

TD1

1- Random walk in 1D

A particle can move by steps on a 1D line. At each time step it makes one step forward with probability p , or one step backward, with probability $(1-p)$. The length of a step is a constant l . At time 0, the particle is at the origin at $x=0$.

- What is on the average the distance that the particle has travelled after N time-steps ?
- What is the standard deviation of the distance ?

One will use the properties of the binomial law of probability.

2- System of N free particles

We recall that a free particle in a box of volume $V = L_x L_y L_z$ obeys the stationary Schrödinger equation :

$$-\frac{\hbar^2}{2m} \nabla^2 \phi = \varepsilon \phi$$

The solutions are

$$\phi = \frac{1}{\sqrt{V}} \exp(i\vec{k} \cdot \vec{r})$$

$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$

On the box boundaries the wave function is zero so one must have periodic boundary conditions. This defines the stationary modes inside the box with 3 quantum numbers n_i , $k_i = \frac{2\pi n_i}{L_i}$, and the energy of a mode is given by

$$\varepsilon_{n_x, n_y, n_z} = \frac{2\pi^2 \hbar^2}{mV^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$

Rmk : there are two ways of modifying the energy level, either by modifying the volume V (by doing some work), or by modifying the values of n_x, n_y, n_z (by exchanging heat).

- Verify that the energy levels are close enough to use the continuous approximation, for an electron of energy 1eV located inside a box of $L = 1$ mm.
- Compute the density of energy state $\rho(E)$.

We now put N free particles in the box.

- Give the expression of the total energy E as function of the modes k_j of the particles.
- Give the density of energy states $\rho(E)$.
- Comment the result.

3- Another derivation of the semi-classical representation

- Considering all the possible energy states of a single free particle inside a box, give the expression of the average of an observable A (using the continuous approximation). Derive from this expression the density of state $\rho(\epsilon)$ in the phase space (\vec{r}, \vec{p}) .

NB : use the relation $\vec{p} = \hbar \vec{k}$

- Show that one recovers the same expression as when invoking the Heisenberg relation of uncertainty like we did in the course.
- Which derivation do you prefer ?

4- System of N independent $1/2$ -spins

We recall that particles like electrons or protons have a magnetic moment which is given by $\vec{\mu} = g\mu_B \vec{S}$. For an electron $g=2$ and $\mu_B = e\hbar/2m$ (Bohr magneton), S is the spin operator with $S_z = \pm 1/2$. The interaction hamiltonian with a magnetic field B on the axis z is $H = -\vec{\mu} \cdot \vec{B} = -g\mu_B S_z B$. There are two energy levels $\epsilon_{\pm} = \mp \mu B$.

We consider an ensemble of N $1/2$ -spins interacting with a magnetic field B , but not interacting together.

- What is the number of microstates ?
- Determine the energy of the microstates and their probabilities
- Give the average of the energy and its standard deviation.
- When N is very large give an approximate expression of the probability distribution of the energy of the system.

TD 2

1- Entropy of the ideal gaz in microcanonical statistics.

Let's consider again an assembly of N (large number) non-interacting particles in an insulated box of given volume. This system has a given value of energy E , volume V and number of particles N (microcanonic description).

We want to find the expression of the temperature, pressure and chemical potential for the equilibrium state of the system.

- Find the expression of the number of microstates of the system.
- Show that its entropy is given by (use the Stirling formula)

$$S(N, V, E) = Nk \left\{ \frac{5}{2} + \ln \left(\frac{V}{N} \left(\frac{4mE}{3Nh^2} \right)^{3/2} \right) \right\}$$

- Derive the expressions of $T(N, V, E)$ and of the pressure $P(N, V, E)$.
- Show that the chemical potential may be written

$$\mu(N, V, E) = kT \ln \left(\frac{N \lambda_T^3}{V} \right)$$

$$\lambda_T = \frac{h}{\sqrt{2\pi mkT}}$$

What is the physical unit of λ_T , what can be its physical interpretation ?

2- Solid cristal

A solid cristal is modeled by an ensemble of N harmonic oscillators (distinguishable because they are localised on different nodes of the cristal), their Hamiltonian is given by

$$H = \sum_{i=1}^N \left(\frac{\vec{p}_i^2}{2m} + \frac{1}{2} m \omega^2 \vec{q}_i^2 - \varepsilon_0 \right)$$

ε_0 represents the attractive potential which ensures the stability of the cristal. The cristal is an isolated system with energy E (microcanonical description).

