PHYSICS 210A : STATISTICAL PHYSICS
HW ASSIGNMENT #3 SOLUTIONS

(1) Consider an ultrarelativistic ideal gas in three space dimensions. The dispersion is $\varepsilon(\boldsymbol{p}) = pc$.

(a) Find T, p, and μ within the microcanonical ensemble (variables S, V, N).

(b) Find F, S, p, and μ within the ordinary canonical ensemble (variables T, V, N).

(c) Find Ω, S, p, and N within the grand canonical ensemble (variables T, V, μ).

(d) Find G, S, V, and μ within the Gibbs ensemble (variables T, p, N).

(e) Find H, T, V, and μ within the S-p-N ensemble. Here $\mathsf{H} = E + pV$ is the enthalpy.

Solution :

(a) The density of states $D(E,V,N)$ is the inverse Laplace transform of the ordinary canonical partition function $Z(\beta,V,N)$. We have

$$Z(\beta,V,N) = \frac{V^N}{N!}\bigg(\int\!\frac{d^3\!p}{h^3}\,e^{-\beta pc}\bigg)^{\!N} = \frac{V^N}{N!}\,\frac{\beta^{-3N}}{\pi^{2N}(\hbar c)^{3N}}\ .$$

Thus,

$$D(E,V,N) = \int\limits_{c-i\infty}^{c+i\infty}\!\frac{d\beta}{2\pi i}\,Z(\beta,V,N)\,e^{\beta E} = \frac{V^N}{N!}\,\big(\pi^{2/3}\hbar c\big)^{-3N}\,\frac{E^{3N-1}}{(3N-1)!}\ .$$

Taking the logarithm, and using $\ln(K!) = K\ln K - K + \mathcal{O}(\ln K)$ for large K,

$$S(E,V,N) = k_{\rm B}\ln D(E,V,N) = Nk_{\rm B}\ln\!\bigg(\frac{V}{N}\bigg) + 3Nk_{\rm B}\ln\!\bigg(\frac{E}{N}\bigg) - 3Nk_{\rm B}\ln a\ ,$$

where $a = 3\pi^{2/3}e^{-4/3}\hbar c$ is a constant. Inverting to find $E(S,V,N)$, we have

$$E(S,V,N) = \frac{aN^{4/3}}{V^{1/3}}\,\exp\!\bigg(\frac{S}{3Nk_{\rm B}}\bigg)\ .$$

From the differential relation

$$dE = T\,dS - p\,dV + \mu\,dN$$

we then derive

$$\begin{aligned}
T(S,V,N) &= +\bigg(\frac{\partial E}{\partial S}\bigg)_{\!V,N} = \frac{a}{3k_{\rm B}}\bigg(\frac{N}{V}\bigg)^{\!1/3}\exp\!\bigg(\frac{S}{3Nk_{\rm B}}\bigg)\\
p(S,V,N) &= -\bigg(\frac{\partial E}{\partial V}\bigg)_{\!S,N} = \frac{a}{3}\bigg(\frac{N}{V}\bigg)^{\!4/3}\exp\!\bigg(\frac{S}{3Nk_{\rm B}}\bigg)\\
\mu(S,V,N) &= +\bigg(\frac{\partial E}{\partial N}\bigg)_{\!S,V} = \frac{a}{3}\bigg(\frac{N}{V}\bigg)^{\!1/3}\bigg(4 - \frac{S}{Nk_{\rm B}}\bigg)\exp\!\bigg(\frac{S}{3Nk_{\rm B}}\bigg)\ .
\end{aligned}$$

Note that $pV = Nk_{\rm B}T$.

