Science and Technology Faculty

Physics Department

Handout of the subject:
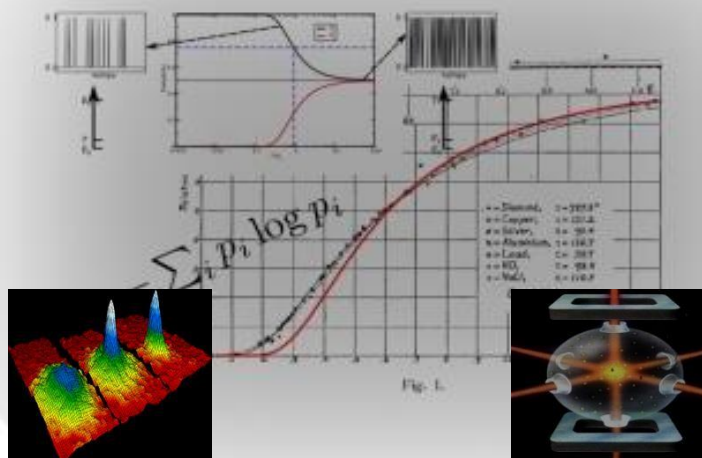
3rd year Bachelor's degree

(LMD)

Statistical Physics
Courses & Applications

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Chapter III Maxwell-Boltzmann's Perfect Gas

Chapter IV Bose and Fermi Perfect Gases

Annex

Statistical physics is a probabilistic approach that allows us to study the macroscopic or thermodynamic properties (such as temperature, pressure, etc.) of a physical system, in equilibrium! This system is composed of a very large number of particles, so it has a very large number of degrees of freedom. Phenomenological, its macroscopic properties are described by the laws of thermodynamics. We can also define statistical physics as the branch of physics that uses probability and statistical methods, and the laws of physics that apply at the microscopic level (such as classical mechanics, quantum mechanics, etc.) to study systems consisting of very large numbers of particles. We know that matter consists of particles (atoms, molecules and ions) and that the state in which these particles are found (position and speed) is responsible for the phenomena observed on a macroscopic scale (human scale). For example, the notion of temperature is related to the kinetic energy or the average speed of the particles: the greater their speed the hotter the body made up of particles seems (example: gas theory perfect

$$\left(\overline{E_c} = \frac{1}{2}m\overline{v}^{-2} = \frac{1}{2}k_bT \right)$$

Statistical physics refers to the study or understanding of the properties of *macroscopic* systems (solids, liquids, gases, magnets (spin system),...) with a number $N=Na = 6, 02.10^{23}$ of elements.

Similarly, the notion of density or density is related to the average distance between particles, and the notion of pressure is related to the amount of motion that these particles can transmit to any face.

The purpose of statistical physics is the study of the behavior of the particles that make up physical bodies in relation to the quantities observed on a human scale. The study of the behaviour of particles is called microscopic. The observed quantities are said to be macroscopic. These are measurement results.

Along with quantum mechanics and relativity, statistical physics is one of the pillars of modern physics. It is based on the laws of relativity and quantum mechanics to explain the collective behavior of particle assemblies in the limit where the number of particles is very large. It uses the laws of probability and statistics to explain the behavior of this large number of constituents. The latter (particles) can be atoms, molecules, ions, etc.

Thermodynamics is based on postulates, these are the principles of thermodynamics. Also statistical physics is also constructed from postulates, which are the reasonable assumptions

chosen a priori. The basis of this choice makes it possible to reproduce, and understand, a large number of properties of macroscopic bodies. Since statistical physics takes into account the properties of microscopic constituents, then thermodynamics only deals with the macroscopic properties of bodies, it is a more complete science than the latter.

The main objectives of statistical physics can be summarized in the following three points:

➢ Statistical physics gives a rational understanding of thermodynamics from the characteristics of the microscopic constituents of a system and their interactions.

➢ Statistical physics makes it possible to calculate the dependence of thermodynamic quantities (specific heat, ... etc.) in terms of temperature and transport properties (heat, electricity, ... etc.).

➢ Statistical physics gives a complete explanation for phase transition phenomena.

This course is intended for students in the third year of fundamental physics. He is interested in classical statistical physics.

So this course is an introduction to statistical physics. In the first chapter, we give some reminders of thermodynamics, probabilities and statistics, and we demonstrate some relationships that we will need in the following chapters. In the second chapter, we will develop a formalism (micro and macro state) that allows us to calculate the entropy and thermodynamic properties of an isolated system (constant energy), and to find the results of thermodynamics from its Hamiltonian. In the third and fourth chapters, we will develop how to determine the energy of a closed system that can exchange energy with the external environment and we will generalize by taking into account the spin of particles (Fermi-Dirac and Bose-Einstein statistics). We will also study the radiation of the black body (perfect gas of photons) .

I. Introduction

This chapter discusses reminders on probability methods and statistics, thermodynamics, and we will introduce some important and necessary relationships in this course.

I.2   Introduction to statistical methods

I.2.1   Combinatory analysis

➢   **Permutations:** the number of permutations of N objects is given by

$$P = N(N-1)(N-2)...1 = N!$$ (I.1)

For example: the number of permutations of three numbered objects in the racks is: 3!=6 ≡ /1/2/3/,/1/3/2/,/2/1/3/,/2/3/1/,/3/1/2/,/3/2/1/.

➢ **Arrangements:** the number of arrangements is the number of ways to choose n objects from *N* objects taking into account the order of taking, it is given by

$$A_N^n = \frac{N!}{(N-n)!}$$ (I.2)

For example: Let be 4 balls numbered from 1 to 4. The number of possible cases of taking two balls out of the 4, taking into account the order of taking, is:

$$A_4^2 = \frac{4!}{(4-2)!} = 12 \equiv (1,\ 2),(1,3),(1,4),(2,1),(2,3),(2,4),(3,1),(3,2),(3,4),(4,1),(4,2),(4,3)$$

Note that (1, 2) and (2, 1) are considered as two different cases.

➢ **Combinations**: the number of combinations is the number of choosing n objects from N objects without taking into account the order of taking, it is given by:

$$C_N^n = \frac{N!}{(N-n)!n!}$$ (I.3)

For example: we take the previous example without taking into account the order, i.e. (1, 2) and (2, 1) are counted as a single combination. So the number of combinations is:

$$C_N^n = \frac{N!}{(N-n)!n!} \equiv (1,\ 2),(1,\ 3),(1,\ 4),(2,\ 3),(2,\ 4),(3,\ 4).$$

I.2.2 Concept of probability and statistics

Statistical physics is based on probability and statistics, because we are interested in systems composed of very large numbers of particles. Therefore, the value of an experimentally observed physical quantity corresponds to its most probable value.

➤ **Probability in case of discrete events:**

Note the possible configurations (or event) of a system by $ji >$, and the number of experiments for this system to be in one of these configurations by n_i. Then the probability of finding the system in a $/i >$ configuration is

$$P_i = \frac{n_i}{N}, \qquad\qquad N = \sum_i n_i. \qquad (I.4)$$

Note: In the general case, the total number of experiments N can be finite or infinite.

For example: If you toss a coin *N* times. We denote by n_1 and n_2 the number of times to obtain heads and tails, respectively. Then, the probabilities of getting flip-flop are given by

$$P_{n_1} = \frac{n_1}{N}, \qquad\qquad P_{n_2} = \frac{n_2}{N}. \qquad (I.5)$$

➤ **Basic properties**

➤ *Normalization:* the normalization conditions in both cases are written, respectively

$$\sum_i P_i = \frac{\sum_i n_i}{N} = 1 \qquad (I.6)$$

$$\int_{-\infty}^{+\infty} \rho(x_1, x_2,..., x_N) dx_1 dx_2 ... dx_N = \int dP(x_1, x_2,..., x_N) = \frac{1}{N}\int dn(x_1, x_2,..., x_N) = 1. \qquad (I.7)$$

➤ *Addition:* If the two events *e*1 and *e*2 are *compatible*, then the probability is given by

$$P(e_1 \cup e_2) = P(e_1) + P(e_2) - P(e_1 \cap e_2). \qquad (I.8)$$

If two the two events $e1$ and $e2$ are *incompatible*, then the probability is given by

$$P(e_1 \cup e_2) = P(e_1) + P(e_2).$$ (I.9)

If the event depends on a continuous parameter x, then the probability is given by

$$P(a \le x \le b) = \int_a^b \rho(x)dx.$$ (I.10)

➢ **Mean value:**

If the events are discrete, then the mean value of a quantity f is defined by

$$f = \sum_m P_m f_m.$$ (I.11)

If the events are continuous, then the average value of a quantity f is defined by

$$f = \int_{-\infty}^{+\infty} \rho(x) f(x) dx.$$ (I.12)

➢ **Variance:** In the case of discrete events, the variance is defined by

$$\sigma^2 = \overline{\left(f - \overline{f}\right)^2} = \overline{f^2} - \left(\overline{f}\right)^2.$$ (I.13)

In the case of continuous events, the variance is defined by

$$\sigma^2 = \int_{-\infty}^{+\infty} \rho(x)\left(f(x) - \overline{f}\right)^2 dx = \overline{\left(f(x)\right)^2} - \left(\overline{f(x)}\right)^2.$$ (I.14)

Standard deviation: is defined by: $\sigma = \sqrt{\sigma^2}$

➢ **Binomial distribution:** We use the binomial distribution if we have only two possible types of events (A and B of probability P_A and P_B for example). The probability of having n times A and $N - n$ times B is given by:

$$P(N,n) = C_N^n P_A^n P_B^{N-n}$$ (I.15)

where N is the number of experiments performed. It can be shown that:

the binomial probability is normalized:

$$\sum_{n=0}^{N} P(N,n) = 1.$$

The mean value of n is $\bar{n} = NP_A$

The variance is given by $\sigma^2 = NP_A P_B$.

The standard deviation $\sigma = \sqrt{NP_A P_B}$

the relative uncertainty on the average value is

$\Delta \frac{n}{\bar{n}} \propto \frac{1}{\sqrt{N}}$

➢ **Gaussian distribution:** This distribution is applied to continuous events. The Gaussian probability density is given as follows:

$$\rho(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-x_0)^2}{2\sigma^2}}. \tag{I.16}$$

where x_0 is the central value of the distribution and σ is the width at mid-height of $\rho(x)$. It can be shown that:

Gaussian probability is normalized $\int_{-\infty}^{+\infty} \rho(x)dx = 1$

The mean value of x is: $\bar{x} = x_0$ The

variance is given by σ^2

The standard deviation is σ

The binomial law becomes the Gaussian law when $N \gg n \gg 1$

➢ **Poisson's law:** Rare events (very small probability event) follow the law of Fish

$$P(n) = \mu^n \frac{e^{-\mu}}{n!}. \tag{I.17}$$

where n is the number of events of the same type. It can be shown that:

poisson's law is normalized: $\sum_{n=0}^{\infty} P(n) = 1$

the binomial law becomes Poisson's law when $P_A \ll P_B$ and $N \gg n \gg 1$

➢ **One-Dimensional Random Walk:** Consider a particle that moves, by discrete steps, on the *x-axis*. It is noted that the length of each step is Δl, and that the particle can move either to the left or to the right.

➢ It is assumed that the probability for the particle to make a step to the right is P_1, and a step to the left is P_2. Then, the probability for the particle to make *n*1 steps to the right and *n*2 steps to the left (*N*=*n*1+*n*2 steps) follows the binomial law.

$$P(N,n_1) = \frac{N!}{n_1!(N-n_1)!}P_1^{n_1}P_2^{N-n_1} \tag{I.18}$$

si $P_1 = P_2 = \frac{1}{2}$.

$$P(N,n_1) = \frac{N!}{n_1!(N-n_1)!}\left(\frac{1}{2}\right)^N. \tag{I.19}$$

➢ Average displacement values are given by $\overline{n_1} = \overline{n_2} = NP_1 = N/2.$, the average position after N displacement is at the origin.

➢ The variance $\sigma^2 = NP_1P_2 = N/4$, Therefore, the relative uncertainty is $\frac{\sigma}{n_1} = 1/\sqrt{N}$

I.2   Mechanical elements

We will introduce the different formalisms to describe the classical dynamics in the phase space.

I.2.1   Lagrangian Formalism

Let's say N particles.

According to Newton's law (where *qi* are the position variables and V the potential in which they are):

$$m\ddot{q}_i = F_i = -\frac{\partial V(\{q_j\})}{\partial qi} \tag{I.20}$$

with i varying from to 3N

The kinetic energy of the system is then:

$$T\left(\{q_j\}\right) \;=\; \frac{1}{2}m\sum_j \dot{q}_j^2.$$

(I.21)

Hence with the Newtonian equation:

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_i} = \frac{d}{dt}\left(mq_i\right) \; = m\ddot{q}_i$$

(I.22)

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_i} - \frac{\partial V\left(\{q_i\}\right)}{\partial q_i} \; = 0$$

(I.23)

The Lagrangian is introduced:

$$L\left(\{q_j\},\{\dot{q}_j\},\, t\right) = T\left(\{q_j\},\{\dot{q}_j\},\, t\right) - V\left(\{q_j\},\, t\right)$$

(I.24)

Note: q_j and are considered independent because they are the variables of a Lagrangian a not the variables of an equation of motion that would connect them.

Marks:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_i \dot{q}_i \frac{d}{\partial q_i} + \sum_i \ddot{q}_i \frac{d}{\partial \dot{q}_i}$$

(I.25)

Newton's equation then gives

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$$

(I.26)

This is Lagrange's equation (scalar, so different from Newton's). Properties:

$-\; q_i$ et $\dot{q}_i$ are on the same plane

$-$ lagrange's equation is shape invariant by changing coordinates

I.2.2   Hamiltonian Formalism

We define *3N* quantity *{p_i}* by

$$p_i = \left. \frac{\partial L}{\partial \dot{q}_i} \right|_{\{q_j\}\, fixes} \tag{I.27}$$

It is the generalized pulse that gives a relation q_i $q_i \{q_j\}, \{p_j\}, t$

We then define the Hamiltonian (by Legendre transformation for L to eliminate the variable q_i

Gold

$$H\left(\{q_j\},\{p_j\},t\right) = \sum_i p_i \dot{q}_j \left(\{q_j\},\{p_j\},t\right) - L\left(\{q_j\},\{\dot{q}_i\left(\{q_j\},\{p_j\},t\right)\},t\right) \tag{I.28}$$

$$dH = \sum_i \left(\dot{q}_i dp_i + p_i d\dot{q}_i - \frac{\partial L}{\partial q_i} dq_i - \frac{dL}{d\dot{q}_i} d\dot{q}_i \right) - \frac{\partial L}{\partial t} dt. \tag{I.29}$$

$$= \sum_i \left(\dot{q}_i dp_i - \frac{\partial L}{\partial q_i} dq_i \right) - \frac{\partial L}{\partial t} dt. \tag{I.30}$$

Or

$$dH = \sum_i \left(\frac{\partial H}{\partial q_i} dp_i + \frac{\partial H}{\partial p_i} dp_i \right) + \frac{\partial H}{\partial t} dt. \tag{I.31}$$

Hence by identification:

$$\dot{q}_i = \frac{\partial H}{\partial q_i} \tag{I.32}$$

$$\frac{\partial L}{\partial q_i} = -\frac{\partial H}{\partial q_i}$$

$$\frac{\partial L}{\partial t} = -\frac{\partial H}{\partial t}$$

Or $\dfrac{\partial L}{\partial q_i} = \dfrac{d}{dt} \dfrac{\partial L}{\partial \dot{q}_i} = \dfrac{d}{dt} p_i = \dot{p}_i$. Donc :

$$\begin{cases} \dot{q}_i = \dfrac{\partial H}{\partial p_i} \\[2mm] \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \end{cases}$$

Properties:

– p_i and q_i are on the same plane (one does not explicitly derive from the other)

– first order equation in *t*

– given *6N* initial conditions, there is only one solution

– two trajectories in the phase space cannot intersect

I.3   Thermodynamics Reminders

Thermodynamics is a phenomenological description of the macroscopic properties of a physical system in equilibrium. Its main purpose is to describe the transformations between the two forms of energy: heat and work. In this section, we present the most important points in this subject. For more details, see reference [1].

