
Problem Set 1

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

$$F = Nk_B T \left[\ln \left(\frac{N}{V} \Lambda_T^3 \right) - 1 \right], \quad (1)$$

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

- (a) Quickly rederive the result of Eq. (1).
- (b) Give a definition of the adsorption 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 adsorption 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 dN_a/dT). Interpret your result.