PHYSICS 140A : STATISTICAL PHYSICS
MIDTERM EXAM SOLUTIONS

Consider a classical gas of indistinguishable particles in three dimensions with Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \Big\{ A\,|\boldsymbol{p}_i|^3 - \mu_0 H S_i \Big\} \ ,$$

where A is a constant, and where $S_i \in \{-1\,,\,0\,,\,+1\}$ (*i.e.* there are three possible spin polarization states).

(a) Compute the free energy $F_{\textsf{gas}}(T,H,V,N)$.

(b) Compute the magnetization density $m_{\textsf{gas}} = M_{\textsf{gas}}/V$ as a function of temperature, pressure, and magnetic field.

The gas is placed in thermal contact with a surface containing $N_{\textsf{s}}$ adsorption sites, each with adsorption energy $-\Delta$. The surface is metallic and shields the adsorbed particles from the magnetic field, so the field at the surface may be approximated by $H=0$.

(c) Find the Landau free energy for the surface, $\Omega_{\textsf{surf}}(T,N_{\textsf{s}},\mu)$.

(d) Find the fraction $f_0(T,\mu)$ of empty adsorption sites.

(e) Find the gas pressure $p^*(T,H)$ at which $f_0 = \frac{1}{2}$.

Solution :

(a) The single particle partition function is

$$\zeta(T,V,H) = V\!\int\!\frac{d^3\!p}{h^3}\, e^{-Ap^3/k_{\rm B}T} \sum_{S=-1}^{1} e^{\mu_0 H S/k_{\rm B}T} = \frac{4\pi V k_{\rm B}T}{3Ah^3}\cdot\Big(1 + 2\cosh(\mu_0 H/k_{\rm B}T)\Big) \ .$$

The N-particle partition function is $Z_{\textsf{gas}}(T,H,V,N) = \zeta^N/N!$, hence

$$\boxed{F_{\textsf{gas}} = -Nk_{\rm B}T\left[\ln\!\left(\frac{4\pi V k_{\rm B}T}{3NAh^3}\right) + 1\right] - Nk_{\rm B}T\ln\!\Big(1 + 2\cosh(\mu_0 H/k_{\rm B}T)\Big)}$$

(b) The magnetization density is

$$\boxed{m_{\textsf{gas}}(T,p,H) = -\frac{1}{V}\,\frac{\partial F}{\partial H} = \frac{p\mu_0}{k_{\rm B}T}\cdot\frac{2\sinh(\mu_0 H/k_{\rm B}T)}{1 + 2\cosh(\mu_0 H/k_{\rm B}T)}}$$

We have used the ideal gas law, $pV = Nk_{\rm B}T$ here.

(c) There are four possible states for an adsorption site: empty, or occupied by a particle with one of three possible spin polarizations. Thus, $\Xi_{\textsf{surf}}(T,N_{\textsf{s}},\mu) = \xi^{N_{\textsf{s}}}$, with

$$\xi(T,\mu) = 1 + 3\,e^{(\mu+\Delta)/k_{\rm B}T} \ .$$

Thus,

$$\boxed{\Omega_{\mathsf{surf}}(T, N_{\mathsf{s}}, \mu) = -N_{\mathsf{s}} k_{\mathrm{B}} T \ln\Big(1 + 3\, e^{(\mu+\Delta)/k_{\mathrm{B}}T}\Big)}$$

(d) The fraction of empty adsorption sites is $1/\xi$, *i.e.*

$$\boxed{f_0(T,\mu) = \frac{1}{1 + 3\, e^{(\mu+\Delta)/k_{\mathrm{B}}T}}}$$

(e) Setting $f_0 = \frac{1}{2}$, we obtain the equation $3\, e^{(\mu+\Delta)/k_{\mathrm{B}}T} = 1$, or

$$e^{\mu/k_{\mathrm{B}}T} = \tfrac{1}{3}\, e^{-\Delta/k_{\mathrm{B}}T} \ .$$

We now need the fugacity $z = e^{\mu/k_{\mathrm{B}}T}$ in terms of p, T, and H. To this end, we compute the Landau free energy of the gas,

$$\Omega_{\mathsf{gas}} = -pV = -k_{\mathrm{B}} T\, \zeta\, e^{\mu/k_{\mathrm{B}}T} \ .$$

Thus,

$$\boxed{p^*(T,H) = \frac{k_{\mathrm{B}} T\, \zeta}{V}\, e^{\mu/k_{\mathrm{B}}T} = \frac{4\pi (k_{\mathrm{B}}T)^2}{9Ah^3} \cdot \Big(1 + 2\cosh(\mu_0 H/k_{\mathrm{B}}T)\Big)\, e^{-\Delta/k_{\mathrm{B}}T}}$$