PHYSICS 140A : STATISTICAL PHYSICS
HW SOLUTIONS #6

(1) Consider a two-dimensional gas of identical classical, noninteracting, massive relativistic particles with dispersion $\varepsilon(\boldsymbol{p}) = \sqrt{\boldsymbol{p}^2c^2 + m^2c^4}$.

(a) Compute the free energy $F(T, V, N)$.

(b) Find the entropy $S(T, V, N)$.

(c) Find an equation of state relating the fugacity $z = e^{\mu/k_\mathrm{B}T}$ to the temperature T and the pressure p.

Solution :

(a) We have $Z = \zeta^N/N!$ where A is the area and

$$\zeta(T) = \int \frac{d^2\!x\, d^2\!p}{h^2}\, e^{-\beta\sqrt{p^2c^2+m^2c^4}} = \frac{2\pi A}{(\beta hc)^2}\left(1 + \beta mc^2\right) e^{-\beta mc^2} \quad .$$

To obtain this result it is convenient to change variables to $u = \beta\sqrt{p^2c^2 + m^2c^4}$, in which case $p\, dp = u\, du/\beta^2c^2$, and the lower limit on u is mc^2. The free energy is then

$$F = -k_\mathrm{B}T\, \ln Z = -Nk_\mathrm{B}T \ln\!\left(\frac{k_\mathrm{B}^2T^2A}{2\pi\hbar^2c^2N}\right) - Nk_\mathrm{B}T \ln\!\left(1 + \frac{mc^2}{k_\mathrm{B}T}\right) - Nk_\mathrm{B}T + Nmc^2 \quad .$$

where we are taking the thermodynamic limit with $N \to \infty$.

(b) We have

$$S = -\frac{\partial F}{\partial T} = Nk_\mathrm{B} \ln\!\left(\frac{k_\mathrm{B}^2T^2A}{2\pi\hbar^2c^2N}\right) + Nk_\mathrm{B} \ln\!\left(1 + \frac{mc^2}{k_\mathrm{B}T}\right) + \frac{Nk_\mathrm{B}^2T}{mc^2 + k_\mathrm{B}T} + 2Nk_\mathrm{B} \quad .$$

(c) The grand partition function is

$$\Xi(T, V, \mu) = e^{-\beta\Omega} = e^{\beta pV} = \sum_{N=0}^{\infty} Z_N(T, V, N)\, e^{\beta\mu N} \quad .$$

We then find $\Xi = \exp\left(\zeta A\, e^{\beta\mu}\right)$, and

$$p = \frac{(k_\mathrm{B}T)^3}{2\pi(\hbar c)^2}\left(1 + \frac{mc^2}{k_\mathrm{B}T}\right) e^{(\mu - mc^2)/k_\mathrm{B}T} \quad .$$

Note that our system obeys the ideal gas law, *viz.*

$$n = \frac{\partial(\beta p)}{\partial\mu} = \frac{p}{k_\mathrm{B}T} \quad \Longrightarrow \quad p = nk_\mathrm{B}T \quad .$$

(2) A box of volume V contains N_1 identical atoms of mass m_1 and N_2 identical atoms of mass m_2.

(a) Compute the density of states $D(E, V, N_1, N_2)$.

(b) Let $x_1 \equiv N_1/N$ be the fraction of particles of species #1. Compute the statistical entropy $S(E, V, N, x_1)$.

(c) Under what conditions does increasing the fraction x_1 result in an increase in statistical entropy of the system? Why?