- For one oscillator in 1D $H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2 - \varepsilon_0$, we recall that the energy states are given by $E_n = (n + \frac{1}{2}) \hbar \omega - \varepsilon_0$. Show that the density of energy states

may be written $\rho(E) = \frac{1}{\hbar \omega}$

- We now want to find the density of microstates in the phase space $\rho(q, p)$.

The method is to use the coordinates $X = \sqrt{\frac{m\omega^2}{2}}q$, $P = \frac{p}{\sqrt{2m}}$, such that

$$X^2 + P^2 = E + \varepsilon_0 = R^2$$

Show that in this space the density of microstates is $dN(X,P) = \frac{2\sqrt{E + \varepsilon_0}}{\hbar\omega} dR$

(number of energy states in the energy band $\Delta E = 2RdR$)

Conclude that the density of states in the phase space (q,p) is uniform

$$\rho(q,p) = \frac{1}{h}$$

- c) Give the number of microstates for the assembly of N oscillators in the 3D space and write it on the form

$$\Omega(N,E) = \frac{1}{h^{3N}} \int_{V_r} d^{3N}q d^{3N}p$$

The integration domain is defined for $H(\{p_i, q_i\}) \leq E$

- d) Show that the number of microstates of energy $< E$ is

$$\Omega(E,N) = \frac{1}{h^{3N}} \left(\frac{2}{\omega}\right)^{3N} V_{6N}(\sqrt{E + \varepsilon_0})^{6N}$$

where V_{6N} is the volume of the sphere of radius unity in a 6N space.

- e) Give the expression of the entropy $S(N,E)$
 f) Derive the expression of the temperature $T(N,E)$ and show that the chemical potential is given by

$$\mu(N,E) = -\varepsilon_0 + 3kT \ln\left(\frac{\Theta}{T}\right)$$

$$\Theta = \frac{\hbar\omega}{k}$$

3- Sublimation

We shall now consider a system formed of two parts, one perfect gaz and a solid cristal, as those described in the two previous exercices. The system is isolated from the exterior and in equilibrium. The total energy is the sum of the energy of the two system $E = E_1 + E_2$, it is constant, and the number of particules is constant $N = N_1 + N_2$.

- a) We denote by $Z(N,V,E)$ the number of microstates of the system. Show that

$$Z(N,V,E) = \sum_{\substack{N_1 + N_2 = N, \\ E_1 + E_2 = E}} Z_1(N_1, V_1, E_1) Z_2(N_2, E_2)$$

Z_1 and Z_2 are the numbers of microstates for the gaz and for the solid, respectively.

- b) Using the postulate of the maximum of entropy, find the most probable values of the internal variables E_1 and N_1 (for the gaz). Show that when the equilibrium is reached

$$T_1 = T_2 = T$$

$$\mu_1 = \mu_2$$

Find the expression of the gaz pressure P_s as a function of T , λ_T , Θ and ε_0 . This is called the *saturating vapor tension*.

c) Plot the variation of P_s as a function of T . Comment the figure, and explain why the physically acceptable domain is for $kT < \varepsilon_0$.

TD 3 Canonical systems

1) Isotope separation

A cylinder of radius R and height H contains N particles of mass m forming a perfect gas at temperature T . This cylinder rotates around its axis with a constant angular velocity ω . In permanent regime we shall assume that a particle located at distance r from the axis has a radial acceleration $\omega^2 r$.

