Once fixed ϵ the ratio

$$\frac{\Gamma_\epsilon(r)}{\Sigma(r)} = 1 - (1-\epsilon)^d,$$

will tend to 1 for $d \to \infty$.

3. Remembering that
$$\frac{\partial S}{\partial U} = \frac{1}{T},$$
compute the relation between U and T.

4. Denoting with $v = \frac{V}{N}$ the specific volume and introducing the **thermal wave length** of the gas $\lambda = \frac{h}{\sqrt{2m\pi k_B T}}$ show that
$$S = Nk_B \left[\ln\left(\frac{v}{\lambda^3}\right) + \frac{5}{2} \right].$$

5. If the initial system is at equilibrium, dividing it in two part by a wall (in two volumes V_1 and V_2 with $V_1 + V_2 = V$) one obtains two systems at the same temperature, with the same density and pressure. Show that
$$S\left(U, V, N\right) = S\left(U, V_1, N_1\right) + S\left(U, V_2, N_2\right)$$
meaning that the entropy is extensive and that the Gibbs factor is necessary to guarantee this result.

Additivity of the Entropy

Let us divide the closed system in two parts, A and B, in such a way that N_A and $N_B = N - N_A$ are fixed as well as V_A and $V_B = V - V_A$. The system remains isolated so $E_A + E_B = E$ but exchange of energy between the subsystems is allowed. The energy function (the Hamiltonian for mechanical systems) can be expressed as two local terms and an interaction one. The latter can be, in general, neglected if the interactions are short ranged[1]

$$H(\mathbf{x}) = H_A(\mathbf{x}_A) + H(\mathbf{x}_B) + H_I(\mathbf{x}) \simeq H_A(\mathbf{x}_A) + H(\mathbf{x}_B).$$

The partition function can be expressed as

$$\begin{aligned}
\Gamma(E) &= \Delta \int D\mathbf{x}_A D\mathbf{x}_B \delta(E - H_A(\mathbf{x}_A) - H(\mathbf{x}_B)) = \\
&= \Delta \int_{\Delta E_a} dE_A D\mathbf{x}_A D\mathbf{x}_B \delta(E_A - H_A(\mathbf{x}_A)) \delta(E - H_A(\mathbf{x}_A) - H(\mathbf{x}_B)) = \\
&= \Delta \int_{\Delta E_A} dE_A \int D\mathbf{x}_A \delta(E_A - H_A(\mathbf{x}_A)) \int D\mathbf{x}_B \delta(E - E_A - H(\mathbf{x}_B)) = \\
&= \frac{1}{\Delta} \int_{\Delta E_A} dE_A \Gamma_A(E_A) \Gamma_B(E - E_A) = \frac{1}{\Delta} \int_{\Delta E_A} dE_A W(E_A).
\end{aligned}$$

A qualitative analysis of $W(E_A)$ can be given observing that

$$\Gamma(E) \simeq \Sigma(E) \sim \xi^N,$$

where ξ is a typical length in the phase space. So $W(E_A)$ is the product o a factor rapidly increasing and another rapidly decreasing in E_A and we expect this function to be sharply peaked around a given value E_A^*

$$\left(\frac{\partial \Gamma_A}{\partial E_A}\right)_{E_A = E_A^*} = 0,$$

$$\left(\frac{\partial^2 \Gamma_A}{\partial E_A^2}\right)_{E_A = E_A^*} < 0.$$

The following inequalities hold

$$\Gamma(E) \geq \frac{1}{\Delta} \int_{E_A^*}^{E_A^* + \Delta} dE_A W(E_A^*) = W(E_A^*),$$

$$\Gamma(E) \leq \frac{1}{\Delta} \int_{\Delta E_A} dE_A W(E_A^*) = \frac{\Delta E_A}{\Delta} W(E_A^*),$$

[1] To give a intuitive explanation of this fact, we give a raw estimation of the way the three terms scale with the number of particles. The two local terms are extensive and scale as

$$H_A \sim N, \; H_B \sim N.$$

Also the spatial volume, at fixed density, scales in the same way, so being ℓ a typical length of the system

$$V \propto \ell^d \sim N \Longrightarrow \ell \sim N^{\frac{1}{d}},$$

where $d$is the spatial dimension. The interaction term between the two systems involves only the particles close to the contact surface. This means that this term scales as the surface

$$H_I \sim \ell^{d-1} \sim N^{\frac{d-1}{d}},$$

so H_I can be safely neglected in the thermodynamic limit.

$$S_A\left(E_A^*\right)+S_B\left(E-E_A^*\right)+k_B\ln\leq S\left(E\right)\leq S_A\left(E_A^*\right)+S_B\left(E-E_A^*\right)+k_B\ln\frac{\Delta E_A}{\Delta}.$$