Solution :

(a) Following the method outlined in ch. 4 of the Lecture Notes, we rescale all the momenta $\boldsymbol{p}_i$ with particle labels $i \in \{1, \ldots, N_1\}$ as $p_i^\alpha = \sqrt{2m_1 E}\, u_i^\alpha$, and all the momenta p_j with particle labels $j \in \{N_1 + 1, \ldots, N_1 + N_2\}$ as $p_j^\alpha = \sqrt{2m_2 E}\, u_j^\alpha$. We then have

$$D(E, V, N_1, N_2) = \frac{V^{N_1+N_2}}{N_1!\, N_2!} \left(\frac{\sqrt{2m_1 E}}{h}\right)^{N_1 d} \left(\frac{\sqrt{2m_2 E}}{h}\right)^{N_2 d} E^{-1} \cdot \tfrac{1}{2} \mathit{\Omega}_{(N_1+N_2)d} \quad ,$$

where $\mathit{\Omega}_M = 2\pi^{M/2}/\Gamma(M/2)$ is the surface area of a unit sphere in M dimensions. Thus,

$$D(E, V, N_1, N_2) = \frac{V^N}{N_1!\, N_2!} \left(\frac{m}{2\pi\hbar^2}\right)^{\frac{1}{2}Nd} \frac{E^{\frac{1}{2}Nd-1}}{\Gamma(Nd/2)} \quad ,$$

where $N = N_1 + N_2$ and $m \equiv m_1^{N_1/N} m_2^{N_2/N}$ has dimensions of mass. Note that the $N_1!\, N_2!$ term in the denominator, in contrast to $N!$, appears because only particles of the same species are identical.

(b) Using Stirling's approximation $\ln K! \simeq K \ln K - K + \mathcal{O}(\ln K)$, we find

$$\frac{S}{k_{\mathrm{B}}} = \ln D = N \ln\left(\frac{V}{N}\right) + \tfrac{1}{2}Nd \ln\left(\frac{2E}{Nd}\right) - N\left(x_1 \ln x_1 + x_2 \ln x_2\right) + \tfrac{1}{2}Nd \ln\left(\frac{m_1^{x_1} m_2^{x_2}}{2\pi\hbar^2}\right) + N\left(1 + \tfrac{1}{2}d\right) \quad ,$$

where $x_2 = 1 - x_1$.

(c) Using $x_2 = 1 - x_1$, we have

$$\frac{\partial S}{\partial x_1} = N \ln\left(\frac{1 - x_1}{x_1}\right) + \tfrac{1}{2}Nd \ln\left(\frac{m_1}{m_2}\right) \quad .$$

Setting $\partial S/\partial x_1$ to zero at the solution $x = x_1^*$, we obtain

$$x_1^* = \frac{m_1^{d/2}}{m_1^{d/2} + m_2^{d/2}} \quad , \quad x_2^* = \frac{m_2^{d/2}}{m_1^{d/2} + m_2^{d/2}} \quad .$$

Thus, an increase of x_1 will result in an increase in statistical entropy if $x_1 < x_1^*$. The reason is that $x_1 = x_1^*$ is optimal in terms of maximizing S. When $m_1 = m_2$, we have $x_1^* = x_2^* = \frac{1}{2}$.

(3) Consider a monatomic gas of N identical particles of mass m in three space dimensions. The Hamiltonian of each particle is

$$\hat{h} = \frac{\boldsymbol{p}^2}{2m} + \hat{h}_{\rm el} \quad ,$$

where $\hat{h}_{\rm el}$ is an electronic Hamiltonian with $(g+1)$ levels: a nondegenerate ground state at energy $\varepsilon_0 = 0$ and a g-fold degenerate excited state at energy $\varepsilon_1 = \Delta$.

(a) What is the single particle partition function ζ. Assume the system is confined to a box of volume V.

(b) What is the Helmholtz free energy $F(T, V, N)$?

(c) What is the heat capacity at constant volume $C_V(T, V, N)$? Interpret your result.

Solution :

(a) Integrating over momentum and summing over electronic states,

$$\zeta(T, V) = \frac{V}{\lambda_T^3} \left(1 + g\, e^{-\Delta/k_{\rm B}T}\right) \quad ,$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_{\rm B}T}$ is the thermal de Broglie wavelength.