(b) The Helmholtz free energy is

$$\begin{aligned} F(T,V,N) &= -k_{\rm B}T\ln Z \\ &= 3Nk_{\rm B}T - Nk_{\rm B}T\ln\left(\frac{V}{N}\right) - 3Nk_{\rm B}T\ln(3k_{\rm B}T) + 3Nk_{\rm B}T\ln a \ , \end{aligned}$$

and from

$$dF = -S\,dT - p\,dV + \mu\,dN$$

we read off

$$\begin{aligned} S(T,V,N) &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_{\rm B}\ln\left(\frac{V}{N}\right) + 3Nk_{\rm B}\ln(3k_{\rm B}T) + 3Nk_{\rm B}\ln a \\ p(T,V,N) &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_{\rm B}T}{V} \\ \mu(T,V,N) &= +\left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_{\rm B}T\ln\left(\frac{V}{N}\right) - 3k_{\rm B}T\ln(3k_{\rm B}T) + (4+3\ln a)\,k_{\rm B}T \ . \end{aligned}$$

(c) The grand potential is $\Omega = F - \mu N = -k_{\rm B}T\ln\Xi$, where

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(\beta,V,N) = \exp\left\{V e^{\mu/k_{\rm B}T}\left(\frac{k_{\rm B}T}{\pi^{2/3}\hbar c}\right)^3\right\} .$$

Thus,

$$\Omega(T,V,N) = -\frac{V}{\pi^2}\cdot\frac{(k_{\rm B}T)^4}{(\hbar c)^3}\cdot e^{\mu/k_{\rm B}T} \ .$$

The differential is

$$d\Omega = -S\,dT - p\,dV - N\,d\mu \ ,$$

and therefore

$$\begin{aligned} S(T,V,\mu) &= -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = \frac{V}{\pi^2}\cdot\frac{(k_{\rm B}T)^3}{(\hbar c)^3}\cdot e^{\mu/k_{\rm B}T}\cdot\left(4k_{\rm B} - \frac{\mu}{T}\right) \\ p(T,V,\mu) &= -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = \frac{(k_{\rm B}T)^4}{\pi^2(\hbar c)^3}\cdot e^{\mu/k_{\rm B}T} \\ N(T,V,\mu) &= -\left(\frac{\partial\Omega}{\partial \mu}\right)_{T,V} = \frac{V}{\pi^2}\cdot\left(\frac{k_{\rm B}T}{\hbar c}\right)^3\cdot e^{\mu/k_{\rm B}T} \ . \end{aligned}$$

Note that $p = -\Omega/V$.

(d) The Gibbs free energy is

$$\begin{aligned} G(T,p,N) &= F + pV \\ &= Nk_{\rm B}T\ln p - 4Nk_{\rm B}T\ln(k_{\rm B}T) + Nk_{\rm B}T\left(4 + 3\ln(\tfrac{1}{3}a)\right) \end{aligned}$$

The differential of G is

$$dG = -S\,dT + V\,dP + \mu\,dN\ ,$$

and therefore

$$\begin{aligned} S(T,p,N) &= -\left(\frac{\partial G}{\partial T}\right)_{p,N} = -Nk_{\rm B}\ln p + 4Nk_{\rm B}\ln(k_{\rm B}T) - Nk_{\rm B}\ln(\tfrac{1}{3}a) \\ V(T,p,N) &= +\left(\frac{\partial G}{\partial p}\right)_{T,N} = \frac{Nk_{\rm B}T}{p} \\ \mu(T,p,N) &= +\left(\frac{\partial G}{\partial N}\right)_{T,p} = k_{\rm B}T\ln p - 4k_{\rm B}T\ln(k_{\rm B}T) + k_{\rm B}T\left(4 + 3\ln(\tfrac{1}{3}a)\right)\ . \end{aligned}$$

Note that $\mu = G/N$.

