DS 5:
The Grand Canonical Ensemble

Philip Cherian

October 20, 2023

1 The grand partition function

(a) Let us begin with the definition of Z_{GC} that you've seen in class:

$$Z_{\text{GC}} = \sum_r e^{-\beta(E_r - \mu N_r)}, \tag{1}$$

where r specifies a microstate, and μ is the chemical potential. Use this to show that we can define a thermodynamic potential, the Grand Potential:

$$\Lambda = -\frac{1}{\beta} \ln Z_{\text{GC}}. \tag{2}$$

(b) Show that the natural variables of Z_{GC} are T, μ, and V. (*Hint*: Natural variables are a set of appropriate variables that allow to compute other state functions by partial differentiation of the thermodynamic potentials.)

(c) Use this to argue that

$$\Lambda = V\Lambda_{\text{pp}}, \tag{3}$$

where Λ_{pp} is the Grand Potential per particle. (*Hint*: Thermodynamic potentials are extensive.)

(d) Given the above results, conclude that

$$\Lambda = -PV. \tag{4}$$

(e) Calculate the Grand Partition Function for an ideal gas, and therefore derive the following relation between the chemical potential and the pressure:

$$e^{-\beta\mu} = \frac{1}{\beta P \lambda_T^3}, \tag{5}$$

where λ_T is the thermal de Broglie wavelength $\lambda_T = \sqrt{h^2/2\pi m T}$.

2 Adsorption of a non-relativistic electron gas

Consider a non-relativistic electron gas (spin-1/2) of mass m at temperature T and pressure P at equilibrium with some adsorbing surface with N_s absorbing sites. The surface is magnetic, so that the energy of the adsorbed electron is $E = -\Delta - \mu_B \sigma h$, where $\sigma = \pm 1$ is the spin, and h is the surface magnetic field.

(a) Compute the grand potential of the gas Λ_{gas}.

(b) Compute the grand potential of the surface Λ_{surf}. (*Hint*: each adsorption site can be in one of three states: empty, occupied with an up-spin, or occupied with a down-spin.)

(c) Find an expression for the fraction of occupied adsorption sites, $f(p, T, \Delta, h)$.

(d) Find the surface magnetisation $\mu_B(N_{\text{surf},\uparrow} - N_{\text{surf},\downarrow})$.

3 Classical gas of two species

Suppose a classical gas comprises two species A And B, with different energies:

$$E_A = \frac{\mathbf{p}^2}{2m} \qquad E_B = \frac{\mathbf{p}^2}{4m} - \Delta. \tag{6}$$

(a) Find the grand potential of the two species, $\Lambda(T, V, \mu_A, \mu_B)$.

(b) Find the number densities $n_A(T, \mu_A, \mu_B)$ and $n_B(T, \mu_A, \mu_B)$.

(c) If the reaction $2A \rightleftharpoons B$ is allowed, what is the relation between μ_A and μ_B, and also n_A and n_B?

(d) If initially $n_A = N$ and $n_B = 0$, what is n_A at equilibrium?