I.3.1   Définitions et notions de base

The historical definition of thermodynamics is the science of heat and thermal machines, and according to Boltzmann is the science of large systems in equilibrium. The main purpose of this science is to describe the transformations between the two forms of energy, mechanical work and heat. In this session, we give the main notions of thermodynamics (2nd year course). United Kingdom

➢   **thermodynamic system**

A part of the universe surrounded by a closed surface (a gas enclosed in a balloon). It is a system composed of a very large number of particles (atoms, molecules, etc.), described by a set of variables (thermodynamic or macroscopic variables) that describe the properties and behavior of the latter. These variables are classified into extensive and intensive variables. This system can be: insulated if it cannot exchange heat or work or matter with the outside, open, if it can exchange heat, work and matter with the outside, or closed if it can exchange heat and work with the outside but not matter.

➢   **Macroscopic or thermodynamic variables:**

Using a small number of parameters, the thermodynamic properties of a system can be described. These parameters can be determined by taking measurements at our scale, they are called macroscopic variables. For example: absolute temperature *T*, pressure *P*, volume *V*, ... etc. The thermodynamic variables necessary to write, completely, the behavior of a system, composed of g different types of particles, are: $\left\{ T, p, V, N_1, \ldots, N_g \right\}$

(where N_i is the number of particles of type i).

➢ **Extensive variables:**

These variables vary if two systems are combined, such as the volume *V*, the number of particles *N*, the total energy *E*, the magnetization *M*. etc. If two identical thermodynamic systems are combined, for example, all the associated extensive variables increase by double.

➢ **Intensive variables:**

These variables do not vary if two identical systems are combined, such as temperature T, pressure P, μ chemical potential, electric field, $\vec{E}$ etc. The ratio of two extensive variables is an intensive variable (e.g. particle number density n = N/V).

➢ **Classic mechanics**

The position and motion of a particle are described by 6 variables. For example, a loose particle is described by: the position $\vec{q} = (x; y; z)$ and the pulse $\vec{p} = (p_x; p_y; p_z)$, where $\vec{p} = md\vec{q}/dt$. If the system is composed of *N* free particles, then its state is fully described by *6N* variables (where *6N* degrees of freedom in phase space).

➢ **Quantum mechanics**

The state of a particle is described by its wave function (solution of Schrödinger's equation) and quantum numbers, see section.

➢ **photograph**

A macroscopic state is the configuration associated with given values of the macroscopic parameters.

➢ **Microscopic:**

A microscopic state is determined by the data of a complete set of parameters (quantum numbers for example) that make it possible to uniquely determine the configuration of the system on the microscopic scale.

➢ **System in equilibrium:**

If its macroscopic variables do not vary over time.

➢ **Thermodynamic process:**

A thermodynamic process is any change or succession of changes in the state of macroscopic variables. It is:

    (a) cyclic if its initial and final states are the same.

    (b) quasi-static if the system goes through a succession of equilibrium states.

    (c) reversible if its thermodynamic path can be reversible ($dQ = T\,dS$).

    (d) isothermal: $dT = 0$.

    (e) isobaric: $d\,p = 0$.

    (f) isochore: $dV = 0$.

    (g) adiabatic: $dQ = 0$...etc.

➢ **Ideal gas**

    A gas is called an ideal gas if the mutual interactions between its molecules are negligible.

Low pressure helium is a good approximation of a perfect gas. Its equation of state is:

$$PV = Nk_b T \tag{I.33}$$

where N is the number of particles in mole, p is its pressure (in Pascal pa), T is its temperature (in Kelvin K) and k_b is Boltzmann's constant,

$$k_b = 1.38064852 \times 10^{-23}\ \mathrm{J} \cdot \mathrm{K}^{-1}. \tag{I.34}$$

➢ **Van der Waals equation:**

The Van der Waals gas (non-perfect gas) equation of state is given by:

$$\left(p + \frac{aN^2}{V^2} \right)(V - bN)\ = Nk_B T \tag{I.35}$$

where a and b are parameters that depend on the nature of the molecules making up the gas.

➢ **Mechanical work**

It is a macroscopic scale energy transfer that results in a change in macroscopic parameters other than temperature. If the macroscopic variable that varies is the volume ($dW = pdV$), the work is said to be of mechanical origin. In general, the differential element of the work is given by:

$$dW = \sum_i F_i dX_i. \tag{I.36}$$

where F_i and X_i are the force and the generalized displacement.

➢ **Heat:**

It is an energy transfer at the macroscopic scale that results in a change in temperature (and not the other macroscopic parameters). It is said that there is a heat exchange Q. The unit of the heat quantity Q is the joule, where

$$1J = 10^7 \, \text{erg} = 6.242 \times 10^{18} \text{ev}. \tag{I.37}$$

➢ **Kinetic theories of gases:**

The purpose of the kinetic theory of gases is to explain the macroscopic behavior of a gas based on the characteristics (movement, ... etc) of its constituents (atoms, molecules, ...). This theory makes it possible to give a microscopic interpretation of the macroscopic variables (T and P).

➢ **Pressure:**

The unit of pressure (p) is the force per unit area. In the IS, its unit is Pascal (*Pa*), where 1 Pa=1N/m^2 = 1kg/ms^2,   1 bar = 10^5 Pa ,1 atm = $1.01325\text{x}10^5$ Pa

According to the kinetic theory of gases, the pressure results from the shocks of the particles on a surface wall S, therefore, it is related to their quantities of movement.

$$\vec{F} = p \, d\vec{S} \tag{I.38}$$

➢ **Temperature:**

In the kinetic theory of gases, it is directly related to the kinetic energy of particles. In the first chapter, we will derive the relationship between temperature and internal energy. For the perfect gas, for example, we can show that

$$U = \frac{3}{2} k_b T. \tag{I.39}$$

➤ **State function**

A state function is a physical quantity that depends only on the initial state and the final state (does not depend on the transformation path).

➤ **Internal energy**

The total energy of a conservative mechanical system is given by the sum of the kinetic energy and the potential energy of the particles that constitute it. This energy is called internal energy (denoted by U) in thermodynamics, where

$$dU = \delta W + \delta Q \tag{I.40}$$

➤ **Thermal capacity**

The heat capacity C is the energy that must be given to a system to increase its temperature by one kelvin. The unit of *C* is joule per kelvin (*J/K*),

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V, \qquad\qquad C_V = \left.\frac{\partial H}{\partial T}\right|_P, \tag{I.41}$$

where C_V is the isochoric heat capacity, C_p is the isobaric heat capacity and *H* is the enthalpy.

➤ **Entropy**

Entropy is an extensive state function, the unit of which is joule per kelvin (*J/K*). According to statistical physics, it can be interpreted as the measure of disorder of a system at the microscopic scale. It is defined by:

$$S = k_b \ln \Omega. \tag{I.42}$$

where Ω is the number of microscopic states accessible for a system.

For reversible processes, the variation in entropy is related to the variation in the amount of heat by,

$$dS = \frac{\delta Q}{T}. \tag{I.43}$$

➤ **Preservative system:**

A conservative system is a system whose energy is conserved.

➤ **Quasi-static transformation:**

If the evolution of the system is such that it always remains in thermodynamic equilibrium.

➢ **Chemical potential**

The chemical potential m describes the variation of the energy of a system with respect to its
quantity of matter. It has the dimension of a molar energy *J/mol.*

I.3.2   Principles of thermodynamics

➢ **Zero principle**

If two systems are in thermodynamic equilibrium with a third system, then all three systems are in
equilibrium with each other.

➢ **First principle:**

This principle announces the conservation of the total energy of a system. During a
thermodynamic process, the change in the internal energy of a system results in:

$$\Delta U = Q + W .$$

The differential form of this principle is given by

$$dU = \delta Q + \delta W \tag{I.44}$$

and $\int_c dU = U_f - U_i$ The total energy does not depend on the path followed, it depends on

• whether the initial state is final. So, U is a state function. On the other hand, *W* and *Q*
depend on the path followed, so they are not state functions.

➢ **Second principle:**

➢ **Clausius statement:** There is no process whose only result is to transfer heat from a cold
body to a hot body. It is possible to pass the heat from a cold body to a hot body but it is
necessary to provide work (refrigerator for example).

➢ **Kelvin-Planck statement:** There is no transformation whose only result is to produce
work from a single heat source at constant temperature. This means that it takes at least
two sources at different temperatures to carry out a conversion of heat energy into
mechanical energy (Carnot cycle for example).

➢ **Clausius' theorem:** For quasi-static cycles (Carnot), the following relation is verified:

$$\int \frac{\delta Q_{qs}}{T} = 0. \tag{I.45}$$

where is the_{amount} of heat exchanged quasi-statically with the system at the point in the cycle,
where the temperature is T.

The entropy S is defined by the relation

$$dS = \frac{\delta Q_{qs}}{T}, \quad \text{et} \quad \int dS = 0 \qquad (I.46)$$

Entropy is, therefore, a state function (or an extensive variable), because it does not depend on the path followed (it depends only on the initial state and the final state). It makes it possible to reformulate the second principle as follows: The entropy of an isolated system can only increase. If the process is reversible $\Delta \tilde{n} = 0$, if the process is irreversible $\Delta \tilde{n} > 0$.

➤ **Entropy of a perfect gas:** Consider a perfect gas consisting of N particles (N constant therefore $dN = 0$). The infinitesimal variation of U is

$$dU = TdS - PdV, \quad \text{ou} \quad \delta Q = TdS, \quad\quad\quad \delta W = -PdV.$$

in addition $PV = Nk_bT,$ $U = \frac{3Nk_bT}{2}.$

So

$$dS = \frac{3}{2}Nk_b \frac{dT}{T} + Nk_b \frac{dV}{V}. \qquad (I.47)$$

we can show that

$$S(T,P) = Nk_b \left\{ s_0\left(T_0, P_0\right) + \ln\left(\frac{T}{T_0}\right)^{5/2}\left(\frac{P_0}{P}\right) \right\} \qquad (I.48)$$

Where $s_0(T_0;P_0)$ is an arbitrary constant that is determined using the third principle of thermodynamics .

➤   **3rd Principle:**

The entropy of a solid or pure liquid in thermodynamic equilibrium is zero at absolute zero (Nernst statement).

I.3.3   Status Functions in Thermodynamics

A state function is a thermodynamic quantity that does not depend on the path followed, but it depends only on the initial state and the final state. In this paragraph, we give some state functions that allow us to calculate the thermodynamic properties of macroscopic systems.

➤ **Internal energy**

The internal energy is a function of the extensive parameters S, V , N_1, ..., N_r (where N_i is the number of type i particles):

$$U = U(S,V, N_1,..., N_r). \qquad (I.49)$$

Each extensive parameter corresponds to an intensive parameter equal to the derivative of *U* with respect to this parameter:

Temperature
$$T = \left(\frac{\partial U}{\partial S}\right)\Big|_{V,N,...,N_r} \qquad (I.50)$$

Pression.
$$P = -\left(\frac{\partial U}{\partial V}\right)\Big|_{S,N,...,N_r} \qquad (I.51)$$

Chemical potential.
$$\mu_j = -\left(\frac{\partial U}{\partial N_j}\right)\Big|_{S,N,...,N_{j-1},N_j,N_{j+1},...,N_r} \qquad (I.52)$$

So,

$$dU = TdS - PdV + \sum_{j=1}^{r} \mu_j dN_j. \qquad (I.53)$$

For a perfect gas, $N_j = cst$, then $dU = TdS - PdV$.

➤ **Enthalpy** *H(S, P, N)***:**

With Constant volume
$$H = U + PV = TS + \sum_{j=1}^{r} \mu_j dN_j \qquad (I.54)$$

$$T = \left(\frac{\partial H}{\partial S}\right)\Big|_{P,N,...}, \qquad V = \left(\frac{\partial H}{\partial P}\right)\Big|_{S,N,...}, \qquad \mu_j = -\left(\frac{\partial H}{\partial N_j}\right)\Big|_{S,N,...} \qquad (I.55)$$

➤ **Free energy** *F(T,V, N)***:**

Constant temperature

$$F = U - TS = -PV + \sum_{j=1}^{r} \mu_j dN_j \qquad (I.56)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)\bigg|_{V,N,\dots}, \qquad P = -\left(\frac{\partial F}{\partial V}\right)\bigg|_{S,N_j,\dots}, \qquad \mu_j = \left(\frac{\partial F}{\partial N_j}\right)\bigg|_{T,V,\dots} \qquad (I.57)$$

➢ **Free Enthalpy** *G(T, P, N)*:

With constant temperature and pressure

$$G = U + PV - TS = \sum_{j=1}^{r} \mu_j dN_j \qquad (I.58)$$

$$S = -\left(\frac{\partial G}{\partial T}\right)\bigg|_{P,N,\dots}, \qquad V = -\left(\frac{\partial G}{\partial P}\right)\bigg|_{S,N_j,\dots}, \qquad \mu_j = \left(\frac{\partial G}{\partial N_j}\right)\bigg|_{T,P,\dots} \qquad (I.59)$$

➢ **High potential** *Φ (T;V; m)*:

When we are interested in Bose or Fermi gases, we often use the great potential *Φ*:

$$\Phi = F - \mu N = -PV, \qquad (I.60)$$

$$d\Phi = -SdT - PdV - Nd\mu \qquad (I.61)$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)\bigg|_{V,\mu,\dots}, \qquad P = -\left(\frac{\partial \Phi}{\partial V}\right)\bigg|_{T,\mu,\dots}, \qquad \mu_j = -\left(\frac{\partial \Phi}{\partial \varpi}\right)\bigg|_{T,V,\dots} . \qquad (I.62)$$

I.4   Exercises and Issues

Exercise #1:

1- What is the probability for two people to have the same birthday in a class of N=30 people?

2- What is the probability that this will happen at least once among your classmates in your years of schooling (we assume that it is 30 different people each year?

Exercise #2:

A walker moves to a right by randomly jumping left or right (equiprobably) a distance a from where he is . We take as the origin of the coordinates the place where it is at time t=0. The amount of time that elapses between each of its jumps is denotedby.