(e) The enthalpy is

$$\begin{aligned} \mathsf{H}(S,p,N) &= E + pV \\ &= 4N\left(\tfrac{1}{3}a\right)^{3/4} p^{1/4} \exp\!\left(\frac{S}{4Nk_{\rm B}}\right)\ . \end{aligned}$$

From

$$d\mathsf{H} = T\,dS + V\,dp + \mu\,dN\ ,$$

we have

$$\begin{aligned} T(S,p,N) &= +\left(\frac{\partial \mathsf{H}}{\partial S}\right)_{p,N} = \frac{\left(\tfrac{1}{3}a\right)^{3/4} p^{1/4}}{k_{\rm B}} \exp\!\left(\frac{S}{4Nk_{\rm B}}\right) \\ V(S,p,N) &= +\left(\frac{\partial \mathsf{H}}{\partial p}\right)_{S,N} = N\left(\frac{a}{3p}\right)^{3/4} \exp\!\left(\frac{S}{4Nk_{\rm B}}\right) \\ \mu(S,p,N) &= \left(\frac{\partial \mathsf{H}}{\partial N}\right)_{S,p} = \left(\tfrac{1}{3}a\right)^{3/4} p^{1/4}\left(4 - \frac{S}{Nk_{\rm B}}\right) \exp\!\left(\frac{S}{4Nk_{\rm B}}\right)\ . \end{aligned}$$

(2) Consider a surface containing $N_{\sf s}$ adsorption sites which is in equilibrium with a two-component nonrelativistic ideal gas containing atoms of types A and B . (Their respective masses are $m_{\sf A}$ and $m_{\sf B}$). Each adsorption site can be in one of three possible states: (i) vacant, (ii) occupied by an A atom, with energy $-\Delta_{\sf A}$, and (ii) occupied with a B atom, with energy $-\Delta_{\sf B}$.

(a) Find the grand partition function for the surface, $\Xi_{\rm surf}(T, \mu_{\sf A}, \mu_{\sf B}, N_{\sf s})$.

(b) Suppose the number densities of the gas atoms are $n_{\sf A}$ and $n_{\sf B}$. Find the fraction $f_{\sf A}(n_{\sf A}, n_{\sf B}, T)$ of adsorption sites with A atoms, and the fraction $f_0(n_{\sf A}, n_{\sf B}, T)$ of adsorption sites which are vacant.

Solution :

(a) The surface grand partition function is

$$\Xi_{\rm surf}(T, \mu_{\sf A}, \mu_{\sf B}, N_{\sf s}) = \Big(1 + e^{(\Delta_{\sf A}+\mu_{\sf A})/k_{\rm B}T} + e^{(\Delta_{\sf B}+\mu_{\sf B})/k_{\rm B}T}\Big)^{N_{\sf s}} .$$

(b) From the grand partition function of the gas, we have

$$n_{\sf A} = \lambda_{T,{\sf A}}^{-3}\, e^{\mu_{\sf A}/k_{\rm B}T} \qquad , \qquad n_{\sf B} = \lambda_{T,{\sf B}}^{-3}\, e^{\mu_{\sf B}/k_{\rm B}T} ,$$

with

$$\lambda_{T,{\sf A}} = \sqrt{\frac{2\pi\hbar^2}{m_{\sf A} k_{\rm B}T}} \qquad , \qquad \lambda_{T,{\sf B}} = \sqrt{\frac{2\pi\hbar^2}{m_{\sf B} k_{\rm B}T}} .$$

Thus,

$$\begin{aligned}
f_0 &= \frac{1}{1 + n_{\sf A}\,\lambda_{T,{\sf A}}^3\, e^{\Delta_{\sf A}/k_{\rm B}T} + n_{\sf B}\,\lambda_{T,{\sf B}}^3\, e^{\Delta_{\sf B}/k_{\rm B}T}}\\
f_{\sf A} &= \frac{n_{\sf A}\,\lambda_{T,{\sf A}}^3\, e^{\Delta_{\sf A}/k_{\rm B}T}}{1 + n_{\sf A}\,\lambda_{T,{\sf A}}^3\, e^{\Delta_{\sf A}/k_{\rm B}T} + n_{\sf B}\,\lambda_{T,{\sf B}}^3\, e^{\Delta_{\sf B}/k_{\rm B}T}}\\
f_{\sf B} &= \frac{n_{\sf B}\,\lambda_{T,{\sf B}}^3\, e^{\Delta_{\sf B}/k_{\rm B}T}}{1 + n_{\sf A}\,\lambda_{T,{\sf A}}^3\, e^{\Delta_{\sf A}/k_{\rm B}T} + n_{\sf B}\,\lambda_{T,{\sf B}}^3\, e^{\Delta_{\sf B}/k_{\rm B}T}} .
\end{aligned}$$

