

Elements of Statistical Mechanics

Thermodynamics describes the properties of macroscopic bodies. Statistical mechanics allows us to obtain the laws of thermodynamics from the laws of mechanics, classical or quantum, applied at its minimum constituents.

Please note that the definition of each size thermodynamics involves the interaction between macroscopic bodies and is therefore closely dependent on the time scale of evolution of the system.

First, we note that in the time needed for the measurement of a magnitude thermodynamics, the variables that describe the system change microscopically enormously. The thermodynamic quantities are time averages of properties in the overall system and are subject to the imprecise nature of its measurement of a random quantity, inaccuracies or that can only be reduced at the cost of increased measurement time. We say that a system is isolated if there is no interaction between it and the environment. Properly, no system meets that definition. We observe, however, that the interactions between the system and the environment, by which we designate there is all that it is not the system, they are generally mediated by the surface of the system. Increasing the size of the system, therefore, the time of interaction between the system and the environment increase. Therefore, once again, the system may be said or isolated or less depending on the time of observation. Similarly, for a system that evolves thermodynamically in its interior, is in some cases possible to divide it into subparts such that in the time scale of evolution of the system subsystems constituents can be considered isolated from each other, then it is possible to define thermodynamic quantities.

A system of N point-like constituents is described according to classical mechanics the set of $6N$ variables that describe for each instant of time positions and moments. The set of all the values that these variables can assume is that the phase space. A microstate of the system is therefore represented by a point in space $6N$ dimensional phases and the temporal evolution of the system by a curve in the phase space.

Obviously there is a one to one correspondence between a thermodynamic and a section of the curve in the phase space, or equivalently exist due to the complexity of the system different microscopic states such that the average of a quantity over a time interval of their evolution as give result in the same value. Therefore, to take account of our inability to prepare the system in a state determined microscopically consider a function $\rho(\mathbf{x}, \mathbf{p})$ in phase space, and this function represents the density of probability that a state macroscopically determined match microstates in the volume $d\mathbf{x}d\mathbf{p}$ centered around \mathbf{x}, \mathbf{p} .

By definition must be $\int \rho(\mathbf{x}, \mathbf{p}) d\mathbf{x}d\mathbf{p} = 1$.

The conservation of ρ time ago that is worth the continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \rho v = 0$$

where \mathbf{v} is extended to the vector (\dot{x}, \dot{p}) .

In steady state we then $\nabla \rho v = 0$, specializing:

$$\frac{\partial}{\partial x} \rho \dot{x} + \frac{\partial}{\partial p} \rho \dot{p} = 0$$

Or

$$\dot{x} \frac{\partial \rho}{\partial x} + \dot{p} \frac{\partial \rho}{\partial p} + \rho \left(\frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} \right) = 0$$

but the Hamiltonian mechanics, along the trajectories of the system:

$$\begin{aligned} \dot{x} &= \frac{\partial H}{\partial p} & \Rightarrow & \quad \frac{\partial \dot{x}}{\partial x} = \frac{\partial^2 H}{\partial x \partial p} \\ \dot{p} &= -\frac{\partial H}{\partial x} & \Rightarrow & \quad \frac{\partial \dot{p}}{\partial p} = -\frac{\partial^2 H}{\partial x \partial p} \end{aligned}$$

So, Liouville theorem for a system under stationary conditions the density of probability is a constant along the trajectories of the system:

$$\frac{d\rho}{dt} = 0.$$

The same is true if we consider a system at the quantum level. Expanding the wave function of the system in a comprehensive basis:

$$|\psi\rangle = a_i |\phi_i\rangle$$

the expectation value for a quantity \mathbf{f} it will be given by:

$$\langle \psi | \hat{f} | \psi \rangle = a_i^* a_j \langle \phi_i | \hat{f} | \phi_j \rangle = a_i^* a_j f_{ij}$$

The time evolution of the system is described by the equations:

$$\dot{a}_i = -\frac{i}{\hbar} \langle \phi_i | H | a_j \phi_j \rangle = H_{ij} a_j.$$

The transition to the incomplete description of quantum statistics are made by changing the words in $a_i^* a_j$ relative to the pure states with the terms w_{ji} which represent the statistical average. The evolution of the matrix w in general should return the correct description of the evolution to a pure state, ie, with no statistical uncertainty, therefore:

$$\dot{w}_{ji} = \dot{a}_i^* a_j + a_i^* \dot{a}_j = \frac{i}{\hbar} (a_j a_l^* H_{li}^* - a_i^* H_{jl} a_l) = \frac{i}{\hbar} (wH - Hw).$$

So if w commutes with H then w does not change over time. This is the equivalent of the Liouville theorem.