1. What is the probability of the walker having, after N jumps made, n jumps to the right and N-n to the left?
2. What will then be its position x e is the n function of N ,n and a?
3. How long does it take him to make N jumps?
4. What is the average number of steps to the right?
5. Express the variance of the variable x, defined by: $\sigma_x{}^2 = (\Delta U)^2 - \langle U \rangle^2$, as a function of N and a and then as a function of t ,1 and a

We are now going to look at the behavior of $P(n, N)$ when n and N are very are very large in front of 1, form of a Gaussian law in variable ξ.

How the typical distance reached varies with time.

Exercise #3:

The Maxwell-Boltzmann distribution is given by:

$$f\left(\vec{v}\right) = \sqrt{\left(\frac{m}{2\pi k_b T}\right)^3} \exp\left(-\frac{mv^2}{2k_b T}\right)$$

where *m* is the mass of the particle under consideration, k_b is Boltzmann's constant, *T* is the temperature and $v^2 = v_x^2 + v_y^2 + v_z^2$

(1) Show that *f* is normalized.

(2) Calculate average values:

$$<v_x>, <v_y>, <v_z>, <v_x^2>, <v_y^2>, <v_z^2>, <E_c> \; et \; <v_x v_y>$$

$-$

(E_c is the kinetic energy).

Exercise #4

Application of the binomial law Calculate the probability of obtaining a face number between 3 and 6 when throwing a well-balanced coin 10 times.

Exercise #5:

Consider the following binomial distribution:

$$P(n) = \frac{N!}{n!\,(N-n)!} p^n q^{N-n}$$

N and n are two natural integers (with y $\leq$ y) and p and q are two complementary probabilities.

We place in the case $1\, p \ll 1\ et\ n \ll N$

1) Demonstrate that: $(1 - p)^{N-n} \approx e^{-Np}$

2) Show that: $\frac{N!}{(N-n)!} \approx N^n$

3) Based on the results established in (1) and (2). Show that p(n) can be written:

$$P(n) = \frac{\lambda^n}{n!} e^{-\lambda} \qquad or \quad \lambda = Np$$

Verify the normalization condition and show that λ is none other than $\bar{n}$

Introduction:

Statistical physics makes it possible to make the link between the macroscopic and microscopic worlds. At our scale, we can define a particular configuration of a macroscopic system (macro-state) by giving the value of all its independent thermodynamic variables. For example, for a perfect gas, it is enough to set three parameters chosen from the pressure, volume, and temperature and particle number of the gas. The fourth parameter is then obtained from the ideal gas equation of state.

If we study the system at the level of its constituents, we are interested in the *microscopic world*. It is appropriate at this stage to analyze the main characteristics of the elementary constituents of this body as we have just mentioned them:

They are extremely small. This means that their properties are often dominated by quantum phenomena.

We travel a great deal! Their evolution can therefore not be treated individually but as a particular element of a set with more global properties: this is the object of statistical physics.

Paradoxically, it is easier to introduce statistical physics from quantum mechanics than from classical mechanics.

At any given moment, the particles in a system are in a certain configuration called a *microstate*. The definition of this makes it possible to completely determine the system at the microscopic level. It is important to note that one cannot, in practice, determine the microstate of a macroscopic system. Indeed, consider for example a mole of gas. We have N particles, where N is Avogadro's number ($N = 6,02 \ 10^{23}$). Even if we used classical mechanics to describe the evolution of gas molecules, we would need to know $3N$ positions and $3N$ velocities to be able to fully determine a configuration of this system.

II.1 QUANTUM MICROSTATES

A microstate is a particular microscopic configuration of a system. Rather than introducing this concept formally, let's illustrate it with a few simple examples that will allow us to assimilate this concept.

Atome d'hydrogène.

As part of Bohr's theory, the energy levels of the electron are quantified. The energy of each level is given by:

$$\varepsilon_n = -\frac{13.6}{n^2} \tag{II.1}$$

where n is the main quantum number (for n > 1 excited states). For a given energy state, there are several possible configurations, each defined by the following quantum numbers:

The secondary quantum number l: $0 \leq l \leq n-1$..

The magnetic quantum number m: $-l \leq m \leq +l$.

The spin quantum number s: s = 1/2

The projection of s on the axis (oz) s_z: $-1/2 \leq s_z \leq +1/2$.

Therefore, for the hydrogen atom, a quantum microscopic state is determined by the five quantum numbers $(n;l;m;s;s_z)$. These make it possible to completely describe the system at the microscopic level. Example:

$$si\; n=1 \begin{cases} l=0, m=0, s=1/2, s_z=+1/2 \\ l=0, m=0, s=1/2, s_z=-1/2 \end{cases} \Rightarrow \Omega = 2micro-\acute{e}tats. \tag{II.2}$$

So, if *n = 1*, we have two different quantum microscopic states. If *n = 2*, the degeneration is equal to eight, *etc.* In the state corresponding to *n = 2* , we can therefore associate 8 different microstates.

II.1.2 The one-dimensional harmonic oscillator

The evolution of a weight suspended from a spring around its equilibrium position, after it has been slightly moved away from it, represents an example of a conventional harmonic oscillator. Suppose that the weight has a mass *m* and that it is likely to move in a single direction that we will note *x*. We will assume that the equilibrium position corresponds to *x*=0. This system has the behavior of a harmonic oscillator if its potential energy, *U*, is of the form:

$$U = \frac{1}{2} Kx^2 \tag{II.3}$$

where *K* is a constant. the equation of motion is written:

$$m\frac{d^2x}{dt^2} = -Kx \tag{II.4}$$

where *t* denotes time. The solution to this equation is a sinusoid whose pulsation is given by:

$\omega = \sqrt{\frac{K}{m}}$. The system oscillates around its equilibrium position with the pulse , *i.e.* with a

frequency $\nu = \frac{\omega}{2\pi}$.n . Conventionally, all positive energy values are permitted.

At the microscopic level, there are also systems whose potential energy is a quadratic form of the

coordinates. A very simple example is given by the hydrogen molecule whose two atoms can oscillate along the axis of symmetry of the molecule. The correct description of such systems requires the use of quantum mechanics. As with the hydrogen atom, this theory says that energy levels, and therefore pulses, are quantified. In the case of a one-dimensional harmonic oscillator, the energy levels are given by the expression:

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega \qquad\qquad (\text{II.5})$$

where *n* is a positive integer or zero: this is the quantum number associated with a one-dimensional oscillator.

II.1.3 A free particle in a cubic box

We will often use in this course the example of a free particle, of mass *m* and zero spin, placed in a cubic box on the *L* side (Figure 2). The potential energy of this system is zero inside the box and infinitely repulsive ($U = +\infty$) outside so as to confine the particle inside the cube. As in the two previous examples, the energy of the particle (purely in kinetic form in this case) cannot be any energy. Only certain values are allowed by quantum mechanics. They are given by the expression:

$$\varepsilon_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right) \qquad\qquad (\text{II.6})$$

where n_x, n_y and n_z are strictly positive integers. These are the quantum numbers associated with each of the directions of space: *x*, *y* and *z*.

II.2 Bosons and Fermions

II.2.1 Definitions

Most objects are discernible at the macroscopic level. If this is not the case, we can, without changing their properties in any way, mark them to be able to distinguish them (billiard balls of different colors, for example). This is not the case at the microscopic level where all particles of the same nature are indistinguishable and it is not possible to "mark" them without strongly disturbing them. Thus, to distinguish two hydrogen atoms, it would be necessary to modify the structure of one of them but we would then no longer have the atom in its ground state. Experience shows that all particles in nature have a spin *s* (expressed in units) that is either *integer* or *half integer*. Depending on the value of the spin, the particles belong to two different

families: the *bosons* if *s* is integer, and the *fermions* if it is half-integer. For example, the electron that has a spin equal to 1 2 is a fermion while the photon, which has a spin equal to 1, is a boson. Fermions and bosons have the following properties:

• The wave function of a system consisting of several fermions is *antisymmetric* with respect to particle exchange. This means that the sign of the wave function changes if you swap two particles in space. This property implies that two particles cannot be in the same quantum state. This is called the *Pauli Exclusion Principle*. Fermions are said to obey *Fermi-Dirac statistics*. A determinant is a mathematical object that satisfies these properties:

if we swap two rows or two columns, the determinant changes sign. If two rows or two columns are identical, the determinant is zero. These antisymmetry properties mean that the total wave function of a fermion system can sometimes be represented by a determinant.

• The wave function of a boson system must be *symmetrical with* respect to the exchange of two particles. Multiple bosons can be in the same quantum configuration. They are said to obey the *Bose-Einstein statistic*.

II.2.2 Microstates and spin

In quantum mechanics, a microstate is determined by the data of a complete set of quantum numbers that make it possible to uniquely specify the configuration of the system. Let's go back to the example of a free particle in a cubic box and assume that it has a spin *s*. In this case, the data of the quantum numbers n_x, n_y and n_z is no longer sufficient to describe a microstate. It is necessary to introduce two additional quantum numbers: *s* and s_z, where s_z is the projection of the spin on the *z-axis*. We know that *sz* can only take values between $-s$ and $+s$ per unit jumps. So there are $2s + 1$ possible values of *sz*.

• For a zero spin particle, a microstate is defined by the data of five quantum numbers: n_x, n_y, n_z, $s = 0$ and $s_z = 0$. Since *s* and s_z have the same value for all microstates, they play no role in counting them. The microstates are then completely determined by the simple data of n_x, n_y and n_z.

• When the spin of the particle is non-zero, it is essential to specify the values of *s* and s_z. For example, if $s = 1$ and if it is not a photon, s_z can take 3 values: $-1, 0$ and $+1$. For n_x, n_y and n_z fixed, three microstates can be defined (n_x, n_y, n_z, *s*, s_z):

$$n_x, n_y, n_z, 1, -1; \qquad n_x, n_y, n_z, 1, 0; \qquad n_x, n_y, n_z, 1, +1$$

In the case of independent particles, it is often convenient to consider separately the degrees of freedom related to the spin of the particles, from those related to ordinary space. The reason is simple: you can solve the problem in a first step without dealing with the spin and get the one-particle configurations. These configurations actually correspond to the microstates associated with a zero spin particle. In a second step, some of these configurations are populated with particles, taking into account the statistics they obey (Fermi-Dirac or Bose-Einstein).

II.3 Independent *N-particle* systems

We will now apply the above notions to a few simple examples. Consider a system where one-particle energy levels are evenly spaced and not degenerated when spin is disregarded. Let us take as the origin of the energies the lowest level and as a unit the difference between two consecutive levels. We will, in several cases, study the state of a system consisting of three independent particles whose total energy is equal to three units.
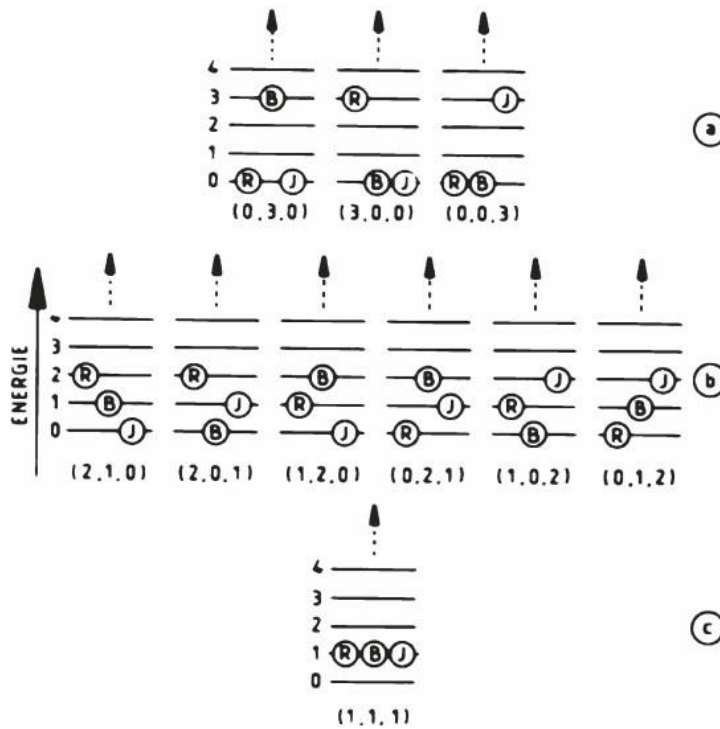
II.3.1 Distinguishable particles

Although unrealistic, this situation is interesting to illustrate how microstates are counted. Suppose one particle is blue (B), the other red (R) and the last yellow

(d) Forget about the nature of particles for now and look at how many different ways three particles can lead to 3 units of energy. There are three possible configurations (Figure II.1):

1- One particle on level 3 and two on level zero.

2- One particle on each of the first three levels.

3- Three particles on the first level.

Now let's consider the nature of the particles and evaluate the number of microstates associated with each configuration. We will note a micro-state by (n_B, n_R, n_J) where n_B, n_R and n_J identify the levels occupied by particles *B, R* and *J*, respectively. For the first configuration, (Figure II.1a), we have three possible microstates: (3.0.0), (0.3.0) and (0.0.3). For the second, we have the 6 possibilities indicated in figure II.1b and for the third configuration we have only one possibility (figure II.1c). In total, for this three-particle system, the degeneration of the energy level is equal to 10 and we have 10 different three-particle microstates.

Figure II.1 *Assessments of the number of discernible microstates*

II.3.2 Identical particles

Now suppose that the particles are indistinguishable. We will consider separately the case of bosons and fermions.

➢ **Bosons**

Suppose all three particles are zero spin bosons. Since there is no restriction for occupancy of one-particle levels (Bose-Einstein statistics), each of the configurations described in section II.3.1 corresponds to only one microstate. Therefore, we only have a total of three microstates (Figure II.2a).

➢ **Fermion**

Finally, suppose that the three particles are spin 1 2 fermions (electrons for example). The Pauli exclusion principle prevents two fermions from having the same quantum numbers. This will reduce the number of possible microstates compared to the Bose-Einstein statistic. Thus, the configuration where we have three particles in state 1 is impossible.

