Problem Set
Adsorption of a gas on a surface

An ideal gas of N monatomic molecules with spin zero and mass m is contained in a box of constant volume V, maintained at the temperature T. The gas is in contact with a surface that can adsorb molecules in A traps. In what follows, we assume that $N \gg A$. We call $-\epsilon_0$ the atom-trap binding energy, and it is assumed that only one atom can be adsorbed per trap.

1 Statistical analysis of the adsorbed atoms

(a) Which formalism is most suitable for studying the adsorbed atoms? What is the relationship between the chemical potential μ_{g} of the gas and the one of the adsorbed atoms μ?

(b) What is the sign of ϵ_0? Show that the total energy of the system can be written as

$$E = -\epsilon_0 \sum_{i=1}^{A} n_i,$$

where n_i is the occupation number of the i^{th} trap. What are the possible values of n_i?

(c) Calculate the grand-canonical partition function Ξ.

(d) Calculate the grand-canonical potential Ω. Deduce from the previous result the average number N_{a} of adsorbed atoms. Check your result by calculating N_{a} directly from Ξ.

(e) Calculate the ensemble-average energy of the adsorbed atoms.

(f) Deduce from the previous results the expression of the entropy S_{a} of the adsorbed atoms as a function of A and N_{a}. Comment on your result.

2 Thermodynamical properties

Within the *Maxwell–Boltzmann approximation*, the free energy of the ideal gas described in the introduction of the Problem takes the form

$$F = N k_{\mathrm{B}} T \left[\ln \left(\frac{N}{V} \Lambda_T^3 \right) - 1 \right], \tag{1}$$

where $\Lambda_T = (2\pi\hbar^2 / m k_{\mathrm{B}} T)^{1/2}$ is the thermal de Broglie wavelength.

(a) Quickly rederive the result of Eq. (1).

(b) Give a definition of the adsorbtion rate of the gas θ. Show that it takes the form

$$\theta = \frac{P}{P + P_0(T)},$$

where P is the pressure of the gas. Give an expression for $P_0(T)$ as a function of the parameters of the problem.

(c) Plot the curves $\theta(P)$, called the *Langmuir adsorbtion isotherms*, for different values of the temperature T.

(d) Calculate the ensemble-average energy E_{T} of the total system.

(e) Deduce from the previous question the heat capacity of the total system C_V. (In your calculation, do not seek for an explicit expression of $\mathrm{d}N_{\mathrm{a}}/\mathrm{d}T$). Interprete your result.