Note that $f_0 + f_{\sf A} + f_{\sf B} = 1$.

(3) Consider a system composed of spin tetramers, each of which is described by the Hamiltonian

$$\hat{H} = -J(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_1\sigma_4 + \sigma_2\sigma_3 + \sigma_2\sigma_4 + \sigma_3\sigma_4) - \mu_0 H(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) .$$

The individual tetramers are otherwise noninteracting.

(a) Find the single tetramer partition function ζ.

(b) Find the magnetization per tetramer $m = \mu_0\langle\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4\rangle$.

(c) Suppose the tetramer number density is $n_{\rm t}$. The magnetization density is $M = n_{\rm t} m$. Find the zero field susceptibility $\chi(T) = (\partial M/\partial H)_{H=0}$.

Solution :

(a) Note that we can write

$$\hat{H} = 2J - \tfrac{1}{2}J(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)^2 - \mu_0 H\,(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) .$$

$\sigma_1+\sigma_2+\sigma_3+\sigma_4$	degeneracy g	energy E
$+4$	1	$-6J-4\mu_0 H$
$+2$	4	$-2\mu_0 H$
0	6	$-2J$
-2	4	$+2\mu_0 H$
-4	1	$-6J+4\mu_0 H$

Thus, for each of the $2^4=16$ configurations of the spins of any given tetramer, only the sum $\sum_{i=1}^4 \sigma_i$ is necessary in computing the energy. We list the degeneracies of these states in the table below. Thus, according to the table, we have

$$\zeta = 6\,e^{-2J/k_B T} + 8\,\cosh\!\left(\frac{2\mu_0 H}{k_B T}\right) + 2\,e^{6J/k_B T}\,\cosh\!\left(\frac{4\mu_0 H}{k_B T}\right) .$$

(b) The magnetization per tetramer is

$$m = -\frac{\partial f}{\partial H} = k_B T\,\frac{\partial \ln \zeta}{\partial H} = 4\mu_0 \cdot \frac{2\,\sinh(2\beta\mu_0 H) + e^{6\beta J}\sinh(4\beta\mu_0 H)}{3\,e^{-2\beta J} + 4\,\cosh(2\beta\mu_0 H) + e^{6\beta J}\cosh(4\beta\mu_0 H)} .$$

(c) The zero field susceptibility is

$$\chi(T) = \frac{16\,n_t\,\mu_0^2}{k_B T} \cdot \frac{1+e^{6\beta J}}{3\,e^{-2\beta J}+4+e^{6\beta J}}$$

Note that for $\beta J \to \infty$ we have $\chi(T) = (4\mu_0)^2 n_t / k_B T$, which is the Curie value for a single Ising spin with moment $4\mu_0$. In this limit, all the individual spins are locked together, and there are only two allowed configurations for each tetramer: $|\uparrow\uparrow\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\downarrow\downarrow\rangle$. When $J=0$, we have $\chi = 4\mu_0^2 n_t / k_B T$, which is to say four times the single spin susceptibility. *I.e.* all the spins in each tetramer are independent when $J=0$. When $\beta J \to -\infty$, the only allowed configurations are the six ones with $\sum_{i=1}^4 \sigma_i = 0$. In order to exhibit a moment, an energy gap of $2|J|$ must be overcome, hence $\chi \propto \exp(-2\beta|J|)$, which is exponentially suppressed.