- Give the expression of the centrifugal force on a particle at distance r from the axis. Give
- the expression of the total energy (kinetic and potential), assuming that the potential energy is zero on the axis.
- Compute the partition function Z of one particle. Derive the internal energy of the gas and give its expression when $\omega \rightarrow 0$. (One will assume that the gas may be treated with the classical continuous approach).
- Give the expression of the specific heat of the gas C_v and its value when $\omega \rightarrow 0$.
- Compute the pressure ratio $P(r)/P(0)$. First give the expression of the density of particles at distance r from the axis $n(r)$ and use the perfect gas equation of state to derive the pressure at distance r .
- Numerical computation : compute $P(R)/P(0)$ for $R = 10$ cm, $\omega = 6000$ turns/mn, for Argon gas with $m = 39,9$ g/mole, $T = 300$ K. Is the effect noticeable ? For which temperature would the pressure ratio $P(R)/P(0) = 2$?
- Numerical computation : this method is used to separate the Uranium isotopes ^{235}U and ^{238}U . Compute the ratio $\frac{n_1(R)/n_1(0)}{n_2(R)/n_2(0)}$, for $R = 20$ cm, $\omega = 10000$ turns/mn, $T = 300$ K.

2) Electrical polarisation of a gas of polar molecules

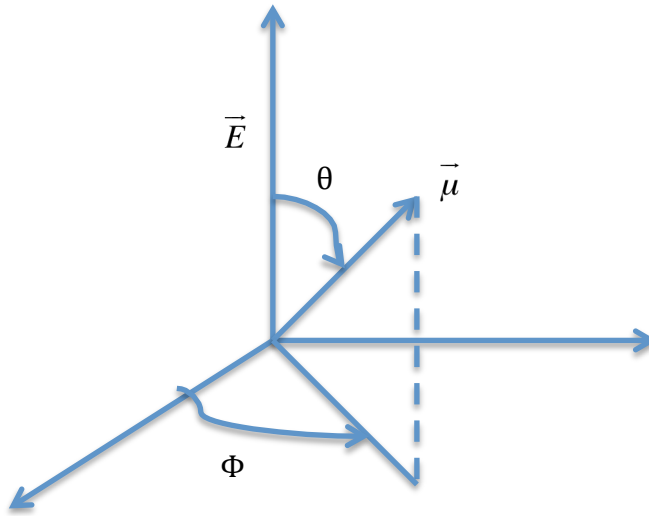
We consider a gas formed of N HCl molecules, considered as rigid objects (we neglect the vibrations) in a box of volume V . Their mass is m and their dipolar moment is denoted by μ ($\mu = 0.36 \cdot 10^{-29}$ C.m).

- The rotation temperature is 15 K for this molecule. Explain under which conditions we can treat the rotation in a classical way.
- In the case where we can disregard the quantification of the rotation energy, the position and orientation of a molecule may be described by 5 coordinates (3 coordinates and the two angles θ and Φ), the two angles allow to precise the orientation of the dipolar moment vector. We denote by p_θ and p_Φ the conjugate coordinates of the two angles. The kinetic energy of rotation is given by

$$K_{rot} = \frac{p_\theta^2}{2I} + \frac{p_\Phi^2}{2I \sin^2 \theta}$$

Compute the canonical partition function Z for the N molecules without interaction. Derive the free energy F and the specific heat C_v at temperature T .

c) The gaz in now in a uniform electric field E , θ denotes the angle between E and the dipolar moment of a molecule.



Write the hamiltonian and find the new partition function at temperature T .
Derive the expression f the free energy and of the specific heat.

d) Give the expression of the electrical polarisation per unit volume $\vec{P} = \frac{N}{V} \langle \vec{\mu} \rangle$

To find the mean dipolar vector , first find the expression of the probability $P(\Omega)d\Omega$ for a molecule to have its dipolar moment in the solid angle $d\Omega$. Then find the expression of \vec{P} and show that the modulus of the polarisation vector

$$\text{is } P = \|\vec{P}\| = -\frac{1}{V} \left(\frac{\partial F}{\partial E} \right)_{T,V}$$

e) Show that in the limit of weak electric fields , the vector P is proportionnal to the electric vector. Derive the expression of the relative permittivity ϵ on the form

$$\epsilon = \lim_{E \rightarrow 0} \left[1 + \frac{P}{\epsilon_0 E} \right]$$

f) Compute numerically ϵ in standard temperature and pressure conditions ($P=100000 \text{ Pa}$, $T=300\text{K}$)

3- Diatomic perfect gaz

The molecules have 3 degrees of freedom of translation, two degrees of rotation and one degree of freedom for the vibration. The hamiltonian is

$$H = \frac{\vec{p}^2}{2m} + \frac{\vec{l}^2}{2I} + \frac{p_r^2}{2m_r} + \frac{1}{2} m_r \omega^2 (r - r_*)^2$$

First term : Kinetic energy of translation

Second term : Kinetic energy of rotation,

Third term : kinetic energy of vibration (m is the reduced mass of the two atoms)

Fourth term : potential energy of vibration where r is the relative coordinate .