(b) We have $F = -k_{\rm B}T \ln Z(T, V, N)$ where $Z = \zeta^N/N!$. Thus,

$$F(T, V, N) = -Nk_{\rm B}T \ln\big(1 + g\, e^{-\Delta/k_{\rm B}T}\big) - \tfrac{3}{2}Nk_{\rm B}T \ln\!\left(\frac{mk_{\rm B}T}{2\pi\hbar^2}\right) - Nk_{\rm B}T \ln\!\left(\frac{V}{N}\right) - Nk_{\rm B}T \quad .$$

where we have used Stirling's rule $\ln K! = K \ln K - K + \mathcal{O}(\ln K)$ for K large.

(c) The heat capacity is

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = -T\,\frac{\partial^2 F}{\partial T^2} = \frac{N\Delta^2}{k_{\rm B}T^2}\left(\frac{1}{g^{-1} + \exp(\Delta/k_{\rm B}T)}\right)^2 + \tfrac{3}{2}Nk_{\rm B} \quad .$$

This expression is a linear sum of the Schottky-like peak from the electronic degrees of freedom and the usual monatomic ideal gas heat capacity.

(4) A surface consisting of $N_{\rm s}$ adsorption sites is in thermal and particle equilibrium with an ideal monatomic gas. Each adsorption site can accommodate either zero particles (energy 0), one particle (two states, each with energy ε), or two particles (energy $2\varepsilon + U$).

(a) Find the grant partition function of the surface, $\Xi_{\rm surf}(T, N_{\rm s}, \mu)$. and the surface grand potential $\Omega_{\rm surf}(T, N_{\rm s}, \mu)$.

(b) Find the fraction of adsorption sites with are empty, singly occupied, and double occupied. Express your answer in terms of the temperature, the density of the gas, and other constants.

Solution :

(a) The grand partition function is

$$\Xi_{\rm surf}(T, N_{\sf s}, \mu) = \Big(1 + 2\, e^{\beta(\mu-\varepsilon)} + e^{\beta(2\mu-2\varepsilon-U)}\Big)^{N_{\rm s}} \quad ,$$

hence

$$\Omega_{\rm surf}(T, N_{\sf s}, \mu) = -k_{\rm B}T \ln \Xi_{\rm surf} = -N_{\sf s} k_{\rm B}T \ln\Big(1 + 2\, e^{\beta(\mu-\varepsilon)} + e^{\beta(2\mu-2\varepsilon-U)}\Big) \quad .$$

(b) Thermal and particle equilibrium with the gas means that the fugacities of the gas and surface are identical, and for the gas we have $z = n\lambda_T^3$. Thus,

$$\begin{aligned}
\nu_0 &= \frac{1}{1 + 2n\lambda_T^3\, e^{-\varepsilon/k_{\rm B}T} + n^2\lambda_T^6\, e^{-(2\varepsilon+U)/k_{\rm B}T}} \\
\nu_1 &= \frac{2n\lambda_T^3\, e^{-\varepsilon/k_{\rm B}T}}{1 + 2n\lambda_T^3\, e^{-\varepsilon/k_{\rm B}T} + n^2\lambda_T^6\, e^{-(2\varepsilon+U)/k_{\rm B}T}} \\
\nu_2 &= \frac{n^2\lambda_T^6\, e^{-(2\varepsilon+U)/k_{\rm B}T}}{1 + 2n\lambda_T^3\, e^{-\varepsilon/k_{\rm B}T} + n^2\lambda_T^6\, e^{-(2\varepsilon+U)/k_{\rm B}T}} \quad .
\end{aligned}$$

(5) A classical gas of indistinguishable particles in three dimensions is described by the Hamiltonian

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

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 $F_{\sf gas}(T, H, V, N)$.

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

The gas is placed in thermal contact with a surface containing $N_{\rm s}$ 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, $\Omega_{\sf surf}(T, N_{\sf s}, \mu)$.

(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

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

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

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

(b) The magnetization density is

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

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, $\Xi_{\sf surf}(T,N_{\sf s},\mu) = \xi^{N_{\sf s}}$, with

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

Thus,

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

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

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

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

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

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

$$\Omega_{\sf gas} = -pV = -k_{\rm B}T\,\zeta\,e^{\mu/k_{\rm B}T} \quad .$$

Thus,

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