If the base $|\phi_i\rangle$ H has a diagonal representation, then w is independent of time only if

$$\epsilon_i \neq \epsilon_j \Rightarrow w_{ij} = 0,$$

and therefore it is possible to find a basis in which both w and H simultaneously have diagonal representation.

Catered Liouville's theorem, n is the quantum equivalent are sufficient to determine the shape of the density of probability. The distributions that we will use can be obtained from the above two hypotheses under equivalent: that states of equal energy have equal a priori probabilities, ie that the distribution statistically maximizes the entropy of the system. Given a set of mutually exclusive events, the entropy associated with the distribution of probability is given by:

$$S = \sum -w_i \ln(w_i)$$

which is obviously a positive magnitude, since $w_i \leq 1$.

A microcanonical ensemble is said if his energy is assigned. For the study of the statistical distribution of this set, therefore, we can limit ourselves to states that meet the requirement $\epsilon = E$, since otherwise w anything. We introduce the Lagrange function that includes the constraint $\sum w_i = 1$

$$\mathcal{F} = \sum w_i \ln(w_i) + \alpha(\sum w_i - 1)$$

in order that \mathcal{F} takes an extremal value then:

$$\frac{\partial \mathcal{F}}{\partial w_i} = \ln(w_i) + 1 + \alpha = 0 \Rightarrow w_i = e^{-1-\alpha} = \text{costante}$$

and α can be derived from the condition of the bond:

$$\sum w_i = 1 \Rightarrow w_i = 1/N \Rightarrow \alpha + 1 = -\ln(1/N) = S$$

As already said the condition of maximization of entropy coincides with the statistical assumption of equivalence of states of equal energy. We can arrive at a similar definition of entropy for the microcanonical ensemble even in the context of classical mechanics:

$$S = \ln \int_{\Gamma(E)} dx dp$$

Where $\Gamma(E)$ designates the set of points of the phase space of energy E . Evident that this definition of entropy depends on the unit of measure. To eliminate this equivocity and divides the integral for getting \hbar^{3N} also a correspondence between the value obtained from classical mechanics and the value obtained by quantum mechanics in the classical regime.

Now suppose we divide an isolated thermodynamic system into two parts. For the case of advanced, the system realizzer with equal probability to each of the microstates $|i, j\rangle$ which verify the relationship $\epsilon_{1i} + \epsilon_{2j} = E$.

Therefore, the probability to find a part in a state i is proportional to the number of ways in which the other party can achieve a state of energy $E - \epsilon_i$. therefore,

$$w_{1i} \propto e^{S_2(E - \epsilon_{1i})} = e^{\alpha - S_2(E_2) + \frac{dS_2}{dE_2}(E - E_2 - \epsilon_{1i})}$$

where we took advantage of the fact that the fluctuations around the energy E of a thermodynamic system are small to expand the function $S(E)$. But $dS/dE = \beta$ and thermodynamics $1 / T$.

Therefore we have:

$$w_i = e^{-\alpha - \beta \epsilon_i}$$

where α is the normalization factor:

$$e^{-\alpha} = \frac{1}{\sum_i e^{-\beta \epsilon_i}}$$

and the sum in the denominator is called the partition function. From the expression of entropy

$$S = - \sum_i w_i \ln(w_i) = \sum_i (\alpha + \beta \epsilon_i) e^{-\alpha - \beta \epsilon_i} = \alpha + \beta E \Rightarrow \alpha = S - \beta E = -\beta F$$

we get that α which is linked to the function of Helmholtz, F , for which we can rewrite the distribution:

$$w_i = e^{\beta(F - \epsilon_i)}$$

This distribution is called the canonical distribution. Suppose now that a part of the system can communicate with the rest not only energy, but also matter. Then, generalizing the arguments of the first and the expansion of the entropy

$$S(E, n) = S(E_0, n_0) + \beta(E - E_0) - \beta\mu(n - n_0)$$

we get

$$w_{n,i} = e^{-\beta(\Omega + n\mu - \epsilon_{n,i})}$$

where Ω is the usual normalization factor, which one can derive the expression of entropy:

$$S = \sum_{n,i} \beta(\Omega + n\mu - \epsilon_{n,i}) e^{-\beta(\Omega + n\mu - \epsilon_{n,i})} = \beta(\Omega + N\mu - E)$$

or

$$\Omega = \frac{S}{\beta} - N\mu + E = PV.$$

Insieme statistico	Distribuzione	Fattore di normalizzazione
microcanonico	$w_i = e^{-S}$	e^{-S}
canonico	$w_i = e^{\beta(F - \epsilon_i)}$	$e^{\beta F} = e^{-S + \beta E}$
grancanonico	$w_{n,i} = e^{-\beta(\Omega + n\mu - \epsilon_{n,i})}$	$e^{-\beta\Omega} = e^{-S + \beta(E - \mu)}$

