

## SOLUTIONS TP-A

(a)  $H=U+PV$ ; Use  $U=TS-pV+uN$  gives  $H=TS+uN=TS+G$  ( $u$  is  $\mu$ )

(b)  $dH=dQ+T(dS)+u(dN)=T(dS) + V(dP)+u(dN)$

Thus  $\left(\frac{\partial H}{\partial T}\right)_P$  = heat capacity at constant P.

For  $\left(\frac{\partial H}{\partial P}\right)_T$  use  $G=H-TS$  and  $\left(\frac{\partial G}{\partial P}\right)_T = V = \left(\frac{\partial(H-TS)}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T$ .

G also has a Maxwell relation from

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ \& } \left(\frac{\partial G}{\partial T}\right)_P = -S \text{ giving } \left(\frac{\partial S}{\partial P}\right)_T = \left(-\frac{\partial V}{\partial T}\right)_P$$

Thus  $\left(\frac{\partial H}{\partial P}\right)_T = V - TV\beta = V - T\left(\frac{\partial V}{\partial T}\right)_P$

(c) For  $P(V-bN)=NkT$

$$\left(\frac{\partial H}{\partial P}\right)_T = bN \text{ which gives } \Delta H = bN(P_2 - P_1) = bN\left(\frac{NkT}{V_2 - bN} - \frac{NkT}{V_1 - bN}\right)$$

## SOLUTION TP-B

Spin 1 particles are bosons and you can put any number in a level. The spin degeneracy is  $g_s = 3$ .

There are 11 configurations such that 6 particles have total energy  $U = 6\varepsilon$ .

Let  $N_j$  equal number of particles in level with energy  $j\varepsilon$ .

The number of ways of putting bosons in levels (any number in a level) for a choice of  $\{N_0, N_1, \dots, N_6\} \equiv \vec{N}$  is  $\Omega_K(\vec{N})$  for each configuration  $K$ . This is given by:

$$\Omega_K(\vec{N}) = \prod_j \frac{(g_s - 1 + N_j)!}{(g_s - 1)! N_j!}$$

Configuration $K$	Distribution of Energy as	$\Omega_K(\vec{N})$
1.	$(5, 0, 0, 0, 0, 0, 1)$	63
2.	$(4, 1, 0, 0, 0, 1, 0)$	135
3.	$(4, 0, 1, 0, 1, 0, 0)$	135
4.	$(3, 2, 0, 0, 1, 0, 0)$	180
5.	$(4, 0, 0, 2, 0, 0, 0)$	90
6.	$(3, 1, 1, 1, 0, 0, 0)$	270
7.	$(2, 3, 0, 1, 0, 0, 0)$	180
8.	$(3, 0, 3, 0, 0, 0, 0)$	100
9.	$(2, 2, 2, 0, 0, 0, 0)$	216
10.	$(1, 4, 1, 0, 0, 0, 0)$	135
11.	$(0, 6, 0, 0, 0, 0, 0)$	28

$$\text{Mean number } \langle N_j \rangle = \frac{\sum_{K=1}^{11} N_j \Omega_K(\vec{N})}{\sum_{K=1}^{11} \Omega_K(\vec{N})}$$

$$\langle \vec{N} \rangle = (2.83, 1.60, 0.830, 0.410, 0.205, 0.088, 0.041)$$

**Solution TP-C1**

(a) The density of states of a photon gas is

$$D(\varepsilon)d\varepsilon = \alpha V \varepsilon^2 d\varepsilon,$$

where  $\alpha$  is a constant.

Hence the partition function

$$F = - \int D(\varepsilon) \ln(1 - e^{-\beta\varepsilon}) d\varepsilon, \quad (1)$$

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} F \quad (2)$$

$$= -\frac{\alpha}{\beta} \int \varepsilon^2 \ln(1 - e^{-\beta\varepsilon}) d\varepsilon, \quad (3)$$

Integrating by parts we have

$$p = \frac{1}{3V} \int_0^\infty V \alpha \varepsilon^2 \frac{\varepsilon}{e^{\beta\varepsilon} - 1} d\varepsilon = \frac{U}{3V}.$$

(b) For thermal radiation, we have

$$U(T, V) = u(T)V.$$

Using the following formula of thermodynamics

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v - p$$

we get  $u = \frac{T}{3} \frac{du}{dT} - \frac{u}{3}$ , i.e.  $u = \gamma T^4$ , where  $\gamma$  is a constant.

