IF/UFRJ
Statistical Mechanics - 2025/1 – Raimundo

Problem Set #5 – The Grand-Canonical Ensemble

21/4/2025

1. Consider a classical ideal gas of monatomic molecules.

   (a) Show that the grand partition function is given by

   $$\mathcal{Z} = \mathrm{e}^{zZ_1},$$

   where z is the fugacity, and $Z_1 = V/\Lambda^3$ is the partition function for a single molecule, with $\Lambda = \left(h^2/2\pi m k_B T\right)^{1/2}$.

   (b) Show that the average number of molecules is

   $$\langle N \rangle = zZ_1$$

   (c) Obtain the equation of state in terms of $\langle N \rangle$.

2. A fluid can coexist in the liquid and gas (vapour) phases. In order to describe this coexistence, we adopt a very simple model, in which we treat the liquid as a "gas" of independent molecules such that (i) the interaction of each molecule with the others is represented by a constant potential, $-\phi$; (ii) each one of the N molecules of the liquid moves freely in a total volume $V_\ell = N_\ell \, v_0$, where v_0 is the (constant) volume per molecule in the liquid phase. The vapour of this liquid (N_g molecules in a volume V_g) is treated as a usual ideal gas.

   (a) Treat each subsystem (liquid and vapour) in the *canonical* ensemble, and show that the vapour pressure is given by

   $$P = \frac{k_\mathrm{B}T}{v_0}\,\mathrm{e}^{-\beta\phi}.$$

(b) Treat each subsystem (liquid and vapour) in the *grand-canonical* ensemble, and reobtain the above result. Comment on the differences between the approaches in (a) and (b).

(c) Discuss physically the behaviour of P at low and high temperatures.

3. A monatomic gas coexists in equilibrium with the solid phase. Assume the energy per atom necessary to transform solid in gas is η, and adopt the Einstein model for solids, namely each atom vibrates around its equilibrium position with frequency ω, being therefore represented by a three-dimensional harmonic oscillator. Determine the vapour pressure, P, as a function of temperature, T, for this system, and sketch $P(T)$. Discuss physically the low- and high-temperature limits.

4. Consider a monatomic crystal, made up of N atoms. The atoms may be located in two kinds of positions: normal (filled circles in Fig. 1) or interstitial (empty circles). Assume there are an equal number, N, of both kinds of positions, but the energy of an atom on an interstitial position excedes by ε that of an atom on a normal position.

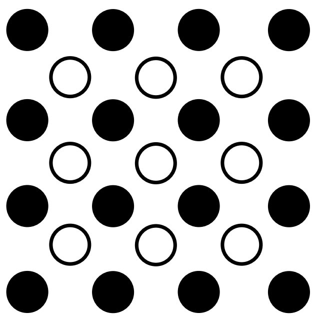

Figure 1: Problem 4 - Lattice sites are represented by full circles, while intersticial sites are represented by empty circles.

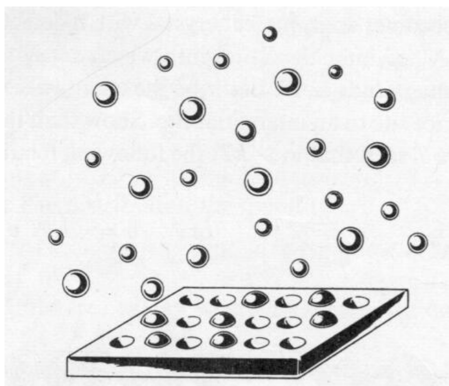

Figure 2: Problem 5 -Gas molecules are adsorbed on a surface.

(a) Show that the partition function for this system can be written as

$$Z = \sum_n \Omega(n)\, \mathrm{e}^{-\beta n \varepsilon} \equiv \sum_n \zeta(n), \qquad (1)$$

where n ($1 \ll n \ll N$) is the number of occupied interstitial positions, and $\Omega(n)$ is the number of ways these positions can be occupied.

(b) Show that the leading contribution to $\Omega(n)$ is

$$\Omega(n) \sim \left(\frac{N}{n}\right)^{2n}. \tag{2}$$

(c) Since $\Omega(n)$ increases rapidly with n, while $\exp(-\beta n\varepsilon)$ decreases rapidly with n, one expects a sharp maximum of $\zeta(n)$ at some n^*. Show that

$$\frac{n^*}{N} \approx \mathrm{e}^{-\beta\varepsilon/2}, \tag{3}$$

and that the Helmholtz free energy becomes

$$A \approx -k_{\mathrm{B}}T \ln \zeta(n^*). \tag{4}$$

(d) Alternatively, we can calculate the Helmholtz free energy by first calculating the entropy, S, associated with displacing n atoms to interstitial positions, and using $A = E - TS$. Show that imposing A to be a minimum yields the same n^* as in (c).

5. A surface with M sites can adsorb atoms of an ideal gas (single atoms with mass m) at a temperature T and pressure P; see Fig. 2. An adsorbed atom has energy $-\varepsilon_0$, relative to the free case.

   (a) Obtain an expression for the *surface coverage*, θ, (i.e., the ratio of the number of adsorbed atoms by M, the number of adsorbing sites) as a function of P, T, and ε_0.

   (b) Discuss physically the behaviour of θ in the limits $P \to 0$ and $P \to \infty$.