All the entropies scale as the number of particles of the relative systems, while the last term scales as the logarithm of the number of particles so it can be neglected in the thermodynamic limit. So the additivity of the entropy is recovered

$$S\left(E\right)=S_A\left(E_A^*\right)+S_B\left(E-E_A^*\right).$$

Internal energy and its fluctuations for a subsystem

The value E_A^* is also the energy of system A at equilibrium. This can be seen easily computing the average in the microcanonical ensemble with total energy E fixed

$$\begin{aligned}
U_A &= \left\langle H_A\right\rangle=\int D\mathbf{x}\,\rho_{mc}\left(\mathbf{x}\right)H_A\left(\mathbf{x}_A\right)\simeq\frac{1}{\omega\left(E\right)}\int D\mathbf{x}\,\delta\left(E-H_A\left(\mathbf{x}_A\right)-H_B\left(\mathbf{x}_B\right)\right)H_A\left(\mathbf{x}_A\right)= \\
&= \frac{1}{\omega\left(E\right)}\int dE_A\int D\mathbf{x}_A\,\delta\left(E-H_A\left(\mathbf{x}_A\right)\right)H_A\left(\mathbf{x}_A\right)\int D\mathbf{x}_B\,\delta\left(E-H_A\left(\mathbf{x}_A\right)-H_B\left(\mathbf{x}_B\right)\right)= \\
&= \frac{1}{\Gamma}\int dE_A\int D\mathbf{x}_A\,\delta\left(E-H_A\left(\mathbf{x}_A\right)\right)H_A\left(\mathbf{x}_A\right)\Gamma_B\left(E-H_A\left(\mathbf{x}_A\right)\right)= \\
&= \frac{1}{\Gamma\Delta}\int dE_AE_A\Gamma_A\left(E_A\right)\Gamma_B\left(E-E_A\right)=\frac{1}{\Gamma\Delta}\int dE_AE_AW\left(E_A\right)= \\
&= \frac{1}{\Gamma\Delta}\int dE_AE_Ae^{\ln W\left(E_A\right)}.
\end{aligned}$$

As discussed before, the function $W\left(E_A\right)$ is sharply peaked around a point E_A^*, so the saddle point approximation can be used to recover a Gaussian pdf

$$\begin{aligned}
U_A &\simeq \frac{1}{\Gamma\Delta}\int dE_AE_Ae^{\ln W\left(E_A^*\right)+\frac{1}{2}\left(\frac{d^2\ln W\left(E_A\right)}{dE_A^2}\right)_{E=E_A}\left(E-E_A^*\right)^2}\propto \\
&\propto \int dE_AE_Ae^{-\frac{\left(E-E_A^*\right)^2}{2\sigma_U^2}}=E_A^*.
\end{aligned}$$

The variance is

$$\sigma_U^2=-\frac{1}{\left(\frac{d^2\ln W\left(E_A\right)}{dE_A^2}\right)_{E=E_A^*}},$$

to give an estimation ve notice that for large N the partition funcion scales as

$$\Gamma\left(E\right)\sim\left(\frac{E}{\Delta}\right)^Nh\left(V,N\right)\Rightarrow\ln\Gamma\left(E\right)\sim N\ln\left(\frac{E}{\Delta}\right)+\ln h\left(V,N\right),$$

so

$$\begin{aligned}
\frac{d\ln W\left(E_A\right)}{dE_A} &= \frac{d\ln\Gamma_A\left(E_A\right)}{dE_A}+\frac{d\ln\Gamma_B\left(E-E_A\right)}{dE_A}= \\
&= \frac{N_A}{\Delta}\frac{d\ln\left(\frac{E_A}{\Delta}\right)}{d\frac{E_A}{\Delta}}-\frac{N-N_A}{\Delta}\frac{d\ln\left(\frac{E-E_A}{\Delta}\right)}{d\frac{E_A}{\Delta}}= \\
&= \frac{N_A}{E_A}-\frac{N-N_A}{E-E_A},
\end{aligned}$$

which has to be zero in the extremal point (the average energy)

$$\frac{d\ln W\left(E_A^*\right)}{dE_A}=0\Rightarrow\frac{E_A^*}{N_A}=\frac{E-E_A^*}{N-N_A}=\epsilon.$$

The second derivative is

$$\left(\frac{d^2 \ln W\left(E_A\right)}{dE_A^2}\right)_{E=E_A^*} = -\left(\frac{N_A}{E_A^2}+\frac{N-N_A}{\left(E-E_A\right)^2}\right)_{E=E_A^*} = -\frac{N}{N_A\left(N-N_A\right)}\frac{1}{\epsilon^2}.$$

We are now able to evaluate the magnitude of the fluctuations

$$\sigma_U^2 = \frac{N_A\left(N-N_A\right)\epsilon^2}{N} = \frac{\left(N-N_A\right)U_A^2}{NN_a},$$

$$\boxed{\frac{\sigma_U}{U_A} \sim \sqrt{\frac{\left(N-N_A\right)}{NN_a}} \underset{N\gg N_A}{\rightarrow} \frac{1}{\sqrt{N_A}}}.$$

The relative fluctuations of the energy go to zero as the inverse of the square root of the number of particles