In summary, the sets microcanonical, canonical and grandcanonical are models of closed systems, respectively, which are open to the exchange of heat, open to the exchange of heat and mass transfer. The normalization factors are related to the functions $S, -\beta F, e^{-\beta\Omega}$ which, as is known from thermodynamics take maximum value for each of the three types of systems in equilibrium conditions.

We will apply now the distribution grandcanonical to find the thermodynamic functions of systems of identical particles. Fermions are particles whose wavefunction is antisymmetric with respect to exchange of two positions.

In formulas, designated $\mathbf{x} = r, s$ the set of coordinates that describe the position and spin,

$$P_{ij} \Psi(x_1 \dots x_i \dots x_j \dots x_n) = \Psi(x_1 \dots x_j \dots x_i \dots x_n) = -\Psi(x_1 \dots x_i \dots x_j \dots x_n).$$

A consequence of this is that in the description of the independent states of the two particles can not occupy the same state. For several reasons, this description is by far the most common and therefore occupies a special position. If the states are independent, we can consider each state as a thermodynamic system at hand, then for each of the states we have,

$$w_{n,i} = e^{\beta(\Omega_i + n\mu + n\epsilon_i)}$$

$$\Omega_i = -T \ln \left(\sum_n e^{\beta n(\mu + \epsilon_i)} \right)$$

but the sum is reduced to only two terms, since the possible values of the number of jobs for fermions are 0 and 1.

Therefore,

$$\Omega_i = -T \ln(1 + e^{\beta(\mu - \epsilon_i)})$$

$$n_i = \sum n w_{n,i} = \frac{e^{\beta(\mu - \epsilon_i)}}{1 + e^{\beta(\mu - \epsilon_i)}} = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$$

and each thermodynamic property is obtained as the sum of the contributions of each state / subsystem. Bosons are identical particles such that the wave function that describes them is symmetric with respect to the exchange of the coordinates. The description in terms of independent states, there are no limits to the occupation numbers of bosonic states. Thus the sum Ω that describes contains all possible values of the index n ,

$$\Omega_i = -T \ln\left(\frac{1}{1 - e^{\beta(\mu - \epsilon_i)}}\right)$$

$$n_i = \sum n w_{n,i} = \frac{e^{\beta(\mu - \epsilon_i)}}{1 - e^{\beta(\mu - \epsilon_i)}} = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$$

The numbers n_i define the relationship of the probability of finding in each state i . As can be seen, bosons and fermions differ in the sign in the denominator, in the case of fermions, the positive sign ensures that n_i is always less than 1. In the case of bosons, instead, in order that the expression makes sense, μ must be less than all energy levels. Note also that $e^{\beta(\epsilon_i - \mu)} \ll 1$, ie for small values of the occupation numbers, the two distributions take values close to the Boltzmann distribution $e^{-\beta \epsilon_i}$.

We could also obtain the distribution of Boltzmann, Fermi-Dirac and Bose-Einstein from the maximization of entropy, for giving good that the distribution of probability is a function of the energy alone. Let a system of N independent particles. We wonder what is the distribution of the occupation numbers of the states of the system that maximizes the entropy under the constraint that the sum of the occupation numbers is N , and that the energy of the system is the set point E .

To obtain the sought formula, we divide the energy eigenstates into groups such that each group has the same energy in less than a macroscopic indeterminacy and are irrelevant? $\epsilon_j e \bar{G}_j$ respectively the energy value and the cardinality of each group. The system is then described macroscopically by the number N_j of particles occupying each group j , or the number of

average employment $n_j = N_j / G_j$. $n_j = N_j / G_j$. The diversities in the statistical behavior of the particles arises from the way in which you count the macroscopic states of the system.