In effect, if for the first electron is therefore not possible to put a third electron on the same energy level. The first configuration leads to 2 microstates while the second gives 8 microstates because, for each electron, we have the choice between 2 values of s_z, which gives a degeneration of $2 \times 2 \times 2 = 8$ (figure II.2b).
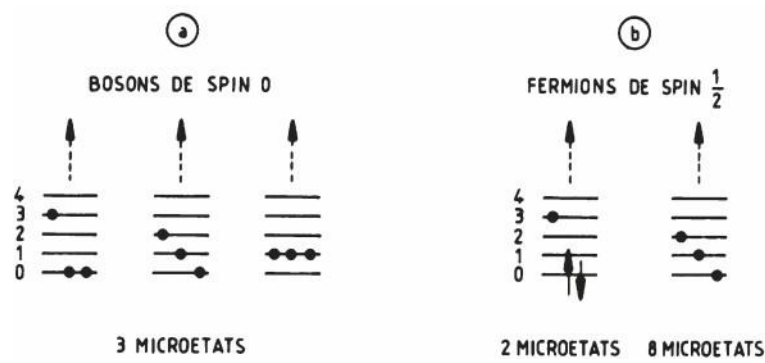
Figure II.2 *Assessments of the number of indistinguishable microstates*

II.4 Phase Space

II.4.1 Phase Space Definition

To determine, in a unique way, the evolution of a conventional system consisting of N particles, it is sufficient to know the position $\vec{q_i}\,t$ and the speed $\vec{v_i}\,t$ (or more generally, the pulse $\vec{p_i}\,t$) of each particle at the instant t. The position and pulse vectors of the three-dimensional particle i are given by

$$\vec{q_i}(t) = \begin{pmatrix} x_i(t) \\ y_i(t) \\ z_i(t) \end{pmatrix}, \qquad\qquad \vec{p_i}(t) = \begin{pmatrix} p_{x_i}(t) \\ p_{y_i}(t) \\ p_{z_i}(t) \end{pmatrix}, \qquad\qquad \text{(II,7)}$$

The set q_i, p_i can be interpreted ~~as a~~ point in a 6N dimensional space called phase space. A trajectory in this space is defined by the curve

$\vec{q_i}\,t$, $p_i\,t$ which describes the temporal evolution of the system. The quantities $q_i\,t$ and $p_i\,t$ are determined using Hamilton-Jacobi equations:

$$\begin{cases} \dot{\vec{q_i}} = \dfrac{\partial H}{\partial \vec{p_i}} \\[2mm] \dot{\vec{p_i}} = -\dfrac{\partial H}{\partial \vec{q_i}} \end{cases} \qquad\qquad \text{(II.8)}$$
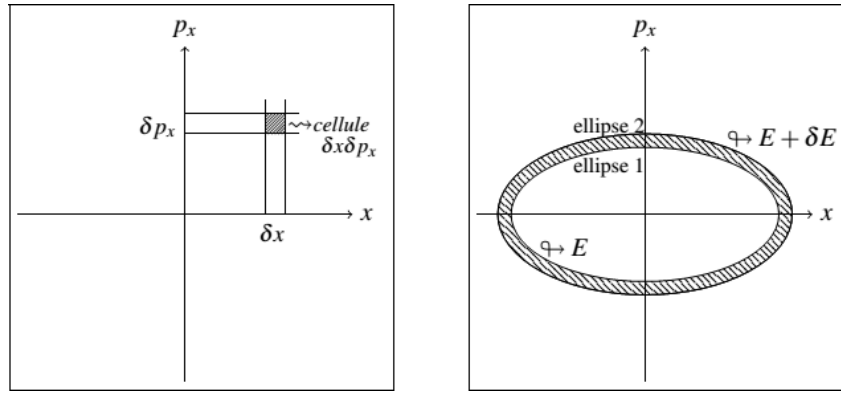
FIGURE II.3 – Two-dimensional phase space (left), and one-dimensional harmonic oscillator phase space (right).

where *H* is the Hamiltonian of the system (corresponds to the total energy of the system On isolated systems, *H* does not explicitly depend on time, so we write behalf of

$$E = H\left(q_i(t), \, p_i(t)\right)$$. (II.9)

The phase space can be subdivided into volume elements $d^{3N}q\,d^{3N}p$. Each element of this space is called *a Phase Space Cell*. If *N* = 1 (phase space of a single particle), the size of a cell is $d^3q\,d^3p\,dxdydz\ dp\,dp\,dp\,dp$. Fig. (II.3) (left) represents a two-dimensional phase space and a cell in that space (particle moves on the *x-axis* for example).

The phase space can be subdivided into volume elements $d^{3N}q\,d^{3N}p$. Each element of this space is called the phase space cell. If N = 1 (phase space of a single particle), the size of a cell is *d³qd³ p = (dxdydz) (d pₓd pᵧd p_z).* (left) represents a two-dimensional phase space and a cell in this space (particle moves on the x-axis for example).

II.4.2 Harmonic Oscillator Phase Space

Consider a conventional one-dimensional harmonic oscillator. The Hamiltonian of this system is given by:

$$H(x, p_x) \; = \frac{p_x^2}{2m} + \frac{k}{2}x^2 = E = C^{ste}$$ (II.10)

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where *m* is the mass of the particle and *k* is the stiffness constant of the oscillator.

The total energy of the system is conserved because the Hamiltonian *H* does not explicitly depend on time. According to the eq. (II.9), the phase space is an ellipse whose size depends on energy. The two semi-axes of this ellipse are given by:

$$a = \sqrt{2mE}, \qquad b = \sqrt{\frac{2E}{k}}. \qquad (\text{II.11})$$

The area σ of this ellipse is given by:

$$\sigma = \pi ab = 2E\pi r \sqrt{\frac{m}{k}}. \qquad (\text{II.12})$$

The energy of a system is always defined with an uncertainty If the energy of the system is between *E* and *E* *E*, the trajectories in the phase space will all be between the two ellipses 1 and 2, see Fig. (II.3) (right).

II.4.3 Volume and area of phase space

In the general case, we define the total volume of the phase space at *6N* dimensions and the surface areabetween *E* and *E* *E*, of an isolated Hamiltonian system *H*, by

$$\omega(E) = \int\limits_{H(q_i,p_i)\leq E} d^{3N}q d^{3N}p = \int\limits_{H(q_i,p_i)\leq E} d\omega \qquad (\text{II.13})$$

$$\sigma(E) = \int\limits_{E=H(q,p)} d\sigma \qquad (\text{II.14})$$

where $\approx$ and $\approx$are the volume and surface elements, respectively.

If the energy of the system is between *E* and *E* *E,* then the volume of the phase space in this case is given by:

$$\Delta\omega = \int\limits_{E\leq H(q,p)\leq E+\Delta E} d^{3N}q d^{3N}p = \int\limits_{E\leq H(q,p)\leq E+\Delta E} d\omega \qquad (\text{II.15})$$

If $\Delta E \rightarrow 0$ (very small), then we can write

$$\Delta\omega = \omega(E + \Delta E) - \omega(E) \approx \left.\frac{\partial\omega}{\partial E}\right|_{V,N} \Delta E. \tag{II.16}$$

According to *Cavalieri's theorem (If the plane figures, determined by the intersections of two solids with any plane parallel to a given fixed plane, have the same area, then the two solids have the same volume),* then the volume between two surfaces, separated by ΔE, of area $\sigma(E)$ is given by

$$\Delta\omega = \sigma(E)\Delta E. \tag{II.17}$$

So,

$$\sigma(E) = \frac{\partial\omega(E)}{\partial E}. \tag{II.18}$$

II.5 Postulates of statistical physics

Statistical physics is built on *assumptions*. These are reasonable assumptions chosen *a priori*. The justification of the merits of this choice is made a posteriori by verifying that this theory makes it possible to reproduce, and to understand, a large number of properties of macroscopic bodies. Thermodynamics is also based on postulates: these are the principles of thermodynamics. Since statistical physics takes into account the properties of microscopic constituents, while thermodynamics only deals with the macroscopic properties of bodies, it is a more complete science than the latter.

➢ **Postulate 1: Equiprobability of microscopic states**

All microscopic states accessible to an isolated macroscopic system in equilibrium are equiprobable.

So the probability that this system is in a given microscopic state is

$$p(E) = \frac{1}{\Omega(E)} \tag{II.19}$$

where Ω is the total number of microscopic states.

➤ **Postulate 2: Ergodic principle**

The average of any parameter calculated in a statistical manner is equal to the average of that parameter taken over a set of identical systems.

If W is the number of microscopic states accessible to the system for an energy between E and E $E_,$. According to the first postulate, the time spent in each microstate is the same t t/Ω . Then the probability is given by

$$p = \frac{\Delta t}{t} = \frac{t/\Omega}{t} = \frac{1}{\Omega} \qquad (\text{II.20})$$

If we consider a set of N identical systems (copies of our system), where N is very large. The number of copies in state i is denoted by n i. So the probability of finding the system

$$p = \frac{n_i}{N} = \frac{1}{\Omega} \qquad (\text{II.21})$$

So in both visions the probability is the same

II.6 Statistical entropy

We have already noticed that $\Omega(E)$, the number of microstates accessible to a system whose energy is equal to E, is an important quantity in statistical physics. We will now clarify this quantitatively by relating $\Omega(E)$ to a quantity that is familiar to us in thermodynamics: *entropy*. It should be noted that $\Omega(E)$ is an extremely large number for macroscopic systems whose temperature is not close to absolute zero.

II.6.1 Boltzmann formula

Consider an isolated system consisting of two subsystems A and B. The number of microscopic states of each subsystem is noted by $\Omega_1(E_1)$ and $\Omega_2(E_2)$, respectively. The two systems can exchange heat (energies can vary), particles or their volumes can vary. It is assumed that these two systems are statistically independent, so the total number of microscopic states is given by

$$\Omega(E)= \Omega_1(E_1) \text{x } \Omega_2(E_2) \tag{II.22}$$

From a macroscopic point of view and according to the second principle of thermodynamics, the entropy of an isolated system composed of two sub-systems is the sum of the entropies of the latter two,

$$S(E,) = S_1(E_1)+ S_2(E_2) \text{ et } dS = dS_1 + dS_2. \tag{II.23}$$

On the other hand, at thermodynamic equilibrium the entropy of an isolated system is maximum, i.e.

$$\begin{cases} S = S_{max} \\ dS = dS_1 + dS_2 = 0 \end{cases} \tag{II.24}$$

If we compare the two macroscopic and microscopic points of view, we deduce that the entropy must be proportional to the logarithm of the number of microscopic states, then

$$S(E,V,N) = k_b \ln\Omega(E,V,N) \tag{II.25}$$

where k_b is a proportionality constant of the same dimension as the entropy, which is called the Boltzmann constant. This equation is very important in statistical physics (Boltzmann's formula) because it makes it possible to calculate the thermodynamic properties (temperature, pressure, ... etc.) of a system from its Hamiltonian using the following relations:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N}, \qquad \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,V}, \qquad -\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{E,N}. \tag{II.26}$$

II.6.2 Calculation of the statistical entropy of a perfect gas

the entropy of a perfect gas is written in the form

$$S(E) = Nk_b \left\{ \frac{3}{2} + \ln \left[\frac{V}{h^3} \left(\frac{4\pi mE}{3N} \right)^{3/2} \right] \right\} \qquad (\text{II.27})$$

II.6.3 **Gibbs paradox** Consider a container isolated from the external environment divided into two parts, of volumes V_1 and V_2, separated by a wall. The first part contains N_1 particles of a monoatomic perfect gas, the second contains N_2 of a *different nature*. We assume that both gases are at the same temperature. Now let's remove the wall. The accessible volume becomes $V=V_1+V_2$. The change in entropy is worth:

$$\Delta S = S_1 - S_2 = N_1 k_b \ln\left(\frac{V_1+V_2}{V_1}\right) + N_2 k_b \ln\left(\frac{V_1+V_2}{V_2}\right) > 0. \qquad (\text{II.28})$$

Even in this case, the entropy difference is positive which cannot be correct because the process in this case is reversible(you can always return to the initial state if you put the partition back). According to the second principle of thermodynamics, the entropy difference for reversible processes is zero $\Delta S = 0$. This contradiction is called Gibbs' Paradox.

In classical vision (classical mechanics), particles are discernible. If we number the particles of the gas *A* from 1 to N_1 (i.e. 1,2,...,N_1), and the particles of the gas *B* from N_1+1 to N 1 + N 2 (i.e. N 1 +1,N 1 +2,...,N 1 + N 2), and we remove the separation wall, there will be an irreversible process because the particles will mix and we cannot return to the initial state if we take into consideration the numbering of the particles.   In reality, the particles of an ideal gas are indistinguishable (non-countable) as in quantum mechanics. So the number of microscopic states in this case is given by the number of microscopic states of the classical case (calculated before) divided by $N!$ (Gibbs factor).

$$\Omega \to \frac{\Omega}{N!}. \qquad (\text{II.29})$$

and the entropy of the perfect gas, calculated in the previous section, becomes

$$S(E) = Nk_b \left\{ \frac{5}{2} + \ln \left[\frac{V}{Nh^3} \left(\frac{4\pi mE}{3N} \right)^{3/2} \right] \right\} \qquad (\text{II.30})$$

The argument of the logarithm of this formula contains only intensive quantities, hence, the entropy *S* is an extensive quantity.

$$\Delta S = 0. \tag{II.31}$$

If we calculate the entropy difference (using the new formula) for the two identical gases and their mixtures, we can show that which implies that the new entropy formula is in agreement with the second principle of thermodynamics.

II.7 Representative sets:

Before calculating properties of a system in statistical physics, we need to use all the knowledge we have about the system under study, and then find a set that allows us to make statistical predictions about quantities that we cannot accurately predict.

We identify the contrast between two different physical situations and the corresponding sets, the micro-canonical set and the canonical set.

II.7.1 Micro-canonical assembly:

In the micro-canonical set, we consider a single system isolated from the outside world and we assume its known total energy at a given accuracy. Other mechanical quantities are also specified such as volume and number of particles. That is to say, the micro-canonical assembly is an isolated system (a statistical assembly) of total energy fixed at near, and which does not exchange matter (particles) with the external environment. Then this set represents the equilibrium states of such a (isolated) total energy system set to near, therefore to an in-phase density between the energy states and. Thus, the probability that the system is in a given microscopic state (*r*) of energy and volume is given by:

$$P(E,V) = \begin{cases} \dfrac{1}{\Omega(E_r,V)} & ; E < E_r < E + \delta E \\ 0 & ; ailleurs \end{cases}$$

$\Omega(E_r,V)$ is the total number of microscopic states accessible in the energy range

$$E < E_r < E + \delta E$$

II.7.2 The canonical set:

In the canonical set, we consider a closed system that can exchange energy but not matter with the external environment. For this, we will consider a system (S) in thermal equilibrium with a

tank that behaves as a thermostat (t) for the system (S) (Figure II.4). The temperature (T) of the thermostat is constant despite the possible exchange of temperature with the system.
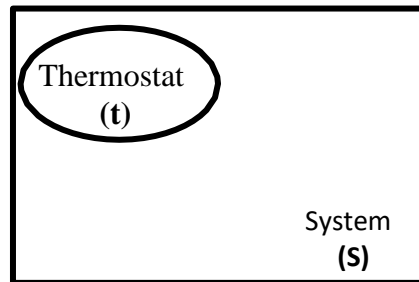
Figure II4.*: thermostat (**t**) in contact with a tank System (**S**)*

Then the canonical assembly makes it possible to study closed systems that exchange only energy with a thermostat because of thermal contact (the evolution of energy or pressure over time), but not matter (constant number of particles) and constant volume. As the set (*S+t*) is isolated and in statistical balance, it can be described by the set micro-canonical. Let E_0 be its total energy (defined as *E* close, this quantity is neglected because it does not affect the results relating to the macroscopic system).

When the energy of a particular micro-state $r(j)$ of system (*S*) equal to E_r, and thermostat (*t*) equal to E_t, within the thermodynamic limit, the total energy of the micro-canonical assembly equal to the sum of the energy of the system (*S*) and the energy of the thermostat (*t*)**:** ($E_0=E_r+E_t$).