(r,p_r) is a couple of conjugate variables.

- a) Recall the spectrum of energy levels for the different terms. Show that for one molecule the partition function can be factorized in

$$Z = Z_{trans} Z_{rot} Z_{vib}$$

Give the explicit expressions of the partition functions.

Recall how the partition function of the N molecules is related to z, in the Maxwell-Boltzmann approximation.

- b) Compute explicitly the partition function in the classical limit. Derive the expression of the mean energy and of the specific heat. Comment.
- c) At low temperature, it is not possible to apply the classical treatment. What is the mean rotation energy when $kT \ll h^2/I$? Same question for the mean energy of vibration when $kT \ll h\omega$.

TD 5 : Perfect versus real gas

Ex 1 : Van der waals equation of state

We recall the equation of state obtained in the course :

$$NkT = \left(p + a \frac{N^2}{V^2} \right) (V - Nb)$$

where a and b are constants, V : volume, N : number of molecules, p : gas pressure.

- a) Show that one of the curves p(V) at constant temperature (isotherms) has an horizontal inflexion point. Give the value of T_c , P_c and V_c for this « critical » point.

Show that

$$\frac{P_c V_c}{RT_c} = \frac{3}{8} = 0,375$$

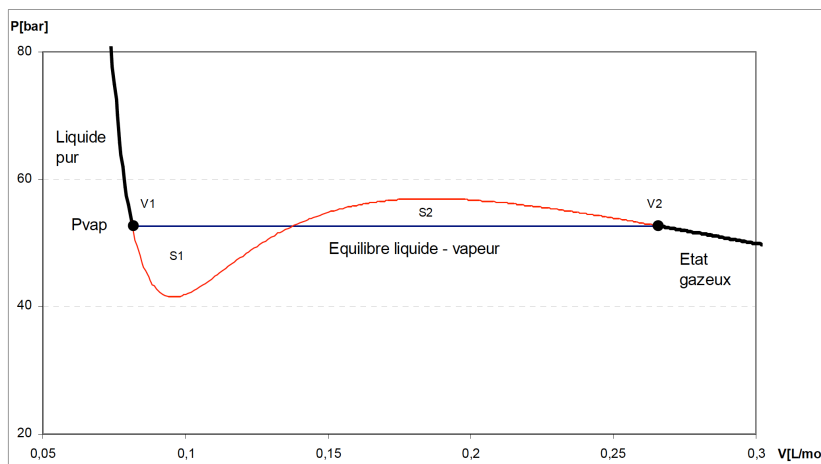
- b) Write the equation of state between reduced coordinates : $p_r = P/P_c$, $T_r = T/T_c$, $V_r = V/V_c$. Give the expression of the compressibility

$$\chi_T = -\frac{1}{V} \frac{\partial V}{\partial p}$$

Plot different isotherms for $T > T_c$, $T = T_c$ and $T < T_c$

- c) When $T > T_c$ a given value of the volume corresponds to one well defined value of the pressure. Discuss the different regimes of compressibility for large and small volumes.
- d) When $T < T_c$, discuss the sign of the compressibility. What happens in the cases where it becomes negative ?

Discuss the plot below (the numerical values are for CO₂ gas at $T = 280$ K which is smaller than the critical temperature)



e) For $T < T_c$, In the domain where the system shows one liquid phase in equilibrium with a gaseous phase (between V_1 and V_2), we recall that the chemical potential is the same in the two phases. Show that the pressure is a constant that depends only on T , called the saturation vapor pressure $P_{sat}(T)$.

f) Show that

$$P_{sat} = \frac{1}{V_2 - V_1} \int_{V_1}^{V_2} P(V) dV$$

This means that the surfaces S_1 and S_2 are equal. This equality allows to compute the value of $P_{sat}(T)$

TD 4 : Grand-canonical systems

Ex. 1 : Langmuir Adsorption isotherms

A perfect gas is in contact with the surface of a solid where molecules can be adsorbed. The number of molecules in the gas is large enough so that the gas thermodynamical properties are not modified when some molecules are adsorbed.

