Statistical Mechanics (M1)

The Grand Canonical Ensemble

1 Fluctuation of the number of particles

Prove the following relationship :

$$\langle (N - \bar{N})^2 \rangle = kT \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T,V} \tag{1}$$

2 The monoatomic ideal gas

Let us consider a monoatomic ideal gas in a volume V, in equilibrium with a heat and particle reservoir of temperature T and chemical potential μ.

a) Show that the grand partition function may be written as : $\Xi = e^{\lambda f}$. Give the expression of the factors λ and f in the exponent.

b) Derive the average number of particles $\langle N \rangle$, the average energy, and the state equation of the gas.

c) Prove that $\overline{\left(N - \bar{N}\right)^2} = \bar{N}$.

d) Let us consider a small subset of V of volume v in such a way that the remaining $V - v$ volume plays the role of a reservoir. Show that the number of n particles inside v is distributed according to the Poisson law :

$$P_n = e^{-\langle n \rangle} \frac{\langle n \rangle^n}{n!} \tag{2}$$

3 Adsorption of an ideal gas on a surface 1

Let us consider a surface presenting N_0 traps ready to adsorb one atom each one. The energy of one adsorbed atom is $-\varepsilon_0 (\varepsilon_0 > 0)$.

I) Considering that the system of adsorbed atoms is in equilibrium with a heat-particle reservoir of temperature T and chemical potential μ :

   a) Obtain the grand partition function, Ξ, the average number of adsorbed atoms N_a, and the corresponding energy.

   b) Obtain the expression of the grand potential, express the entropy S_a as a function of $\langle N_a \rangle$. Compare with the microcanonical entropy of a system of N_a particles adsorbed in N_0 traps.

II) We assume now that the surface is in fact the wall of the recipient of volume V containing the gas and that it is formed of the same atoms as the gas.

   (a) Express the chemical potential as a function of the pressure p, and the temperature T. Derive corresponding isotherms (Langmuir's adsorption isotherms).

   (b) Calculate the average energy of the total systems constituted by the gas and the adsorbed phase.

   (c) Derive the heat capacity at constant volume of the total system as a function of p and T. Give a physical interpretation to the different terms contributing to the heat capacity. We can use the property :

$$\left(\frac{\partial \bar{N}_g}{\partial T} \right)_{V,N} > 0 \tag{3}$$

III) Obtain the expression of θ of point II.a) in the framework of the canonical ensemble.

4 Adsorption of an ideal gas on a surface 2

We will consider a model of adsorption on a surface different from the one in Ex. 3. In this case, the adsorbed atoms are not fixed at localized sites of the surface, but are free of moving on the surface, constituting a 2D monoatomic ideal gas. The energy of an adsorbed particle is now : $E = \frac{p^2}{2m} - \varepsilon_0$, were $p^2 = p_x^2 + p_y^2$, considering that the surface is parallel to the (x, y) plane and with $\varepsilon_0 > 0$ being the adsorption energy per particle.

a) Obtain the average number of adsorbed atoms per unit surface as a function of the pressure p and T, along with the corresponding average energy.

b) Derive the total energy of the systems constituted by the gas and the adsorbed molecules.

c) Derive the heat capacity at constant volume of the global system.

d) Reobtain the average number of adsorbed atoms per unit surface in the framework of the canonical ensemble.

5 System of interacting electrons

A solid has $N \gg 1$ sites that may host 0, 1 or 2 electrons. When one electron is trapped in a site, it has an energy $\varepsilon_0 < 0$, irrespective of the spin orientation. When two electrons are trapped in the same site, then their spins are antiparallel, and the energy of the electron pair is $2\varepsilon_0 + g$, where the interaction energy of the electrons trapped in the same site is $g > 0$and $g < |\varepsilon_0|$. We neglect the interaction between electrons trapped in different sites.

I) Considering that the system of adsorbed atoms is in equilibrium with a heat-particle reservoir of temperature T and chemical potential μ :

   a) Obtain the average number of trapped electrons and the average energy of the solid.

II) Let us suppose now that the number of trapped electrons is fixed and equal to the number of sites N.

   a) Calculate the chemical potential of electrons and the average number, n_0, of empty sites, n_1 of sites containing only one electron and n_2 of sites containing two electrons. Study the low and high temperature limits of these values.

III) The solid is now situated in a constant magnetic field B. Let us call m the magnitude of the magnetic moment of each electron. Obtain the average magnetization of the solid of volume V, considering it in equilibrium with a thermostat of temperature T also acting as a reservoir of electrons of chemical potential μ.