II.8 Exercises & Issues

Exercise #1:

Let there be three equidistant ($\varepsilon_0 = 0, \varepsilon_1 = \varepsilon, \varepsilon_2 = 2\varepsilon$) and non-degenerate, on which two discernible particles (A and B) are distributed. It is assumed that the total energy is $U = 2\varepsilon$

1- represent on a diagram the possible macroscopic deferents, as well as the corresponding complexions. What is the likely state.

2- same question if level 1 has a degeneration equal to 2. Explaining degeneration is also called level static weight. We will check the number of complexions of each macroscopic state and well equal to that given by the general formula of maxwell-Boltzmann

Why can't we calculate the most probable distribution by the general formula maxwell-Boltzmann

Exercise #2:

Establish, in the case of bosons and assuming that the number of particles is large but indeterminate (in the case of photons or phonons) , the position at thermal equilibrium of each level of degeneration. We will put⁰in the following form:

$$N_i^0 = \frac{g_i}{e^{\beta \varepsilon_i} - 1}$$

Or appears a single β

Exercise #3:

Consider a particle with two degrees of freedom. The volume element in the phase space can be written as:

Show that this volume element remains invariant when changing from Cartesian coordinates to polar coordinates:

$$dxdydP_xdP_y = drd\theta dP_rdP_\theta$$

where $P_r = m\dot{r}$ $P_r = I\dot{\theta}$ is the moment of inertia of the particle.

1- Let us now assume that this particle of mass m and attached by a wire of length l to a fixed point.

a. What are the dynamic variables representing the system in the phase space?

b. Find the equation of the phase trajectory. From this deduce the equation of the trajectory. , the branch course

c. Give the temporal equation of motion.

d. Show that Liouville's theorem is true.

Introduction

The velocity distribution of particles constituting a conventional ideal gas at temperature T is an amount that is important to study in detail because it is used within the framework of the kinetic theory of gases. In the first two sections, we saw that the probability that a particle has a pulse between **p** and **p** + d**p**, and is located in a volume d**r** between **r** and **r** + d**r**, is equal to:

$$P(r,p)\,drdp = \frac{1}{\zeta}\frac{drdp}{h^3}e^{-\frac{p^2}{2mk_bT}} \tag{III.1}$$

with $\quad \zeta = \left(\frac{2\pi mkbT}{h^2}\right)^{3/2}V$

III.1 Classic ideal gas

We consider a conventional monoatomic perfect gas, in a container of volume V, consisting of N indistinguishable particles, maintained at temperature T. The total energy of this gas is given by

$$H(q_i,p_i) = \sum_{i=1}^{N}\frac{p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2}{2m} \tag{III.2}$$

In this case, the energy is continuous, it depends on the continuous variables p_{xi}, p_{yi} and p_{zi} (vary between $]-\infty,+\infty[$). Then, to calculate $Z^{(c)}$ we use the canonical partition function $Z^{(c)}$.

➢ **The partition function $Z^{(c)}$**

The canonical partition function is written

$$Z^{(c)}[T,V,N] = \int \frac{d^{3N}q\,d^{3N}p}{N!h^{3N}}e^{-\beta H(q_v,p_v)},$$

$$= \frac{1}{N!h^{3N}}\prod_{i=1}^{N}\int dx_i dy_i dz_i \int_{-\infty}^{+\infty} dp_{x_i} dp_{y_i} dp_{z_i} e^{-\beta\frac{p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2}{2m}} \tag{III.3}$$

with $\quad V = \int dx_i dy_i dz_i \quad$ and $\quad \int_{-\infty}^{+\infty} dp_{x_i} dp_{y_i} dp_{z_i} e^{-\beta\frac{p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2}{2m}} = (2m\pi k_bT)^{3/2}$

The integral on d 3q dx dy dz is obvious because the integral does not depend on these variables, so it is just equal to the volume of the container. To integrate on, we use the following Gaussian

integral

$$\int_{-\infty}^{+\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}$$

(III.4)

where α is a non-zero positive real. So, we show that the canonical partition function of this gas is given by the quantity λ is the thermal wavelength (de Broglie) of this gas.

$$Z^{(c)}[T,V,N] = \frac{V^3}{N!\lambda^{3N}}, \qquad\qquad \lambda = \frac{h}{\sqrt{2m\pi k_b T}}$$

(III.5)

➢ **free energy deficit**

The free energy of this gas is written

$$F[T,V,N] = -k_b T \ln Z^{(c)}[T,V,N],$$

$$= -Nk_b T \left(1 + \ln\left[\frac{V}{N}\left(\frac{2m\pi k_b T}{h^2} \right)^{3/2} \right] \right).$$

(III.6)

where we used Stirling's formula $\ln N! = N \ln N - N$ for N very large.

➢ **Entropy (S)**

The entropy of this system is this is the formula we found in the previous chapter after the Gibbs correction.

$$S = -\frac{\partial F}{\partial T}\bigg|_{V,N}.$$

$$= Nk_b \left(\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{2m\pi k_b T}{h^2} \right)^{3/2} \right] \right).$$

(III.7)

➢ **Pressure (P)**

The electrostatic pressure is given by:

$$p = -\frac{\partial F}{\partial V}\bigg|_{T,N} = \frac{Nk_b T}{V}.$$

(III.8)

which leads to the famous equation of state of the perfect gas $pV = N_k bT$.

➢ **Chemical potential**

The chemical potential is therefore

$$\mu = -\left.\frac{\partial F}{\partial N}\right|_{T,V}.$$

$$= -Nk_b \ln\left[\frac{V}{N}\left(\frac{2m\pi k_b T}{h^2}\right)^{3/2}\right].$$

(III.9)

➢ **Internal energy U**

We can calculate the internal energy by two methods, either by the relation or by evaluating the average energy.

$$U = F + TS = \frac{3}{2}Nk_b T.$$

(III.10)

or either by evaluating the average energy.

$$U = <H> = -\frac{\partial \ln\left(Z^{(c)}[T,V,N]\right)}{\partial \beta} = \frac{3}{2}Nk_b T.$$

(III.11)

this is the formula found in thermodynamics.

III.1 Maxwell-Boltzmann perfect gas

III.1.1 Maxwell-Boltzmann statistics

The probability of finding a system of the canonical set in a microscopic state where we did not take into account the Gibbs factor.

$$dp = \frac{1}{h^{3N}}\rho_c(q_i, p_i)dq^{3N}dp^{3N} = \frac{1}{h^{3N}}\frac{e^{-\beta H(q_i, p_i)}}{Z}dq^{3N}dp^{3N}$$

(III.12)

According to the first postulate of statistical physics (equiprobability of microscopic states), this probability is constant on the energy surface $H(q_i, p_i) = E$ in the phase space. Then,

the probability of finding the system in a microscopic state of energy between E and $E + dE$ is

$$dp = \frac{e^{-\beta H(q_i, p_i)}}{Z} \frac{1}{h^{3N}} \int_{E \leq H \leq E + \Delta E} \frac{dq^{3N} dp^{3N}}{h^{3N}}. \tag{III.13}$$

Where

$$\frac{1}{h^{3N}} \int_{E \leq H \leq E + \Delta E} \frac{dq^{3N} dp^{3N}}{h^{3N}} = \frac{\partial \sum(E)}{\partial E} = \frac{\partial}{\partial E}\left[\frac{1}{h^{3N}} \int_{H(q_i, p_i) \leq E} \frac{dq^{3N} dp^{3N}}{h^{3N}} \right] dE,$$

$$= g(E)dE \tag{III.14}$$

where $\Sigma(E)$ is the volume of phase space divided by h^{3N}, and $g(E)$ is the state density on the energy surface. The latter two are connected by the following relationship

$$\frac{\partial \sum(E)}{\partial E} = g(E) = \Omega(E). \tag{III.15}$$

where $\Omega(E)$ is the number of microscopic states accessible to the system. Therefore, the canonical partition function and probability are expressed as a function of the state density $g(E)$ as follows

$$p(E) = \frac{g(E)}{Z} e^{-\beta E}, \qquad Z = \int_0^{+\infty} g(E) e^{-\beta E} \tag{III.16}$$

In quantum mechanics, the state density $g(E)$ is replaced by the degree of degeneration g_E. The probability given by the eq.(III.16) is the probability of the Maxwell-Boltzmann statistic. It gives us all the information about a physical system if the spin of these constituents is not taken into account.

III.1.2 Maxwell distribution of speeds

These distributions are valid for a *conventional* mono- or polyatomic gas.

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} X + V(\vec{q}_1, \ldots, \vec{q}_N) \tag{III.17}$$

$$dP = (\vec{q}_1, \vec{q}_2, ..., \vec{q}_n, \vec{p}_1, \vec{p}_2, ..., \vec{p}_n) = \frac{1}{Z} \frac{\prod_{i=1}^{N} d\vec{q}_i d\vec{p}_i}{N! h^{3N}} e^{-\beta H(\{\vec{p}_i, \vec{q}_i\})} \tag{III.18}$$

We are interested in the distribution of speeds regardless of positions

$$dP = \left(\vec{p}_1, \vec{p}_2, ..., \vec{p}_n \right) = \frac{1}{Z} \frac{1}{N! h^{3N}} \prod_{i=1}^{N} d\vec{p}_i \int \prod_{i=1}^{N} d\vec{q}_i e^{-\beta H(\{\vec{p}_i, \vec{q}_i\})} \tag{III.19}$$

$$= C \prod_{i=1}^{N} d\vec{p}_i e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}} \tag{III.20}$$

$$dP\left(\vec{v}_1, \vec{v}_2, ..., \vec{v}_n, \vec{v}_1, \vec{v}_2, ..., \vec{v}_n \right) = C' \prod_{i=1}^{N} d\vec{v}_i e^{-\beta \sum_{i=1}^{N} \frac{1}{2} m \vec{v}_i^2} \tag{III.21}$$

For a molecule, we have:

$$dP\left(\vec{v} \right) = C'' e^{-\frac{1}{2} \beta m \vec{v}^2} d\vec{v} \tag{III.22}$$

Gold $\int dP\left(\vec{v} \right) = 1$ from where $C'' = \left(\frac{m}{2\pi kT} \right)^{3/2}$. We deduce the Maxwell distribution of the velocities

We are now interested in average sizes.

Average number of particles with velocities between $\vec{v}$ and $\vec{v} + d\vec{v}$

$$dN\left(\vec{v} \right) = N dP\left(\vec{v} \right) \tag{III.24}$$

This is true because there is no correlation between particle velocities (there is no interaction between velocities)

➢ **distribution of velocities**

$dN\left(\vec{v} \right)$ is isotropic (depends only on $\vec{v}^2$).

$$dN(v_x) = dN(v_y) = \cdots = dN(\vec{v}.\vec{n}) \tag{III.25}$$

$$dN(v_x) = N \left(\frac{m}{2\pi kT} \right)^{3/2} dv_x \int dv_y dv_z e^{-\frac{\beta}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right)}. \tag{III.26}$$

$$= N\sqrt{\frac{m}{2\pi kT}}dv_x e^{-\frac{\beta}{2}mv_x^2} \tag{III.27}$$

We obtain a Gaussian centered on: the velocity distribution is well isotropic.

➢ **Average quadratic speed**

$$\overline{v_x^2} = \sqrt{\frac{m}{2\pi kT}}\int_{-\infty}^{+\infty} v_x^2 e^{-\frac{\beta}{2}mv_x^2}dv_x \tag{III.28}$$

➢

$$= \sqrt{\frac{m}{2\pi kT}}\int_{-\infty}^{+\infty} -\frac{\partial}{\partial\alpha}v_x^2 e^{-\alpha v_x^2}dv_x$$

➢

$$= \sqrt{\frac{m}{2\pi kT}}\frac{\partial}{\partial\alpha}\sqrt{\frac{\pi}{\alpha}}$$

➢

$$= \sqrt{\frac{m}{2\pi kT}}\sqrt{\pi}\frac{1}{2}\alpha^{-\frac{3}{2}}$$

➢

$$= \sqrt{\frac{m}{2\pi kT}}\frac{1}{2}\left(\frac{2kT}{m}\right)^{-\frac{3}{2}}$$

➢

$$= \frac{1}{2}\frac{2kT}{m} = \frac{kT}{m}$$

➢

$$\overline{v_x^2} = \frac{kT}{m}, \Delta v_x = \sqrt{\overline{v_x^2} - \overline{v_x}^2} = \sqrt{\frac{kT}{m}} \tag{III.29}$$

➢

Note

$$\overline{E_c} = \overline{\frac{1}{2}mv^2} = \overline{\frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)} = 3\frac{1}{2}m\overline{v_x^2} = \frac{3}{2}kT \tag{III.30}$$

We have the equipartition of energy

Distribution of $\|v\|$

> The probability that $\|v\| = v$ is :

$$dN = \int_{\theta,\varphi} dN(\vec{v})$$

(III.31)

$$= N\left(\frac{m}{2\pi kT}\right)^{3/2} dv \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta v^2 \sin\theta d\theta d\phi e^{-\beta\frac{1}{2}m\vec{v}^2}$$

$$dN = N\left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\beta\frac{1}{2}mv^2} dv$$

> **Most probable value $\tilde{v}$ of v**

$$\frac{d}{dv}\left[\frac{dN(v)}{dv}\right] \propto \frac{d}{dv}\left[v^2 e^{-\frac{\beta}{2}mv^2}\right]$$

(III.32)

$$= 2ve^{-\frac{\beta}{2}mv^2} + v^2\left(-\frac{\beta}{2}mv^2\right)e^{-\frac{\beta}{2}mv^2}$$

$$\frac{d}{dv}\left[\frac{dN(v)}{dv}\right] = 0 \Leftrightarrow \frac{\beta m}{2}\tilde{v}^2 = 1$$

$$\Leftrightarrow \tilde{v}^2 = \frac{2}{\beta m} = \frac{2kT}{m}$$

$$\Leftrightarrow \bar{v} = \sqrt{\frac{2kT}{m}}$$

(III.33)

> **Average value $\bar{v}$ of v**

$$\bar{v} = \frac{1}{N}\int_0^{+\infty} N(v) dv$$

(III.34)

$$= \int_0^{+\infty}\left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\beta\frac{1}{2}mv^2} dv$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} + \frac{2}{\beta m}\left[\frac{e^{-\beta\frac{1}{2}mv^2}}{\beta m}\right]_0^{+\infty}$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} + \frac{2}{\beta^2 m^2}$$

$$= \sqrt{\frac{8kT}{\pi m}}$$

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}, \quad \overline{v^2} = \frac{3kT}{m}, \quad \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}. \tag{III.35}$$

The Maxwell distribution of velocities occurs in:

- Kinetic theory of gases.
- Collisions (then describe *the Boltzmann equation approach to equilibrium*)
- Transport properties such as coefficients involved in phenomenological equations such as heat diffusion (conductivity coefficient), and hydrodynamics with viscosity.