## Solution TP-C2

a) The canonical partition function is:

$$Z_{can} = \frac{1}{N!} \left[ \prod_{i=1}^{3N} \int_0^L dx_i \int_{-\infty}^{\infty} dp_i \right] \exp - \left[ \sum_{i=1}^{3N} \frac{p_i^2}{2m} + Nu_{pot}(v) \right] / k_B T. \quad (1)$$

(Note that we left out a constant factor of  $h^{3N}$  which one needs to make  $Z_{can}$  dimensionless).

Treat molecules as billiard balls and place them one by one into the container of volume  $V$ , so that the 1st molecule can occupy volume  $V = L^3$ , the 2nd molecule:  $V - v_c$ , the 3rd molecule:  $V - 2v_c$ , and so on:

$$\frac{1}{V^N} \left[ \prod_{i=1}^{3N} \int_0^L dx_i \right] = \prod_{m=1}^{N-1} \left(1 - m \frac{v_c}{V}\right) \simeq 1 - \left(\sum_{m=1}^{N-1} m\right) \frac{v_c}{V} = 1 - \frac{(N-1)N}{2} \frac{v_c}{V} \simeq \left(1 - \frac{N}{2} \frac{v_c}{V}\right)^N, \quad (2)$$

where we used  $N \gg 1$  and  $v_c \ll V$ .

Hence

$$\begin{aligned} Z_{can} &= \frac{1}{N!} \left(V - \frac{N}{2}v_c\right)^N \exp\left(-\frac{Nu_{pot}(v)}{k_B T}\right) \left[\int_{-\infty}^{\infty} dp \exp\left(-\frac{p^2}{2mk_B T}\right)\right]^{3N} \\ &= \frac{1}{N!} \left(V - \frac{N}{2}v_c\right)^N \exp\left(-\frac{Nu_{pot}(v)}{k_B T}\right) (2mk_B T \pi)^{\frac{3N}{2}}. \end{aligned} \quad (3)$$

Using Stirling's approximation we obtain:

$$f(v, T) = -\frac{1}{N} k_B T \log Z_{can} = k_B T [f_0 - \log[(v - v_c/2)T^{3/2}]] + u_{pot}(v), \quad (4)$$

where  $v = V/N$  is the volume per particle, and  $f_0 = -1 - 3/2 \log(2\pi m)$  is the part of the free energy that is independent of  $v$  and  $T$ .

Now,  $(\partial f / \partial v)|_T = -p$  gives

$$\left(p + \frac{\partial u_{pot}}{\partial v}\right) (v - v_c/2) = k_B T, \quad (5)$$

the van der Waals equation of state.

$(\partial f / \partial T)|_v = -s$  gives

$$s = \frac{1}{T} (u_{pot}(v) - f) + \frac{3k_B}{2}, \quad (6)$$

or

$$f = \frac{3}{2} k_B T - T s + u_{pot}(v), \quad (7)$$

which shows that  $u = u_{pot}(v) + \frac{3}{2} k_B T$ , as expected.

**Solution TP-D1**

(a) The partition function takes the form

$$Z_N = \frac{1}{N!} (Z_{1(tr)})^N (Z_{1(mag)})^N, \quad (1)$$

where  $Z_{1(tr)}$  is the translational contribution for a single molecule and  $Z_{1(mag)}$  is the magnetic contribution for a single molecule. The single particle translational partition function can be written  $Z_{1(tr)} = V/\lambda_T^3$ , where  $\lambda_T = h/\sqrt{2\pi m k_B T}$  is the thermal wavelength.

Let us now compute the partition function due to the magnetic degrees of freedom. Each atom will have magnetic energy  $E(s) = -s\mu B$ , where  $-S \geq s \leq S$ . The magnetic partition function for a single atom is

$$Z_{1(mag)} = \sum_{s=-S}^S e^{s\beta\mu B} = \sinh((S + 1/2)\beta\mu B) / \sinh(1/2\beta\mu B). \quad (2)$$

The partition function for the gas is

$$Z_N = \frac{1}{N!} \left(\frac{2V}{\lambda_T^3}\right)^N [\sinh((S + 1/2)\beta\mu B) / \sinh(1/2(\beta\mu B))]^N. \quad (3)$$

(b) The internal energy is given by

$$U = -\left(\frac{\partial \ln Z_N}{\partial \beta}\right) = \frac{3}{2} N k_B T - N \partial_\beta [\sinh((S + 1/2)\beta\mu B) / \sinh(1/2(\beta\mu B))]. \quad (4)$$