For a set of distinguishable particles the number of states that we can build on the basis of single-particle states of G_j is given by

$$\Gamma_j = G_j^{N_j}$$

As already said, the number of maximum employment for fermions is 1. Therefore, the number of macroscopic states that it is possible to obtain G_j been dealing with fermions N_j is the way to choose N_j of G_j states, or

$$\Gamma_j = \binom{G_j}{N_j} = \frac{G_j!}{N_j!(G_j - N_j)!}$$

Bosons are particles indistinguishable, but the number of jobs in each state is arbitrary. If a configuration is represented by a succession of dots and strokes,

o|oo|oo||ooo|oo ...

in which each point represents a boson and all the sudden separation between two states then it can be deduced that the number of distinguishable configurations is given by the number of ways in which you can assign $N_j - 1$ traits to $G_j + N_j - 1$ places.

therefore

$$\Gamma_j = \binom{G_j + N_j - 1}{N_j - 1} = \frac{(G_j + N_j - 1)!}{N_j!(G_j - 1)!}$$

Therefore, the configuration described by n_j is associated to entropy

$$S = \sum_j \ln \Gamma_j$$

Using Stirling's formula for the asymptotic value of the factorial function:

$$\ln(z!) = z \ln(z) - z - \frac{1}{2} \ln(z) + \ln(2\pi) + \omega(z) \approx z \ln(z) - z$$

We obtain:

$$S = \sum_j G_j (n_j \ln n_j \mp (1 \pm n_j) \ln(1 \pm n_j))$$

where the upper sign applies to bosons and the lower sign for fermions . In the limit of small values of n_j , applicable for example to gas at ordinary temperatures , the two entropy formulas become equivalent to each other and to the relationship longer the simplest

$$\Gamma_j = \frac{G_j^{N_j}}{N_j!}$$

$$S = \sum_j G_j (n_j \ln(n_j) + n_j) = \sum_j N_j \ln(en_j)$$

which returns the correct Boltzmann statistics of the factor $N!$ to take account of the identity of the particles (boltzoni) .

To maximize the entropy subject to the constraints

$$\sum_j G_j n_j = N$$

$$\sum_j \epsilon_j G_j n_j = E$$

we form the Lagrange function

$$\mathcal{F} = \sum_j G_j (n_j \ln n_j \mp (1 \pm n_j) \ln(1 \pm n_j)) + \alpha (\sum_j G_j n_j - N) + \beta (\sum_j \epsilon_j G_j n_j - E)$$

getting value for extremal

$$\ln\left(\frac{1 \pm n_j}{n_j}\right) = \alpha + \beta \epsilon_j$$

which is the distribution of identical particles already obtained in above.

As an exercise we calculate the properties of an ideal gas of boltzoni . If the gas is made up of point particles and at temperatures such that we can neglect the quantum corrections we simply :

$$\beta F = -\ln\left(\frac{1}{h^{3N} N!} \int_{\Gamma} e^{-\beta \sum_i \frac{p_i^2}{2m}} dx dp\right)$$

positions on the integral yields simply the volume V , the integral on the moments is factored :

$$\int e^{-\beta \frac{p^2}{2m}} dp = \sqrt{\frac{2m\pi}{\beta}}$$

Finally

we

get:

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

Therefore, we calculate the energy :

$$E = -\frac{\partial}{\partial \beta}(\beta F) = \frac{3N}{2}T,$$

Entropy :

$$S = \beta(E - F) = N \ln\left(\frac{N h^3}{V} \frac{\beta}{2m\pi}\right) + \frac{N}{2}$$

and the pressure of the system:

$$P = -\frac{\partial F}{\partial V} = \frac{NT}{V}$$

If the constituents of the gas are pluriatomici , or temperatures such that the internal electronic structure becomes relevant bisogner have to add terms related to internal degrees of freedom .

$$F = F_{tr} + F_{rot} + F_{vibr+el}$$

and where Ftr is for contributions to translational already calculated for the rotational Frot , which classically is described by :

$$\beta F_{rot} = -\ln \int_{\Omega} e^{-\frac{\beta}{2}(\frac{M_x^2}{I_x} + \frac{M_y^2}{I_y} + \frac{M_z^2}{I_z})} dM = -\ln \left(\sqrt{\frac{2\pi I_x}{\beta}} \sqrt{\frac{2\pi I_y}{\beta}} \sqrt{\frac{2\pi I_z}{\beta}} \right)$$

with Ix, Iy , Iz moments of rotational inertia along the principal axes.

$F_{vibr+el}$ and represents the contribution of the electronic and vibrational states.

To conclude we note that passing from the classical statistical thermodynamics it is necessary to carry out replacements

$$\begin{aligned} S &\rightarrow S/K_b \\ T &\rightarrow K_b T \end{aligned}$$