III.2 Statistique de Fermi Dirac

We consider a quantum perfect gas composed of N fermions of spin 1/2, in a cubic box of volume V, maintained at temperature T using a thermostat. A microscopic state of this system is determined by the following quantum numbers (n_x,n_y,n_z,s,s_z). According to Pauli's exclusion principle, two identical fermions (i.e., have the same quantum numbers) cannot occupy the same microscopic state. So each microscopic state can be occupied by a single particle at most. The system composed of this state can be considered as a system of the grand-canonical assembly (the rest forms the reservoir of particles). Then, the grand-canonical partition function of this subsystem is given by

The average number of fermions occupying a microscopic state is this distribution of number of fermions is called the Fermi-Dirac distribution. The average number of fermions should check the relationship

$$Z_i^{(gc)} = \sum_{n_i=0}^{1} \sum_{\{i\}} e^{-\beta(e_i - \mu n_i)} = 1 + e^{-\beta(e_i - \mu)}$$

(III.36)

The average number of fermions occupying a microscopic state is

$$< n_i >= \frac{1}{\beta} \frac{\partial \ln Z_i^{(gc)}}{\partial \mu} = \frac{e^{-\beta(e_i - \mu)}}{1 + e^{-\beta(e_i - \mu)}}.$$

(III.37)

This fermion number distribution is called the Fermi-Dirac distribution.

The average number of fermions must verify the relationship

$$\sum_{\{i\}} < n_i >= N.$$

(III.38)

When $\{i\} \equiv \{n_x^{(1)}, n_y^{(1)}, n_z^{(1)}; ...\}$ designates all possible microscopic states.

III.3 Bose-Einstein Statistics

Consider, now, a quantum perfect gas composed of N bosons (ie. d particles of integer or zero spin), in a recopier of volume V, maintained at temperature T using a thermostat. As in the previous paragraph, a microscopic state of this system is determined by the quantum numbers (n_x, n_y, n_z, s, s_z). Because particles are bosons, a state

microscopic or a subsystem can be occupied by all particles (no limit on particle number). The subsystem can be considered as a system of the grand-canonical assembly (the other subsystems constitute the particle reservoir). It is assumed that the energy of each particle is ei, then, the energy of N particles is

$$E_{N,i} = Ne_i, \qquad\qquad N = 0, 1, \cdots, \infty$$

(III.39)

So the grand-canonical partition function of this system is

$$Z_i^{(gc)} = \sum_{n_i=0}^{\infty} e^{-N\beta(\mu - e_i)} = \frac{1}{1 - e^{-\beta(\mu - e_i)}}.$$

(III.40)

where we used the sum of a geometric series to find the expression in the second line of this equation.

The average number of particles that occupy a microscopic state is therefore

$$< n_i >= \frac{1}{\beta} \frac{\partial \ln Z_i^{(gc)}}{\partial \mu} = \frac{1}{e^{\beta(e_i-\mu)}-1}.$$

(III.41)

This particle number distribution is called the Bose-Einstein statistic.

III.4 Exercises & Issues

Exercise #1:

We propose to establish the expression of β in maxwell-Boltzmann statics. Let $_1$ be the energy levels. Their degeneration factors andthe$_{number}$ of particles at equilibrium.

   a. write the static expression of the internal energy U.

   b. the state of the system is varied infinitesimally. Write the variation of the internal energy.

   c. the energy levels usually $_{depend}$on the volume but not on the temperature interpret the two terms that intervene in the expressionof

By comparing the thermodynamic relationship ññ = ññño the corresponding relationships obtained by differentiating the relationship $S = K\mathrm{Log(W)}$. Establish the expression of φas a function of the thermodynamic temperature in the case where W corresponds to the maxwell-Boltzmann static.

Exercise #2:

Or a linear harmonic oscillator consisting of a mass m attached to a spring of stiffness constant k, able to move on a horizontal axis (Ox).

   a. What are the dynamic variables representing the system in the phase space?

   b. Give the expression of its total energy E according to its dynamic variables.

   c. Suppose that the oscillator   is mechanically isolated, From question b, deduce the nature of its movement in the phase space?

   d. Demonstrate that the movement of the oscillator is governed by the differential equation: $\ddot{x} + \omega^2 x = 0$ (with • to be determined).And deduce therefrom the frequency of the

        oscillator as a function of *k* and *m*.

1. We consider a set of *N* simple conventional harmonic oscillators without interaction, of the same mass *m* and stiffness constant *k*, in contact with a heat reservoir of fixed temperature T.

    a. What is the nature of the statistical set in question?

    b. Demonstrate that the partition function is written in the form:

$$Z = \left(\frac{k_B T}{h\nu} \right)^N$$

And k_B, h are Boltzmann's and Planck's constants, respectively.

$$\left(\int_{-\infty}^{+\infty} e^{-\alpha y^2} dy = \sqrt{\frac{\pi}{\alpha}} \right)$$

    c. Determine the average energy E

    d. Determine energy fluctuations

    e. Determine free energy

IV.1 Introduction

In quantum mechanics, all information about the state of a system is encoded in the wave function, the latter is a solution of the Schrödinger equation. The wave function of a system composed of N particles (bosons or fermions) is given by

$$\psi_{k_1 \cdots k_N}(\vec{r}_1, \cdots, \vec{r}_N) = \prod_{i=1}^{N} \psi_{k_1}(\vec{r}_i).$$

(IV.1)

where $\psi_{k_i}(\vec{r}_k)$ for i = 1.2,·· · is the one-particle wave function→.and ki are, respectively, the position vectors of each particle and the set of numbers quantum denoting a state at a given particle. The wave function ψ (r→i) can be symmetric or antisymmetric by permutation of numbers 1···N. Symmetric wavefunctions describe the states of whole spin particles, so-called bosons. On the other hand, antisymmetric wavefunctions describe the behavior of half-integer spin particles, which are called fermions. In Dirac's notation, the state vector of the total system is written

$$|k_1, k_2, \cdots, k_N> = |k_1> |k_2> \cdots |k_N> .$$

(IV.2)

where $|k_i>$ is a one-particle state vector.

The wave function is an eigenstate of the Hamiltonian operator Ĥ. For a system composed of free particles, perfect gas for example, it must check

$$\hat{H}|k_1, \cdots, k_N> = E|k_1, \cdots, k_N>. \qquad\qquad E = \sum_{i=1}^{N} \varepsilon_{k_i}.$$

(IV.3)

$$\hat{h}|k_1> = \varepsilon_{k_i}, \qquad\qquad \varepsilon_{k_i} = \frac{\hbar^2 \vec{k}_i^2}{2m}$$

(IV.4)

where $\hat{H}(\vec{r}_1, \cdots, \vec{r}_N, \vec{p}_1, \cdots, \vec{p}_N) = \sum_{i=1}^{N} \hat{h}(\vec{r}_i, \vec{p}_i).$, because the system consists of particles without Interaction

The state vector can be characterized by the occupancy numbers ni instead of the set of quantum numbers $\{k_i\}$. i.e.d

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$$| n_1, \cdots, n_N > \equiv \ | k_1, \cdots, k_N > \ . \tag{IV.5}$$

where n_i is the number of particles that can occupy the state $|k_i>$. We can express this as:

$$\widehat{H}|n_1, \cdots, n_N > \ = E|n_1, \cdots, n_N >, \qquad\qquad E = \sum_{k=1}^{\infty} n_k \varepsilon_k. \tag{IV.6}$$

$$\widehat{N}|n_1, \cdots, n_N > \ = N|n_1, \cdots, n_N >, \qquad\qquad N = \sum_{k=1}^{\infty} n_k. \tag{IV.7}$$

$$\hat{n}_k|n_1, \cdots, n_N > \ = n_k|n_1, \cdots, n_N >, \qquad n_k = \begin{cases} 0,1, & \text{fermions} \\ 0,1,2,\ldots & \text{bosons} \end{cases} \tag{IV.8}$$

where $\widehat{H}$ is the Hamiltonian operator, E is the total energy of the system, $\widehat{N}$ is the number of particles operator, N is the number of particles in the system, nk is the number of particles in the state $|k>$. According to Pauli's exclusion principle, two fermions cannot occupy the same state if they have the same quantum numbers, which explains why

NK On the other hand, bosons can occupy the same state regardless of whether they have the same quantum numbers or not ($n_k = 0.1.2 \cdots$).

Now applying the occupancy number language to derive canonical and grand-canonical partition functions for classical Maxwell-Boltzmann statistics and for Fermi Dirac and Bose Einstein quantum statistics. The occupancy number does not provide information about which particles should occupy a certain state at a particle $|k>$. Therefore, the set $\{n_1, n_2, \cdots\}$ must have a weight to take into account the nature (spin and indistinguishability) of the particles. In the general case, and for any statistic, the canonical and grand-canonical partition functions can be written in the following compact forms:

$$Z^{(c)}[T,V,N] \ = \sum_{\{n_k\}}^{l} g\{n_k\} e^{-\beta \sum_{k=1}^{\infty} n_k \varepsilon_k} \tag{IV.9}$$

$$Z^{(g,c)}[T,V,\mu] \ = \sum_{\{n_k\}}^{l} g\{n_k\} e^{-\beta \sum_{k=1}^{\infty} n_k (\varepsilon_k - \mu)}. \tag{IV.10}$$

Or

$$\sum_{\{n_k\}}^{l} \ \rightarrow \ \sum_{\substack{n_1, n_2, \cdots = 0 \\ n_1 + n_2 + \cdots = N}}^{N} \tag{IV.11}$$

The statistical weight of a set $\{n_1, n_2, \cdots\}$, for each statistic, is given by,

$$g\{n_k\} = \begin{cases} g^{MB}\{n_k\} = \frac{1}{n_1! n_2! \cdots}. & \text{Maxwell-Boltzmann.} \\ g^{BE}\{n_k\} = 1. & \text{Bose-Einstein.} \\ g^{FD}\{n_k\} = \begin{cases} 1 & \text{si tous les } n_k = 0 \text{ où } 1. \\ 0 & \text{par ailleurs.} \end{cases} & \text{Fermi-Dirac} \end{cases}$$

$$\text{(IV.12).}$$

So, the canonical and grand-canonical probabilities are written

$$P^{(c)}\{n_k\} = \frac{g\{n_k\}}{Z^{(c)}} e^{-\beta \sum_{k=1}^{\infty} n_k \varepsilon_k}$$

$$\text{(IV.13)}$$

$$P^{(g.c)}\{n_k\} = \frac{g\{n_k\}}{Z^{(g.c)}} e^{-\beta \sum_{k=1}^{\infty} n_k (\varepsilon_k - \mu)}$$

$$\text{(IV.14)}$$

Let us now calculate, explicitly, the grand-canonical partition functions in all three cases. The Bose-Einstein grand-canonical partition function is

$$\begin{aligned} Z_{BE}^{(g,c)} &= \sum_{n_1, n_2, \cdots = 0}^{\infty} \left(e^{-\beta(\varepsilon_1 - \mu)} \right)^{n_1} \left(e^{-\beta(\varepsilon_2 - \mu)} \right)^{n_2} \cdots \\ &= \prod_{k=1}^{\infty} \sum_{n_k = 0}^{\infty} \left(e^{-\beta(\varepsilon_k - \mu)} \right)^{n_k} \\ &= \prod_{k=1}^{\infty} \frac{1}{1 - z e^{-\beta \varepsilon_k}} \end{aligned}$$

$$\text{(IV.15)}$$

where fugacity $z = e^{\beta\mu}$. To find the last formula, we used the sum of a geometric sequence. With regard to the case of Fermi-Dirac, we have

$$Z_{FD}^{(g,c)} = \sum_{n_1,n_2,\cdots=0}^{\infty} \left(e^{-\beta(\varepsilon_1-\mu)}\right)^{n_1} \left(e^{-\beta(\varepsilon_2-\mu)}\right)^{n_2} \cdots$$

$$= \prod_{k=1}^{\infty} \sum_{n_k=0}^{\infty} \left(e^{-\beta(\varepsilon_k-\mu)}\right)^{n_k}$$

$$= \prod_{k=1}^{\infty} \left(1 + z e^{-\beta\varepsilon_k}\right) \tag{IV.16}$$

In the same way, we calculate the Maxwell-Boltzmann grand-canonical partition function,

$$Z_{MB}^{(g,c)} = \sum_{n_1,n_2,\cdots=0}^{\infty} \left(e^{-\beta(\varepsilon_1-\mu)}\right)^{n_1} \left(e^{-\beta(\varepsilon_2-\mu)}\right)^{n_2} \cdots$$

$$= \prod_{k=1}^{\infty} \sum_{n_k=0}^{\infty} \left(e^{-\beta(\varepsilon_k-\mu)}\right)^{n_k}$$

$$= \prod_{k=1}^{\infty} e^{z e^{-\beta\varepsilon_k}} \tag{IV.17}$$

Once the grand-canonical partition functions are known, the thermodynamic properties can be calculated using the grand-canonical potential

$$\Phi(T,V,\mu) = -k_b T \ln(Z^{g.c}[T,V,\mu] = U - TS - \mu N = -pV. \tag{IV.18}$$

The grand canonical potentials of the three statistics are given by:

$$\Phi_{MB} = -k_b T \sum_{n_k=0}^{\infty} e^{-\beta(\varepsilon_k-\mu)} \tag{IV.19}$$

$$\Phi_{BE} = k_b T \sum_{n_k=0}^{\infty} \ln\left(1 - e^{-\beta(\varepsilon_k-\mu)}\right). \tag{IV.20}$$

$$\Phi_{BE} = -k_b T \sum_{n_k=0}^{\infty} \ln\left(1 + e^{-\beta(\varepsilon_k - \mu)}\right).$$

(IV.21)

We can write the logarithm of the grand-canonical partition function, in these three cases, in the following compact form:

$$q[T,V,\mu] = \ln(Z^{(g.c)}[T,V,\mu]) = \frac{pV}{k_b T} = \frac{1}{a}\sum_{k=1}^{\infty} \ln\left(1 + aze^{-\beta\varepsilon_k}\right).$$

(IV.22)

with

$$a = \begin{cases} +1 & FD \\ 0 & MB \\ -1 & BE \end{cases}$$

(IV.23)

for the Maxwell-Boltzmann statistic, we take the limit of a tends towards zero (and not a=0!).It is shown that the number of particles and the internal energy are given by

$$N(T,V,\mu) = k_b T \frac{\partial}{\partial\mu}\ln Z^{(g.c)}\bigg|_{T,V} = \sum_{k=1}^{\infty}\frac{1}{z^{-1}e^{\beta\varepsilon_k}+a} = <N>.$$

(IV.24)

$$U(T,V,\mu) = -\frac{\partial}{\partial\mu}\ln Z^{(g.c)}\bigg|_{z,V} = \sum_{k=1}^{\infty}\frac{\varepsilon_k}{z^{-1}e^{\beta\varepsilon_k}+a} = <N>.$$

(IV.25)

We all have

$$< N >=< \sum_{k=1}^{\infty} n_k >=\sum_{k=1}^{\infty} < n_k >.$$

$$(IV.26)$$

So,

$$< n_k >= \frac{1}{e^{\beta(\varepsilon_k - \mu)} + a} = -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_k} \ln Z^{(g.c)} \bigg|_{z,V,\varepsilon_{i \neq k}}$$

$$(IV.27)$$

where fugacity z is assumed to be constant, see discussion in next section.

