

## EXAM OF STATISTICAL PHYSICS

January 11<sup>th</sup> 2018*Duration of the exam : Two hours**The use of documents, mobile phones, calculators, . . . , is forbidden.*

## Recommendations :

Read the text carefully and **write** out your answers as *succinctly* and as *clearly* as possible.Check your calculations (dimensional analysis, etc.); do not forget to **reread yourself**.Think to the **information given in the annex**.**Questions related to the lectures ( $\sim 10\text{min}$ )**

1/ Recall the statement of the fundamental postulate of statistical physics.

2/ We consider  $\{|\ell\rangle\}$  the set of microstates (the stationary states in the quantum case); give the occupation probabilities  $P_\ell^*$  of the microstates if the system is isolated and at equilibrium.3/ Recall the Gibbs-Shannon formula for the statistical entropy  $S(\{P_\ell\})$  in the *general* case. Apply this formula to the case of an isolated system and recover the expression of the microcanonical entropy  $S^*$ .**Problem : entropic force ( $\sim 1\text{h}$ )**

We study a large molecule in the presence of smaller atoms (see figure). We show that when the molecule approaches a wall of the container, it undergoes a force resulting from a purely entropic effect. We describe the particles **classically**.

**A. Gas of point particles.**— We first consider the gas of atoms alone (in the absence of the large molecule), which will be, in this first part **A**, modeled as **point** particles of mass  $m$ . We assume the gas to be **isolated** in a container of volume  $V$ .

1/ Describe the microstates of the system. Express the number  $\Phi_N(E)$  of microstates with energies less than  $E$  as a multiple integral.2/ What is the relation between  $\Phi_N(E)$  and the number of accessible states  $\Omega_N(E, V)$  (we assume the energy to be defined with some uncertainty  $\delta E$ )? Show that  $\Omega_N(E, V) \propto V^N E^\eta$  (the prefactor is not requested) and give the value of the exponent  $\eta$ .

**B. Gas of hard-core spheres.**— In this second part, we still consider the gas of atoms, which we now describe as a gas of hard-core spheres, i.e. small **impenetrable spheres** of diameter  $a$ .

1/ **Two atoms.**— A single atom has an accessible volume  $V$ . What is the available volume for a second atom (see figure) ?

2/ By continuing this reasoning (i.e. by introducing by thought atoms one by one), justify that the number of accessible microstates for the gas of  $N$  atoms is of the form

$$\Omega_N(E, V) = C_N(E) \prod_{n=1}^N [V - 2(n-1)b], \quad (1)$$

where we will give the expression of the volume  $b$  as a function of the diameter  $a$  of the spheres. What is the energy dependence of  $C_N(E)$  (without additional calculation) ?

3/ Show that, in the limit  $N \gg 1$  and  $V \gg Nb$ , one has  $\prod_{n=0}^{N-1} (V - 2nb) \simeq V_{\text{eff}}^N$  where  $V_{\text{eff}} = V - Nb$  is the effective volume.

Hint : consider  $\sum_{n=0}^{N-1} \ln(V - 2nb) \simeq \int_0^N \ln(V - 2nb) dn$  and draw  $\ln(V - 2nb)$  for  $n \in [0, N]$ .

4/ **Temperature.**– Recall the definition of the microcanonical temperature  $T^*$  and calculate it. Compare to the perfect gas of point particles (part **A**).

5/ **Equation of state.**– Recall the definition of microcanonical pressure  $p^*$ . Deduce the equation of state. Compare to the perfect gas of point particles. Plot the pressure as a function of the average density  $n = N/V$ . Interpret the divergence of the pressure for a critical value of the density,  $n_c$ , to be determined.

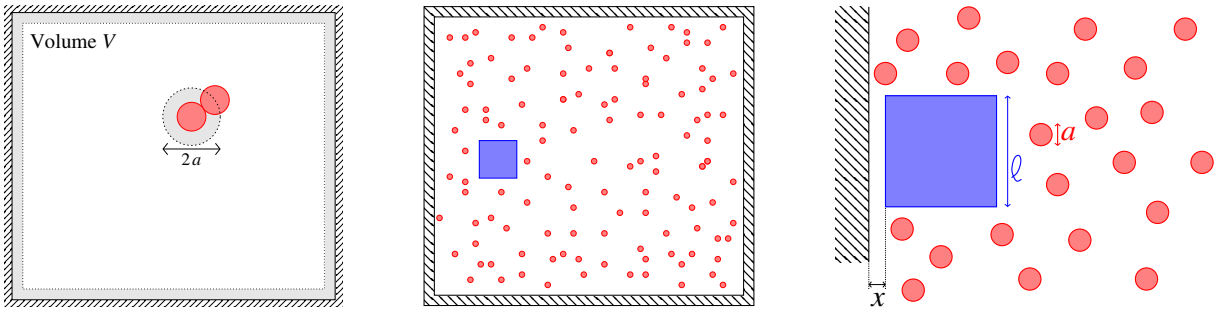


FIGURE 1 – Left : *exclusion volume due to a single atom.* Middle and right : *A large  $\ll$  molecule  $\gg$  (the large cube) of volume  $v = \ell^3$  is in the middle of smaller atoms (small balls) of volume  $(4\pi/3)(a/2)^3$ .*