We assume that each site on the surface can adsorb at most one molecule. The energy of one site is $\epsilon = 0$ if it contains no molecule, $\epsilon = -\epsilon_1$ ($\epsilon_1 > 0$) if one molecule is adsorbed. The adsorption sites are far from each other so that they do not interact. So when n molecules are adsorbed the adsorption energy is $E = -n\epsilon_1$.

I- *Chemical potential of the gas*

We assume that the gas is a perfect gas that can be described in a classical way, the mass of the molecule is m , they have no internal degree of freedom, they occupy a volume V .

- 1) Give the expression of the grand function of partition Q and of the grand potential J of the gas.
- 2) Give the expressions of the pressure, mean number of molecules, mean energy and entropy.
- 3) Show that one recovers the equation of state $PV = \langle N \rangle kT$
- 4) Show that the chemical potential of a molecule in the gas may be written

$$\mu = \mu_0(T) + kT \ln(P / P_0)$$

where P is the gas pressure and P_0 is a standard pressure that is by convention equal to 1 bar, $\mu_0(T)$ is the standard chemical potential. Show that $\mu_0(T) = -kT \ln(f(T))$, and give the expression of the function $f(T)$.

II. *Properties of the solid*

We now study the solid that can adsorb the molecules. The temperature T is given and the chemical potential of the adsorbed molecules μ' is fixed by the condition in the gas at the surface.

- 1) We can you say of μ' ?
- 2) We consider a given adsorption site on the solid surface. Give its grand partition function.
- 3) Derive the grand partition function for the M adsorbed molecules and the grand potential.
- 4) Give the mean number $\langle n \rangle$ of adsorbed molecules and the surface coverage $\langle n \rangle / M = \tau$ as function of ϵ_1 , T and μ' .
- 5) Taking into account the expression of the chemical potential of the molecules in the gas give the expression of $\tau(T, P)$ as function of the temperature and pressure in the gas. Plot qualitatively the variations of τ as a function of P for 2 different temperatures. Discuss the result.

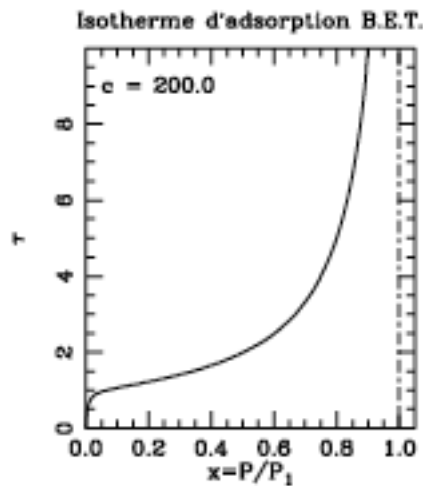
Ex 2. Adsorption isotherm Brunauer-Emmett-Teller (1938)

We now study the case where the number of adsorbed molecules on a given site is not limited. The adsorption energy of the first molecule is ϵ_1 as previously, but the adsorption of other molecules are $-\epsilon_2$ ($0 < \epsilon_2 < \epsilon_1$).

- 1) Compute the grand partition function for the solid.
- 2) Find the expression of the average occupation number $\tau = \langle n \rangle / M$ as a function of the temperature and pressure. Introduce the constant $c = \exp(\beta(\epsilon_1 - \epsilon_2))$, $P_1(T) = P_0 \exp(-\beta(\epsilon_2 + \mu_0(T)))$ and $x = P/P_1(T)$. Show that one must have $x < 1$ and that

$$\tau = \frac{cx}{(1-x+cx)(1-x)}$$

For $c \gg 1$ the variations of τ are as shown in the plot.



What is the meaning of the inflexion at small values of x ? Explain qualitatively the behavior of $\tau(P)$

TD 6 : Applications of the Boltzmann-Saha law

Ex 1 : We consider a plasma formed of hydrogen atoms in thermodynamical equilibrium at temperature T and pressure p.

We define the degree of ionisation as

$$x = \frac{[H^+]}{[H] + [H^+]}$$

where the notation [X] means the number density of atoms X.