IV.2 Bose Perfect Gas

In this section, the thermodynamic properties of an ideal gas of non-relativistic bosons are calculated. The particles of this gas are indistinguishable and do not interact with each other. The energy of each particle is $\varepsilon_{k_i} = \hbar^2 \vec{k}_i^2 / 2m$ (where m is the mass of each). let's calculate now, the logarithm of the grand-canonical partition function (which allows us to calculate the other physical quantities). We all have

$$q(T,V,z) = \ln Z^{(g.c)}(T,V,z) = -\sum_k \ln \left(1 - ze^{-\beta\varepsilon_k}\right).$$

$$(IV.28)$$

where *V* is the volume of the container, and $z=e^{\beta\mu}$ is the fugacity.

To impose constraints on the chemical potential μ is the fugacity z, we use the formula of the average number of particles in a state |k > of energy ε_k derived in the previous section. We know that the latter is positive and cannot exceed the total number of particles in the system, so

$$0 \leq < n_k > \leq N, \qquad \Leftrightarrow \qquad 0 \leq \frac{1}{z^{-1}e^{\beta\varepsilon_k} - 1} \leq N.$$

$$(IV.29)$$

So,

$$z^{-1}e^{\beta\varepsilon_k} = e^{\beta(\varepsilon_k - \mu)} \geq 1$$

$$(IV.30)$$

which implies that $\varepsilon_k \geq \mu$ for all states |k >. i.e.d that the chemical potential of a boson gas must be smaller than the lowest energy $\varepsilon = 0$, then

$$\mu \leq 0, \qquad \Rightarrow \qquad 0 \leq z \leq 1.$$

$$(IV.31)$$

so the chemical potential of a boson gas is zero or negative and the fugacity z is always less than or equal to 1. For a sufficiently large volume, the sum over all single-particle states can be written, approximately, as an integral,

$$\sum_k \rightarrow \int g(\varepsilon) d\varepsilon = \frac{V}{(2\pi)^3} \int d^3 k = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \varepsilon^{1/2} d\varepsilon$$

(IV.32)

then

$$g(\varepsilon) = \frac{d\sum}{d\varepsilon} = \frac{d}{d\varepsilon} \int \frac{d^3 q d^3 p}{h3}.$$

(IV.33)

Then $q(T,V,z)$ becomes

$$q(T,V,z) = -\ln(1-z) - \sum_k \ln(1 - ze^{-\beta\varepsilon_k}).$$

$$= -\ln(1-z) + \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \varepsilon^{1/2} \ln\left(1 - ze^{-\beta\varepsilon}\right) d\varepsilon.$$

$$= -\ln(1-z) - \frac{2\pi V}{h^3} (2m)^{3/2} \frac{2}{3} \beta \int_0^\infty \frac{\varepsilon^{3/2}}{z^{-1} e^{\beta\varepsilon} - 1} d\varepsilon.$$

(IV.34)

where we separated the contribution of the energy state $\varepsilon = 0 \left(-\ln(1-z)\right)$, and we integrated by part to get the last integral. In the same way, it is shown that the number of particles is

$$N(T,V,z) = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{z^{-1} e^{\beta\varepsilon} - 1} + \frac{z}{1-z}. \qquad 0 \le z \le 1, \qquad n \in R.$$

(IV.35)

where $z/(1-z)$ is the number of particles in the energy states $\varepsilon = 0$. To perform the integration on ε, we introduce the following integral representation

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{z^{-1} e^x - 1}, \qquad 0 \le z \le 1,$$

(IV.36)

So,

$$q = q_\varepsilon + q_0.$$

$$q_\varepsilon = \frac{V}{\lambda^3} g_{5/2}(z), \qquad\qquad q_0 = -\ln(1-z).$$

(IV.37)

and

$$N = N_\varepsilon + N_0.$$

$$N_\varepsilon = \frac{V}{\lambda^3} g_{3/2}(z), \qquad\qquad q_0 = \frac{z}{1-z}. \tag{IV.38}$$

where q_ε and q_0 (N_ε and N_0) is the logarithm of the grand-canonical partition function (number of bosons) of the excited states ($\varepsilon > 0$) and zero energy states ($\varepsilon = 0$), respectively.

If the temperature is sufficiently high ($V/\lambda^3 < 1$) and the fugacity z is not very close to 1, it can be shown that N_0 is negligible in front of $N\varepsilon$, and that $0 \le g_2(z) \le \zeta\left(\tfrac{3}{2}\right) = 2.612$,

So

$$N_\varepsilon^{max} = N_\varepsilon \approx 2.612 V \left(\frac{2\pi m k_b T}{h^2} \right)^{3/2} \propto V T^{3/2}. \tag{IV.39}$$

where ζ is Riemann's zéta function

The Bose temperature T_B is the temperature at which the number of bosons in excited states is equal to the total number of particles. So,

$$N = 2.612 V \left(\frac{2\pi m k_b T}{h^2} \right)^{3/2}. \tag{IV.40}$$

This becomes:

$$N_\varepsilon = N \left(\frac{T}{T_B} \right)^{3/2}. \tag{IV.41}$$

The number of bosons in the state $\varepsilon = 0$ is

$$N_0 = N\left[1 - \left(\frac{T}{T_B}\right)^{3/2}\right].$$

(IV.42)

From this relationship, we see that if the temperature T decreases, the number of bosons in the state $\varepsilon = 0$ increases. This phenomenon is called **Bose-Einstein condensation** (bosons accumulate in the low-energy state when T decreases).

Now let's calculate the internal energy,

$$U = -\left.\frac{\partial}{\partial \beta} q\right|_{z,V} = \frac{3}{2} k_b T \frac{V}{\lambda^3} g_{5/2}(z).$$

$$\underset{\substack{T < T_B \\ \mu \to 0}}{\approx} \frac{3}{2} k_b T \frac{V}{\lambda^3} g_{5/2}(z).$$

$$= 1.34 \frac{3}{2} V \left(\frac{2\pi m}{h^2}\right)^{3/2} (k_b T)^{5/2}.$$

(IV.43)

and depending on the Bose temperature, we write

$$U = 0.77 N k_b T \left(\frac{T}{T_B}\right)^{3/2}.$$

(IV.44)

The constant volume heat capacity is

$$C_V = 1.93 N k_b \left(\frac{T}{T_B}\right)^{3/2} = \frac{5}{2}\frac{U}{T}.$$

(IV.45)

Entropy

$$S = -\frac{\partial \Phi}{\partial T}\bigg|_{V,\mu} = \frac{5}{3}\frac{U}{T}$$

(IV.46)

Pressure is

$$p = -\frac{\partial \Phi}{\partial V}\bigg|_{T,\mu} = \frac{2}{3}\frac{U}{V} = 0.0851\frac{m^{3/2}(k_b T)^{5/2}}{\hbar^3}.$$

(IV.47)

So the pressure depends only on the temperature of the system (and not the volume V).We can show that we find the thermodynamic properties of a classic perfect gas (Boltzmann gas) if the temperature is very high and the density is low.

IV.3 Black body radiation

In this section, we study the electromagnetic radiation emitted by a body heated to temperature T (black body), this radiation or these photons constitute a gas of bosons (the photons are spin 1 particles) in a cavity maintained at temperature T. It is assumed that this gas is perfect, because the photons do not interact with each other (the photons are electrically neutral and of zero mass). The photon has two transverse polarizations, so the spin degeneration factor is equal to two (gs = 2). The speed of photons is equal to that of light c, so the energy of each particle is written,

$$\varepsilon = \hbar\omega = h\nu = pc$$

(IV.48)

where ω, ν and p are the pulsation, frequency and pulse of the photon.

Photons can be emitted or absorbed by the walls of the cavity, so the number of photons is variable which requires the use of the grand-canonical assembly to study this system (T and V do not vary). At equilibrium, the free energy of the system is constant, so

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = 0$$

(IV.49)

so the chemical potential of this gas is zero. The average number of photons in a state of energy $\varepsilon = \hbar\omega$

$$<n_\varepsilon> = \frac{1}{e^{\beta_\varepsilon} - 1}$$

(IV.50)

The average number of photons in states where the energy is between ε and ε + dε (where between ω and ω + dω) is therefore,

$$dN = <n\varepsilon> g(\varepsilon)d\varepsilon = \frac{8\pi V}{h^3 c^3}\frac{\varepsilon^2}{e^{\beta\varepsilon} - 1}d\varepsilon.$$

(IV.51)

$$= \frac{1}{\pi^2 c^3}\frac{\omega^2}{e^{\beta\hbar\omega} - 1}d\omega.$$

(IV.52)

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With

$$g(\varepsilon) = g_s \frac{4\pi V}{h^3 c^3} \varepsilon^2.$$

(IV.53)

So the average number of photons in the cavity is

$$N = \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^2}{e^{\beta\hbar\omega} - 1} d\omega .$$

(IV.54)

to perform the integration on ω, we use the following integral representation

$$\int_0^\infty \frac{x^{n-1}}{e^x - 1} dx = \Gamma(n)\zeta(n) .$$

(IV.55)

where $x > 0$ and $\zeta(n) = \sum_{k=1}^\infty \frac{1}{k^n}$ is the Riemann function:

$$\zeta(3/2) = 2.612, \ \zeta(5/2) = 1.341, \ \zeta(3) = 1.202, \ \zeta(5) = 1.037.$$

(IV.56)

We then find:

$$N = 0.24V \left(\frac{k_b T}{\hbar c} \right)^3 .$$

(IV.57)

We define the photon density ($n(\omega) = N/V$) and the energy density

$$\frac{dn(\omega)}{d\omega} = \frac{1}{\pi^2 c^3} \frac{\omega^2}{e^{\beta\hbar\omega} - 1}.$$

(IV.58)

$$\frac{du(\omega)}{d\omega} = \hbar\omega \frac{dn(\omega)}{d\omega} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}.$$

(IV.59)

The variation of the internal energy as a function of the pulse (or wavelength) is

$$dU = \frac{\hbar V}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega.$$

$$= 8\pi hcV \frac{\lambda^{-5}}{1 - e^{\frac{\beta hc}{\lambda}}} d\lambda.$$

(IV.60)

This formula describes the spectral distribution of blackbody radiation energy. It is derived for the first time by Planck, and it agrees with the experimental results.

Now let's look at the low-east-high-frequency limits, respectively, of this distribution

$$dU \approx \frac{k_b T\, V}{\pi^2 c^3} \omega^2 d\omega. \qquad\qquad \hbar\omega \ll k_b T.$$

(IV.61)

$$dU \approx \frac{\hbar V}{\pi^2 c^3} \omega^3 e^{-\frac{\hbar\omega}{k_b T}} d\omega, \qquad\qquad \hbar\omega \gg k_b T.$$

(IV.62)

The first formula is the Rayleigh-Jeans formula, it corresponds to the classical limit where the photons are considered as harmonic oscillators of ω-pulse. The second is the wein formula, in this case the quantum behavior is very important.

To obtain the total energy in the general case, we integrate the eq. (IV.60) on the pulse that varies between zero and infinity. We find

$$U = \frac{k_b^4 V \pi^4}{15\pi^2 c^3 \hbar^3} T^4.$$

(IV.63)

So, the energy is proportional to T 4 which corresponds to Stéphan's law. Radiated energy per unit volume is

$$u = \frac{U}{V} = 7.56 \times 10^{-16} T^4 Jm^{-3}.$$

(IV.64)

Because the chemical potential is zero $\mu = 0$, the free energy corresponds to the high-potential Φ, so we have

$$F = \Phi = \frac{k_b TV}{\pi^3 c^3} \int\limits_0^\infty \omega 2 \ln\left(1 - e^{-\beta \hbar \omega}\right) d\omega,$$

$$= -\frac{4}{3}\frac{\sigma}{c} V T^4. \qquad \text{(IV.65)}$$

Whereby

$$\sigma = \frac{k_b^4 V \pi^4}{60\pi^2 c^2 \hbar^3}. \qquad \text{(IV.66)}$$

And

$$p = -\frac{\partial F}{\partial V}\bigg|_T = \frac{4\sigma}{3c} T^4. \qquad \text{(IV.67)}$$

$$S = -\frac{\partial F}{\partial T}\bigg|_T = \frac{16\sigma V}{3c} T^3. \qquad \text{(IV.68)}$$

We find the internal energy given by the eq. IV.63).

$$U = F + TS = \frac{4\sigma V}{c} T^4 = -3F, \qquad\qquad C_V = \frac{16\sigma V}{c} T^3. \qquad \text{(IV.69)}$$

The equation of state of the photon gas is

$$pV = \frac{U}{3}. \qquad \text{(IV.70)}$$

IV.4   **Fermi Perfect Gas** Nucleons inside the atomic nucleus or electrons in metals can be thought of, approximately, as Fermi perfect gases. In this paragraph, we study the thermodynamic properties of an ideal gas consisting of non-relativistic. For the Fermi-Dirac statistic, we write

$$q(T,V,z) = \sum_k \ln\left(1 + ze^{-\beta\varepsilon_k}\right). \qquad \text{(IV.71)}$$

$$N(T,V,z) = \sum_k \frac{1}{z^{-1}e^{\beta\varepsilon_k} + 1}. \qquad \text{(IV.72)}$$

Because the energy levels are close to each other for a large enough volume, then the sum on k can be replaced by an integral on energy. This becomes:

$$q(T,V,z) = \int_0^\infty g(\varepsilon)d\varepsilon \ln\left(1 + ze^{-\beta\varepsilon_k}\right). \qquad \text{(IV.73)}$$

$$N(T,V,z) = \int_0^\infty g(\varepsilon)d\varepsilon \frac{1}{z^{-1}e^{\beta\varepsilon_k} + 1}. \qquad \text{(IV.74)}$$

with

$$g(\varepsilon) = g_s \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2}, \qquad\qquad gs = 2s+1. \qquad \text{(IV.75)}$$

where s is the spin of the fermions.

Let's introduce, now, the following integral representation,

$$f_n(z) = \frac{1}{\Gamma(n)} = \int_0^\infty \frac{x^{n-1}}{z^{-1}e^x + 1} dx, \qquad 0 \le z \le \infty, \qquad x = \beta\varepsilon. \qquad (IV.76)$$

So,

$$q(T,V,z) = \frac{gV}{\lambda^3} f_{5/2}(z). \qquad (IV.77)$$

$$N(T,V,z) = \frac{gV}{\lambda^3} f_{3/2}(z). \qquad (IV.78)$$

We can show that the internal energy and pressure of this gas are given by,

$$U = \frac{3}{2} Nk_b T \frac{f_{5/2}(z)}{f_{3/2}(z)}. \qquad (IV.79) \qquad p = \frac{2}{3}\frac{U}{V}. \qquad (IV.80)$$

So the pressure is equal to 2/3 times the energy distribution in space. This relationship holds for the classical non-relativistic Maxwell-Boltzmann perfect gas, and the non-relativistic Bose-Einstein perfect gas. It can also be shown that free energy and entropy are given by

$$F = N_k bT \left(\ln(z) - \frac{f_{5/3}(z)}{f_{3/2}(z)} \right) \qquad (IV.81)$$

$$S = N_k b \left(\frac{5}{2} \frac{f_{5/3}(z)}{f_{3/2}(z)} - \ln(z) \right) \qquad (IV.82)$$

IV.5 Exercises & Issues

Exercise#1:

We consider a classical ideal gas in a gravitational field. The energy of each particle at altitude z_i is

$$E_i = \frac{P_i^2}{2m} + mgz_i$$

where g is the gravitational constant.