Temperature

We recover now the equilibrium condition for the temperature. Starting from the same bipartition considered before, with the two systems that can exchange only energy, the W funcion defined above is

$$W\left(E_A\right) = e^{\ln\Gamma_A(E_A)+\ln\Gamma_B(E-E_A)} = e^{\frac{S_A(E_A)+S_B(E-E_A)}{k_B}},$$

the equilibrium condition implies

$$\left.\frac{\partial W}{\partial E_A}\right|_{E_A=E_A^*} = 0 \Rightarrow \left.\frac{\partial S_A\left(E_A\right)}{\partial E_A}\right|_{E_A=E_A^*} + \left.\frac{\partial S_B\left(E-E_A\right)}{\partial E_A}\right|_{E_A=E_A^*} = 0,$$

$$\boxed{\frac{1}{T_A} = \frac{1}{T_B}}.$$

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Configurational entropy

When defining a bipartition, we divided so far the phase space in two spatially-separated parts. Nonetheless, the bipartition can be also non local. For example let us separate the space into the space of the positions and the space of the momenta. The Hamiltonian is

$$H\left(\mathbf{x}\right) = T\left(\mathbf{p}\right) + V\left(\mathbf{q}\right),$$

and the partition function can be decomposed into the kinetic and potential contributions

$$\begin{aligned}
\Gamma &= \Delta\int D\mathbf{p}\int D\mathbf{q}\,\delta\left(E-T\left(\mathbf{p}\right)-V\left(\mathbf{q}\right)\right) = \\
&= \Delta\int dE_K\int D\mathbf{p}\int D\mathbf{q}\,\delta\left(E_K-T\left(\mathbf{p}\right)\right)\delta\left(E-T\left(\mathbf{p}\right)-V\left(\mathbf{q}\right)\right) = \\
&= \Delta\int dE_K\int D\mathbf{p}\,\delta\left(E_K-T\left(\mathbf{p}\right)\right)\int D\mathbf{q}\,\delta\left(E-E_K-V\left(\mathbf{q}\right)\right) = \\
&= \Delta\int dE_K\int D\mathbf{p}\,\delta\left(E_K-T\left(\mathbf{p}\right)\right)\int D\mathbf{q}\,\delta\left(E_P-V\left(\mathbf{q}\right)\right) = \\
&= \frac{1}{\Delta}\int dE_K\Gamma_K\left(E_K\right)\Gamma_{conf}\left(E-E_K\right).
\end{aligned}$$

Following the same steps of we get

$$S\left(E\right) = S_K\left(E_K^*\right) + S_{conf}\left(E-E_K^*\right),$$

where $S_{conf}\left(E-E_K^*\right)$ is called **configurational entropy**.

Mixing entropy, Gibbs paradox and Boltzmann correct counting

In this section we analyze more in detail the role of the $N!$ Gibbs factor that we have introduced to take into account indistinguishable particles. Consider the two following problems:

1. Two identical ideal gases (A and B) have same temperature, density and pressure. They initially occupy two volumes V_A and V_B separated by a wall. The wall is then removed and then again put in its place.
2. Two different gases (A and B) They initially occupy two volumes V_A and V_B separated by a wall. The wall is then removed and then again put in its place.

Let us analyze the two cases without using the $N!$ counting factor.

1. The initial entropy is

$$S_1 = S_A + S_B = k_B \left(N_A \ln V_A + N_B \ln V_B + \frac{3}{2} N_A \ln \frac{E_A}{N_A} + \frac{3}{2} N_B \ln \frac{E_B}{N_B} + N\alpha \right), \tag{1}$$

then when the wall is removed

$$S_2 = k_B \left(N \ln V + \frac{3}{2} N \ln \frac{E}{N} + N\alpha \right), \tag{2}$$

and finally, when the wall is put back in place, since the state is equal to the initial one

$$S_3 = S_1.$$

In this case

$$\frac{E}{N} = \frac{E_A}{N_A} = \frac{E_B}{N_B} = \epsilon,$$

so

$$S_2 - S_1 = k_B \left(N_A \ln \frac{V}{V_A} + N_B \ln \frac{V}{V_B} \right) > 0, \tag{3}$$

this difference is called **mixing entropy**. Finally

$$S_3 = S_1.$$

2. In the second case, the initial entropy is

$$S_1 = S_A + S_B = k_B \left(N_A \ln V_A + N_B \ln V_B + \frac{3}{2} N \ln \epsilon + N_A \alpha_A + N_B \alpha_B \right),$$

and let us suppose that also $\alpha_A = \alpha_B = \alpha$. Removing the wall we obtain again eq. 3. Putting back the wall in this case

$$S_3 = S_2.$$

The calculations for the second case look correct, but in the first case a paradox (Gibbs' paradox) appears since one would expect that $S_2 = S_1$. Introducing the Boltzmann correct counting for identical particles

$$S = k_B \ln \frac{\Gamma}{N!},$$

eqs. 1 and 2 become

$$S_1 = S_2 = k_B \left(N \ln \rho + \frac{3}{2} N \ln \epsilon + N\alpha + N \right).$$