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

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

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,

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

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

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

From the differential relation

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

we then derive

$$T(S,V,N) = +\left(\frac{\partial E}{\partial S}\right)_{\!V,N} = \frac{a}{3k_{\rm B}}\left(\frac{N}{V}\right)^{\!1/3}\exp\!\left(\frac{S}{3Nk_{\rm B}}\right)$$

$$p(S,V,N) = -\left(\frac{\partial E}{\partial V}\right)_{\!S,N} = \frac{a}{3}\left(\frac{N}{V}\right)^{\!4/3}\exp\!\left(\frac{S}{3Nk_{\rm B}}\right)$$

$$\mu(S,V,N) = +\left(\frac{\partial E}{\partial N}\right)_{\!S,V} = \frac{a}{3}\left(\frac{N}{V}\right)^{\!1/3}\left(4 - \frac{S}{Nk_{\rm B}}\right)\exp\!\left(\frac{S}{3Nk_{\rm B}}\right) .$$

Note that $pV = Nk_BT$.

(b) The Helmholtz free energy is

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

and from

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

we read off

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

(c) The grand potential is $\Omega = F - \mu N = -k_BT\ln\Xi$, where

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

Thus,

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

The differential is

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

and therefore

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

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

(d) The Gibbs free energy is

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

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 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

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

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

$\sigma_1+\sigma_2+\sigma_3+\sigma_4$	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	$-6J+4\mu_0 H$

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

(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.

(3) For an ideal gas, find the difference $C_\varphi - C_V$ for the following functions φ. You are to assume N is fixed in each case.

(a) $\varphi(p,V) = p^3\,V^2$

(b) $\varphi(p,T) = p\, e^{T/T_0}$

(c) $\varphi(T,V) = VT^{-1}$

Solution :

In general,

$$C_\varphi = T\left(\frac{\partial S}{\partial T}\right)_{\!\varphi} .$$

Note that

$$đQ = dE + p\, dV .$$

We will also appeal to the ideal gas law, $pV = Nk_{\rm B}T$. Below, we shall abbreviate $\varphi_V = \frac{\partial\varphi}{\partial V}$, $\varphi_T = \frac{\partial\varphi}{\partial T}$, and $\varphi_p = \frac{\partial\varphi}{\partial p}$.

(a) We have

$$đQ = \tfrac{1}{2}fNk_{\rm B}\, dT + p\, dV ,$$

and therefore

$$C_\varphi - C_V = p\left(\frac{\partial V}{\partial T}\right)_{\!\varphi} .$$

Now for a general function $\varphi(p,V)$, we have

$$\begin{aligned} d\varphi &= \varphi_p\, dp + \varphi_V\, dV \\ &= \frac{Nk_{\rm B}}{V}\,\varphi_p\, dT + \Big(\varphi_V - \frac{p}{V}\,\varphi_p\Big)\, dV , \end{aligned}$$

after writing $dp = d(Nk_{\rm B}T/V)$ in terms of dT and dV. Setting $d\varphi = 0$, we then have

$$C_\varphi - C_V = p\left(\frac{\partial V}{\partial T}\right)_{\!\varphi} = \frac{Nk_{\rm B}\, p\,\varphi_p}{p\,\varphi_p - V\varphi_V} .$$

This is the general result. For $\varphi(p,V) = p^3V^2$, we find

$$C_\varphi - C_V = 3Nk_{\rm B} .$$

(b) We have

$$đQ = \big(\tfrac{1}{2}f + 1\big)Nk_{\rm B}\, dT - V\, dp ,$$

and therefore

$$C_\varphi - C_V = Nk_{\rm B} - V\left(\frac{\partial p}{\partial T}\right)_{\!\varphi} .$$

For a general function $\varphi(p,T)$, we have

$$d\varphi = \varphi_p\, dp + \varphi_T\, dT \quad\Longrightarrow\quad \left(\frac{\partial p}{\partial T}\right)_{\!\varphi} = -\frac{\varphi_T}{\varphi_p} .$$

Therefore,

$$C_\varphi - C_V = Nk_B + V\,\frac{\varphi_T}{\varphi_p}\,.$$

This is the general result. For $\varphi(p,T) = p\,e^{T/T_0}$, we find

$$C_\varphi - C_V = Nk_B\left(1 + \frac{T}{T_0}\right).$$

(c) We have

$$C_\varphi - C_V = p\left(\frac{\partial V}{\partial T}\right)_\varphi\,,$$

as in part (a). For a general function $\varphi(T,V)$, we have

$$d\varphi = \varphi_T\,dT + \varphi_V\,dV \quad \Longrightarrow \quad \left(\frac{\partial V}{\partial T}\right)_\varphi = -\frac{\varphi_T}{\varphi_V}\,,$$

and therefore

$$C_\varphi - C_V = -p\,\frac{\varphi_T}{\varphi_V}\,.$$

This is the general result. For $\varphi(T,V) = V/T$, we find

$$C_\varphi - C_V = Nk_B\,.$$

(4) Find an expression for the energy density $\varepsilon = E/V$ for a system obeying the Dieterici equation of state,

$$p(V - Nb) = Nk_B T\,e^{-Na/Vk_B T}\,,$$

where a and b are constants. Your expression for $\varepsilon(v,T)$ should involve an integral which can be expressed in terms of the exponential integral,

$$\mathsf{Ei}(x) = \int\limits_{-\infty}^{x} dt\,\frac{e^t}{t}\,.$$

Solution :

We have

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = T\left(\frac{\partial S}{\partial V}\right)_{T,N} - p = T\left(\frac{\partial p}{\partial T}\right)_{V,N} - p\,,$$

where we have invoked a Maxwell relation. For the Dieterici equation of state, then,

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = \frac{Nk_B T}{V - Nb}\cdot\frac{Na}{Vk_B T}\cdot e^{-Na/Vk_B T}\,.$$

Let $n = N/V$ be the density and $\varepsilon = E/N$ be the energy per particle. Then the above result is equivalent to

$$\frac{\partial \varepsilon}{\partial n} = -\frac{a}{1 - bn}\, e^{-na/k_\mathrm{B}T} \,.$$

We integrate this between $n = 0$ and n, with $bn < 1$. Define the dimensionless quantity $\lambda = a/bk_\mathrm{B}T$ and $t = \lambda(1 - bn)$. Then

$$\varepsilon(n,T) - \varepsilon(0,T) = -\frac{a\, e^{-\lambda}}{b} \int\limits_{(1-bn)\lambda}^{\lambda} \frac{dt}{t}\, e^{t} = \Big\{ \mathsf{Ei}\big((1-bn)\lambda\big) - \mathsf{Ei}(\lambda) \Big\} \frac{a\, e^{-\lambda}}{b}$$

In the zero density limit, the gas must be ideal, in which case $\varepsilon(0,T) = \frac{1}{2} f k_\mathrm{B}T$. Thus,

$$\varepsilon(n,T) = \tfrac{1}{2} f k_\mathrm{B}T - \left\{ \mathsf{Ei}\left(\frac{(1-bn)a}{bk_\mathrm{B}T}\right) - \mathsf{Ei}\left(\frac{a}{bk_\mathrm{B}T}\right) \right\} \cdot \frac{a\, e^{-a/bk_\mathrm{B}T}}{b} \,.$$

In terms of the volume per particle, write $v = V/N = 1/n$.