The heat capacity is

$$C_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N,B} = \frac{3}{2} N k_B - T^2 N \partial_T \partial_T [\sinh((S+1/2)\beta\mu B) / \sinh(1/2(\beta\mu B))]. \quad (5)$$

(c) The magnetization is given by  $M = -(\partial\Phi/\partial B)_{T,N}$  where  $\Phi$  is the free energy for this problem,  $\Phi = -K_B T \ln(Z_N)$  and

$$M = -\left(\frac{\partial\Phi}{\partial B}\right)_{T,N}. \quad (6)$$

## Solution TP-D2

The entropy for a fixed number of molecules of both types ( $N_X, N_Y$ ) ( $N_X + N_Y = N$ ) is given by:

$$\frac{\Omega(N_X, N_Y; U, V)}{\Omega(N_X + N_Y, 0; U, V)} = \frac{N!}{N_X!N_Y!} \equiv \exp\left(\frac{N s_M(x)}{k_B}\right), \quad (8)$$

where  $x = N_X/N$ . Here  $\Omega(N_X + N_Y, 0; U, V)$  is the entropy if all particles are of type  $X$  (same as for the monoatomic ideal gas), and  $s_M(x)$  is the mixing entropy for a specific ( $N_X, N_Y$ ). Note that all position and momentum dependent contributions to the total number of states cancel out in Eq. (8).

We obtain the total mixing entropy by summing over all values of ( $N_X, N_Y$ ):

$$\exp\left(\frac{N s_M^{tot}}{k_B}\right) = \sum_{N_X, N_Y | N_X + N_Y = N} \frac{N!}{N_X!N_Y!} = 2^N, \quad (9)$$

or  $s_M^{tot} = k_B \log 2$ . Here we used the binomial expansion:

$$(a + b)^N = \sum_{N_X, N_Y | N_X + N_Y = N} \frac{N!}{N_X!N_Y!} a^{N_X} b^{N_Y}. \quad (10)$$

Using Stirling's formula we obtain:

$$N s_M(x) = k_B \log\left(\frac{N!}{N_X!N_Y!}\right) \simeq k_B \log\left(\frac{N^N}{N_X^{N_X} N_Y^{N_Y}}\right) = -k_B N \log\left[\left(\frac{N_X}{N}\right)^x \left(\frac{N_Y}{N}\right)^y\right], \quad (11)$$

with  $x = N_X/N, y = N_Y/N, x + y = 1$ . Therefore, the mixing entropy per particle is:

$$s_M(x) = -k_B [x \log x + (1 - x) \log(1 - x)], \quad (12)$$

and  $s_M^{tot}$  can be written as:

$$\exp\left(\frac{N s_M^{tot}}{k_B}\right) = N \int_0^1 dx \exp\left(\frac{N s_M(x)}{k_B}\right). \quad (13)$$

Note that this expression is not exact:  $s_M^{tot} = k_B \log 2$  does not hold under this approximation anymore.

b)

$$\frac{\partial s_M(x)}{\partial x} = -k_B [\log x - \log(1 - x)] = 0 \quad (14)$$

gives  $\log x_{max} = \log(1 - x_{max})$ , or  $x_{max} = 1/2$ . Then

$$s_M^{tot} \simeq s_M(x_{max}) = k_B \log 2. \quad (15)$$

This is the same as our exact result from part (a) - the errors introduced by the Stirling's approximation and by the max term approximation to the integral cancel out! In general, the errors scale as  $\log N/N$  as thus vanish in the thermodynamic limit [we will verify this explicitly in the next section].

c)

$$\frac{\partial^2 s_M(x)}{\partial x^2} \Big|_{x_{max}} = -k_B \left[ \frac{1}{x_{max}} + \frac{1}{1 - x_{max}} \right] = -4k_B. \quad (16)$$

Then under the saddle-point approximation

$$\begin{aligned} N \int_0^1 dx \exp\left(\frac{N s_M(x)}{k_B}\right) &\simeq N \exp\left(\frac{N s_M(x_{max})}{k_B}\right) \int_0^1 dx \exp(-2N(x - x_{max})^2) \\ &\simeq N \exp\left[\frac{N s_M(x_{max})}{k_B} + 1/2 \log(\pi/2N)\right]. \end{aligned} \quad (17)$$

Note that we extended the upper limit of the Gaussian integral to  $+\infty$  (this is possible because  $N \gg 1$ ). The Gaussian correction is indeed of order  $\log N/N$ .