(1) Calculate the grand-canonical partition function $Z^{(gc)}$.

(2) Calculate the pressure variation as a function of altitude z.

Exercise #2:

We propose to determine, in the first order, the deviation of the Bose-Einstein law from that of Maxwell-Boltzmann. The great potential Ω is written:

Ω=-kTzf()

*kB is the Boltzmann constant.

where z is the transition partition function of a Maxwell-Boltzmann gas;

where k is Boltzmann's constant;

$f(v) = \alpha = \frac{N}{z}$, z being the transition partition function of a Maxwell-Boltzmann gas;

$f(v) = \alpha = \frac{N}{z} = -\frac{2}{\sqrt{\pi}} \int_0^{+\infty} \sqrt{x}\, ln\left(1 - e^{(v-x)}\right) dx$ is a function that only depends on v

Establish the expression for the equation of state from $f(v)$

Establish based on $f(v)$ the expressions of :

$f(v) = \alpha = \frac{N}{z}$ is a function dependent only on?

Establish the expression of the equation of state starting from()

Draw upthe expressions of:

-    *s* entropy.

-    internal energy *U*.

-    the constant volume heat capacity C_v

3. Establish a relationship between the pressure P, the internal energy U and the volume V for the Boson gas.

Exercise#3:

The first theoretical calculation of blackbody radiation properties is due to Planck. Instead of reasoning about the quantums of the electromagnetic field (Bose). Planck reasoned about the field sources, i.e. the walls of gravity enclosing the electromagnetic field.

The atoms of the wall, at the temperature T, are likened to harmonic oscillators vibrating at the frequency and obeying the Maxwell-Boltzmann statistic. In this case, the average energy of an oscillator is $\bar{\varepsilon} \frac{hv}{e^{\frac{hv}{kT}} - 1}$

Assuming <u>that</u> the number of oscillators whose frequency is between and is, calculate the energy spectral density   .

$$g(v)dv = \frac{8\pi V}{c^3} v^2 dv$$

At a fixed temperature, study the variation of (,) as a function of (): for low frequencies (Rayleigh-Jeans law).
for high frequencies (Wein's law).

Show thatthe function has a maximum and graphically represent this function. How does the maximum move when the temperature varies?

3. Find the Rayleigh-Jeans law by the energy equipartition theorem.

A1 LIOUVILLE 'S EQUATION

The description of a system of N indistinguishable particles of mass m using the one-body distribution function is an approximation because the correlations between the particles are neglected. The total energy of this system, which we will assume to be made up of point particles obeying classical mechanics, is the sum of the kinetic energy and the potential energy which we will assume to depend only on the coordinates:

$$E = H = \sum_{i=1}^{N} \frac{P_i^2}{2m} + V\left(r_1 + ... + r_N\right).$$

(1)

Quantity H is referred to as the *Hamiltonian* of the system. It corresponds to the expression of the total energy of the system using coordinates and pulses. The quantity $\dfrac{\partial H}{\partial p_i} = \dfrac{p_i}{m} = \dot{r_i}$ is none other than the velocity of the particle i. Newton's equations, which give the dynamic evolution of the particles of the system, can be written $m \; \ddot{r_i} = \dot{p_i} = -\dfrac{\partial H}{\partial r_i}.$

Together these two equations make up what are called *Hamilton's equations*. They are equivalent to Newton's equations. The first set defines the impulse of the particles and the second set gives the dynamic evolution of the particles:

$$\dot{r_i} = \frac{\partial H}{\partial p_i} \qquad et \qquad \dot{p_i} = -\frac{\partial H}{\partial r_i} \qquad i=1 \; à \; N$$

(2)

Let us now express Hamilton's equations in another form by introducing the *N-body* distribution function $f^{(N)}(r_1, p_1, .. , r_N, p_N, t)$. The phase space associated with this problem of N particles has $6N$ dimensions.

The quantity $f^{(N)}(r_1, p_1, . . . , r_N, p_N, t)dr_1 \, dp_1 . . . dr_N \, dp_N$ represents the probability of finding N particles in the elementary volume $dr_1 \, dp_1 . . . dr_N \, dp_N$ at time t^3. Therefore, if we integrate over the entire phase space:

$$\int f^{(N)}\left(r_1, p_1, \; . . . , r_N, p_N, \; t\right) dr_1 dp_1 . . . dr_N dp_N = 1$$

(3)

f

Considering a volume element $dr_1 \, dp_1 .. . dr_N \, dp_N$ centered at $r_1, p_1, .. , r_N, p_N$ at time t, it will become $dr'_1 \, dp'_1 . . . dr'_N \, dp'_N$ centered at $r'_1 \, p'_1 . . . r'_N p'_N$ at time $t+dt$. The quantities $r'_1, p'_1, ..., r'_N, p'_N$

are deduced from $r_1, p_1,...,r_N, p_N$ using the equations of motion. It can be shown that this volume element is invariant in the transformation, *i.e.*:

$$dr'_1\ dp'_1 \ldots dr'_N\ dp'_N = dr_1\ dp_1 \ldots dr_N\ dp_N \tag{4}$$

This simply results from the fact that the Jacobian of the transformation is, to the second order, equal to unity.

Example:

If any property of the system can be calculated from the distribution function $f_p(r,\ p,\ t)$, we need to know its evolution as a function of time. We will, as part of the approximation of independent particles, find the equation that $f_p(r,\ p,\ t)$ satisfies. As a first step, we will neglect particle collisions.

Consider, at time t, the volume element $dr\ dp$ centered at r and p of the phase space. It contains on average $f_p(r,p,t)drdp$ particles. At time $t+dt$, these particles moved under the influence of the mean potential $U(r)$. Indeed, each particle is subjected to a force $\mathbf{F} = -\dfrac{\partial U(\mathbf{r})}{\partial \mathbf{r}}$

The volume element $drdp$ has become $dr'dp'$ and is centered at (r',p'). We deduce r and p of the particle motion equations:

The volume element $d\mathbf{r'}d\mathbf{p'}$ is connected to $d\mathbf{r}\ d\mathbf{p}$ by the following relation:

$$\frac{dr}{dt} = v = \frac{p}{m} \Rightarrow r' = r + \frac{p}{m}dt$$

$$\frac{dp}{dt} = F \Rightarrow p' = p + Fdt \tag{5}$$

wherein J is the Jacobian of transformation. Taking into account (5), it is worth:

$$J = \begin{vmatrix} \frac{\partial x'}{\partial x} & \frac{\partial x'}{\partial y} & \frac{\partial x'}{\partial z} & \frac{\partial x'}{\partial p_x} & \frac{\partial x'}{\partial p_y} & \frac{\partial x'}{\partial p_z} \\ \frac{\partial y'}{\partial x} & \frac{\partial y'}{\partial y} & \frac{\partial y'}{\partial z} & \frac{\partial y'}{\partial p_x} & \frac{\partial y'}{\partial p_y} & \frac{\partial y'}{\partial p_z} \\ \frac{\partial z'}{\partial x} & \frac{\partial z'}{\partial y} & \frac{\partial z'}{\partial z} & \frac{\partial z'}{\partial p_x} & \frac{\partial z'}{\partial p_y} & \frac{\partial z'}{\partial p_z} \\ \frac{\partial p'_x}{\partial x} & \frac{\partial p'_x}{\partial y} & \frac{\partial p'_x}{\partial z} & \frac{\partial p'_x}{\partial p_x} & \frac{\partial p'_x}{\partial p_y} & \frac{\partial p'_x}{\partial p_z} \\ \frac{\partial p'_y}{\partial x} & \frac{\partial p'_y}{\partial y} & \frac{\partial p'_y}{\partial z} & \frac{\partial p'_y}{\partial p_x} & \frac{\partial p'_y}{\partial p_y} & \frac{\partial p'_y}{\partial p_z} \\ \frac{\partial p'_z}{\partial x} & \frac{\partial p'_z}{\partial y} & \frac{\partial p'_z}{\partial z} & \frac{\partial p'_z}{\partial p_x} & \frac{\partial p'_z}{\partial p_y} & \frac{\partial p'_z}{\partial p_z} \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 & \frac{dt}{m} & 0 & 0 \\ 0 & 1 & 0 & 0 & \frac{dt}{m} & 0 \\ 0 & 0 & 1 & 0 & 0 & \frac{dt}{m} \\ \frac{\partial F_x}{\partial x}dt & 0 & 0 & 1 & 0 & 0 \\ 0 & \frac{\partial F_y}{\partial y}dt & 0 & 0 & 1 & 0 \\ 0 & 0 & \frac{\partial F_z}{\partial z}dt & 0 & 0 & 1 \end{vmatrix} \tag{7}$$

Therefore, $J = 1$ implying that:

$$d\mathbf{r'}d\mathbf{p'} = d\mathbf{r}\ d\mathbf{p} \tag{8}$$

A.2 Debye-Einstein model for phonons

In Einstein's model, the atoms of a solid are represented by 3-dimensional quantum harmonic oscillators, which vibrate independently of each other at the same pulsation ω, see section (3.5). It has been shown that the internal energy of the total system and the average value of the excitation levels of each one-dimensional oscillator (in one direction) are given by

$$U(T,N) = 3N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right).$$

(9)

$$<n> = \frac{1}{e^{\beta\hbar\omega} - 1}$$

(10)

This implies that the average energy of a one-dimensional oscillator, of pulsation ω, is

$$<\varepsilon> = \hbar\omega\left(\frac{1}{2} + <n>\right).$$

(11)

By analogy with the photon system, we can interpret <n> as the number of indistinguishable quanta that we call phonons. So phonons are energy bosons

$$\varepsilon = c_s\left|\vec{p}\right|. \qquad\qquad \vec{p} = \hbar\vec{k}.$$

(12)

where c_s is the propagation speed of the phonons, it is equal to the sound speed. So in this interpretation (or Debye's model), the solid is considered an elastic medium traversed by waves, like sound waves, which propagates in both directions

transverse to the speed ct, and in the longitudinal direction at the speed cl. In this case, the density of states g(ω), as a function of the pulsation ω, is written

$$g(\omega) = V\left(\frac{\omega^2}{2\pi^2 c_l^3} + \frac{\omega^2}{\pi^2 c_t^3}\right)$$

(13)

Because the number of normal oscillations is finite (3N), then

$$\int_0^{\omega_c} g(\omega)\,d\omega = 3N, \Rightarrow \omega_c^3 = 18\pi^2 \frac{N}{V}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)^{-1}$$

(14)

We can show that the internal energy and the heat capacity are written,

$$U(T,V,N) = \frac{9N\hbar}{\omega_c^3} \int_0^{\omega_c} d\omega \left(\frac{1}{e^{\beta\hbar\omega}-1} + \frac{1}{2} \right) \omega^3 \tag{15}$$

$$C_V = \frac{9N\hbar^2}{\omega_c^3 k_b t^2} \int_0^{\omega_c} d\omega \frac{\omega^4 e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1 \right)^2} \tag{16}$$

A.3 Stirling's Approximation

The factorial function: $n! = 1 \times 2 \times 3 \times \ldots \times (n-1) \times n$ quickly becomes incalculable when n is big It can nevertheless be assessed with an excellent approximation by noting that:

$$\log n! = \sum_{i=1}^{n} \log i \; \square \int_1^n \log x \, dx = \left[x \log x - x \right]_1^n = n \log n - n + 1 \tag{17}$$

When $n \gg 1$, we get the Stirling approximation:

$$\text{Log } n! = n \text{ Log } n - n \tag{18}$$

which is excellent for the numbers involved in statistical physics. When n is small, a more accurate approximation is sometimes used:

$$\text{Log } n! = n \text{ Log } n - n + \frac{1}{2} \text{Log } (2\pi n) \; soit \; n! = \sqrt{2\pi n} \, n^n \, e^{-n} \tag{19}$$

—

A.4 Gamma function

The following defined integral is called a *gamma function*:

$$\Gamma(n + 1) = \int_0^\infty x^n \, e^{-x} dx \quad \text{pour } n > -1 \tag{20}$$

By integration by parts, we can establish the following relationship:

$$\Gamma(n + 1) = \int_0^\infty x^n \, e^{-x} dx = -[x^n e^{-x}]_0^\infty + n \int_0^\infty x^{n-1} \, e^{-x} dx = n\Gamma(n) \tag{21}$$

if n is integer $\Gamma(1) = \int_0^\infty e^{-x}\,dx = 1$, ➔ $\Gamma(n+1) = n!$ Definition (4) makes it possible to generalize the notion of factorial to non-integer numbers. For n half-integer numbers, we calculate Γn using the recurrence relation (5) and the property $\Gamma\left(\frac{1}{2}\right) = \left(-\frac{1}{2}\right)! = \sqrt{\pi}$ which will be established below. By using the results above, it is deduced, after a change of elementary variable, that:

$$\int_0^\infty x^n\,e^{-\alpha x}dx = \frac{n!}{\alpha^{n+1}} \quad \text{pour } n \text{ entier} \tag{22}$$

A.5 Legendre Transformation

It is well known that a curve in the plane $y=f(x)$ is perfectly defined as long as its derived function f' is known at any point x. There are a number of situations in physics and mathematics where the natural data of the studied problem is the derivative $f'(x)$ rather than the variable x itself. The Legendre transformation is a systematic means that makes it possible to define, without loss of information, a new function whose independent variable will be the slope of the function f at the point x, that is to say $f'(x)$.

Definition: *Let f:*R $\rightarrow$ R be *a bounded function with bounded variation. The Legendre transform of f is the function g defined by one of two relationships:*

$$g\ (f'(x)) \equiv xf'(x) - f(x) \quad or \quad g(f'(x)) \equiv f(x) - xf'(x)\ .$$

The first sign convention is that used in Mathematics, the second is that used in Thermodynamics.

Let's show that this definition is equivalent to the definition which has a clear geometric content:

$$g(p) \equiv max\ (px - f(x))\ ,$$

$g(p)$ is the maximum distance between the straight line of slope p which passes through the origin and the function f. The solution is obtained for x_p such that $p = f'(x_p)$, i.e. the distance between the straight line and the function is maximum at the point x_p where the tangent to f is equal to the slope of the straight line (see Fig. F3). We therefore also

have $g(p) \equiv px_p - f(x_p)$, or $g(f'(x_p)) = f'(x_p)x_p - f(x_p)$, which corresponds to the initial definition. The variables x and $f'(x) \equiv p$ are called *conjugate variables with* respect to the pair of functions f *et* g.
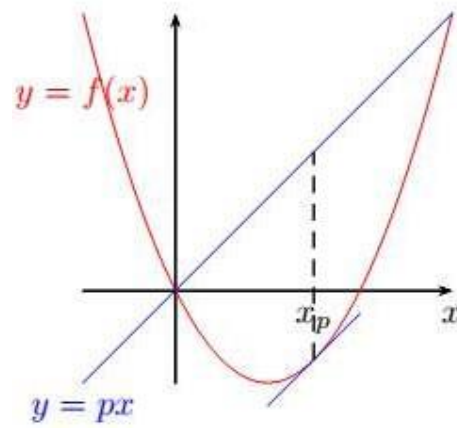
Figure A.5 – Geometric interpretation of the Legendre transform.

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