Using the fact that the plasma remains electrically neutral, find the expression of x as function of T and p. Plot curves at constant x in a (logT, logp) diagram. Put in this diagram the points representing the conditions of the solar interior and solar photosphere. Conclude about the ionization degree of the solar plasma in these two regions.

The ionization energy $\chi_1 = 13,6 \text{ eV}$

Ex. 2

We would like to explain the broadest absorption lines of silicium ions observed in stellar spectra.

Using the Table below, study the variations of the number density of ions Si^{r+} on the excited level s of energy ϵ , for temperatures between 4000 K and 30 000K, and an electronic pressure of 13 Pa, with respect to the total number density of silicium atoms

$$x_s = \frac{[Si_s^{r+}]}{\sum_r [Si^{r+}]}$$

Atom	Potential (eV)		lines	g	Partition function					
	Ionizat.	Excitation			4000K	6000 K	8000K	10 000K	20 000K	30 000K
H	13,6	10,15	Balmer	8		2	2	2	8	60
Si I	8,15	1,90	390,55	1	9	9,5	10,5	11		
Si II	16,34	9,80	412,84 413,09	10	5,5	5,5	6	6	7	
Si III	33,49	18,94	455,26 456,79 457,48	3			1	1	1,5	2
Si IV	45,15	23,93	408,89 411,61	2			2	2	2	2,2

The values are taken from Allen « Astrophysical quantities », 1973

L.H. Aller, « The atmospheres of the Sun and stars », Ronald Press Company, 1963

Knowing that the strongest lines of Si IV are observed in type O9 stars, the lines of Si III in type B2 stars, the lines of Si II in type B7 and the line of Si I in type G5 ones, give an estimate of the effective temperature in the atmospheres of these different spectral classes.

TD 7 : Ideal quantum gas of fermions

Ex 1 : White dwarf

A white dwarf is an evolved star, its mass is typically close to the solar mass whereas its radius is on the order of the radius of the Earth. The main source of energy is nuclear fusion in the core of the star.

Here we shall consider a white dwarf like Sirius B : $M = 2,09 \cdot 10^{30}$ kg ($1,05 M_{\odot}$) and its radius $R = 5570$ km (less than the Earth radius).

We shall study a simple model to recover these characteristics. We shall assume that all the hydrogen in the star has been transformed into 4He in previous nuclear fusions.

The temperature is estimated around $T = 2 \cdot 10^7$ K.

- a) At this temperature the helium atoms are completely ionized (why ?)
- b) Compute the total number of electrons N_e inside the star.
- c) Compute the Fermi energy. Show that one may consider the gas of electrons as non-relativistic perfect gas completely degenerated (quantum gas)
- d) Compute the pressure of the electrons.
- e) Compute the internal energy of the gas of electrons as function of N_e and R . Assuming that the density is uniform compute the gravitational energy of the star. Show that the internal energy and gravitational energy are equal for a given value R_e of the radius. This is the condition of stability of the star. Compute numerically R_e and compare it to the actual value for Sirius B. Are you satisfied with this simple model ?
- f) Compute as a function of N_e , the Fermi momentum p_F of the degenerate gas of electrons. We observe that p_F increases with the density of electrons in the gas. The electrons may become relativistic. To investigate whether the mass of the star could increase without any limit we shall consider the case where the mass energy of the electrons is very small with respect to their total energy (ultra-relativistic electrons). We then have $\varepsilon_F \approx cp_F$, c is the velocity of light.
 - Compute as a function of p_F the mean value of the momentum $\langle p \rangle$ and of the energy $\langle \varepsilon \rangle$ of one electron.
 - Compute The internal energy of the gas of electrons.
 - Show that in the ultra-relativistic limit there is a upper limit for the mass of the white dwarf M_c , above which the star would be instable and collapse. Compute the number of electrons in that limit case and derive M_c . Compare with the value that is obtained when using more realistic models ($M_c \cong 2,9 \cdot 10^{30}$ kg = $1,44 M_{\odot}$). Conclusions.

Ex 2 : Flux of escaping particles

We consider N fermions at low temperature (degenerate case) contained in a volume V . The container has a small hole of surface dS . Compute the flux of particles escaping from the volume V through this small hole (i.e. the number of particles escaping per second per square meter).