**C. Entropic force.**– In this last part, we study the situation where the large molecule of volume  $v \gg b$  is in the presence of  $N$  atoms (middle figure). To simplify the discussion, we consider that the large molecule has a cubic form :  $v = \ell^3$  (with  $\ell \gg a$ ).

1/ We suppose the large molecule at **rest**, at a distance  $x$  from the wall (see figure). What is the new effective volume  $\tilde{V}_{\text{eff}}$  accessible by atom (distinguish the cases  $0 < x < a$  and  $x > a$ ) ?

2/ Deduce the expression of the microcanonical entropy of the *atoms* as a function of  $x$ , which we note  $S^*(x)$ . Plot the entropy  $S^*(x)$  as a function of  $x$  assuming  $V_{\text{eff}} = V - Nb \gg v$ ,  $x \ell^2$ . By using a theorem seen in the course, infer whether the large molecule is attracted or repelled by the wall.

3/ We define the  $\ll$  entropic force  $\gg$  as

$$f(x) \stackrel{\text{def}}{=} T^* \frac{\partial S^*(x)}{\partial x}. \quad (2)$$

Plot  $f(x)$  as a function of  $x$ . Discuss the sign of the force. For  $x < a$ , give a simple expression of the force  $f(x)$  as a function of  $p^*$  defined in the question **B.5** (we assume  $V_{\text{eff}} \gg v, x \ell^2$ ).

## Exercice : 1D quantum harmonic oscillators ( $\sim 50\text{min}$ )

We consider  $N$  independent and identical harmonic oscillators described in the framework of quantum mechanics. The system is assumed to be **isolated**. We recall that the stationary states  $|n\rangle$  for **an** oscillator are identified by an integer  $n \in \mathbb{N}$  and have energies  $\varepsilon_n = \hbar\omega(n + 1/2)$ .

1/ What are the microstates of the system of  $N$  oscillators ?

2/ If the system has an energy  $E_M = \hbar\omega(M + N/2)$ , justify that the total number of accessible microstates is  $\Omega(M, N) = (M + N - 1)!/[M!(N - 1)!]$ .

3/ Deduce the microcanonical entropy  $S^*$ . Simplify the expression by supposing  $N \gg 1$  and  $M \gg 1$  (but be careful : we do **not** assume  $M \gg N$ , which would correspond to a classical approximation).

4/ Calculate the microcanonical temperature  $T^*$ . Show that  $1 + N/M = \exp\{\hbar\omega/(k_B T^*)\}$ . Draw *carefully*  $T^*$  as a function of the excitation energy  $\Delta E = M\hbar\omega$  (we will identify a « classical » regime,  $\Delta E \gg N\hbar\omega$ , and a « quantum » regime,  $\Delta E \ll N\hbar\omega$ ).

5/ We write  $P(n)$  the probability for *one* of the oscillators to be in the  $n^{\text{th}}$  excited state  $|n\rangle$ . Justify that  $P(n) = \Omega(M - n, N - 1)/\Omega(M, N)$ . Simplify the expression assuming  $N, M \gg n$  (we will use  $(N + a)!/N! \simeq N^a$  for  $N \gg a$ ). Check the normalisation.

**6/ Bose-Einstein distribution.**— We now study in which state is, on average, one of the  $N$  oscillators.

a) Express  $\bar{n}$  as a function of  $P(n)$ .

b) In order to calculate the sum, we use the trick  $\sum_{n=1}^{\infty} n q^n = q \frac{d}{dq} \sum_{n=0}^{\infty} q^n$ . Deduce  $\bar{n}$ . Was the result expected ?

c) Express the average occupancy of the  $\bar{n}$  oscillators as a function of the microcanonical temperature (use the result of the question 4). Draw *carefully*  $\bar{n}$  as a function of  $T^*$ .

### Annex

- Stirling formula :  $\ln n! \simeq n \ln n - n$  si  $n \gg 1$ .
- Fundamental equality of *thermodynamics* :  $dE = T dS - p dV + \mu dN$ .