PHYSICS 112
Homework 5 Solutions

1. We have

$$f(\mu+\delta) = \frac{1}{\exp[\beta(\mu+\delta-\mu)]+1} = \frac{1}{\exp[\beta\delta]+1}\,,$$

and similarly (with δ replaced by $-\delta$)

$$f(\mu-\delta) = \frac{1}{\exp[-\beta\delta]+1}\,.$$

Now

$$\frac{1}{e^x+1} = \frac{e^{-x}}{1+e^{-x}} = 1 - \frac{1}{1+e^{-x}}\,,$$

and so, with $x = \beta\delta$, we have

$$\boxed{f(\mu+\delta) = 1 - f(\mu-\delta)\,.}$$

Hence the probability that a state δ above μ is occupied is equal to the probability that a state δ below μ is empty.

2. Let the volume initially occupied by the "A" atoms be V, which we are told is equal to the volume occupied by the the "B" atoms. Hence the initial entropy is given by

$$\frac{S_i}{k_B} = N\left[\frac{5}{2} - \ln\left(\frac{NV_Q^A}{V}\right)\right] + N\left[\frac{5}{2} - \ln\left(\frac{NV_Q^B}{V}\right)\right]\,, \tag{1}$$

where we allow for the possibility of different masses for the A and B atoms and hence different "quantum volumes", V_Q^A and V_Q^B. After diffusive contact is allowed, the atoms occupy a volume $2V$. Hence the final entropy, summing over the entropy of the A atoms and the B atoms, is

$$\frac{S_f}{k_B} = N\left[\frac{5}{2} - \ln\left(\frac{NV_Q^A}{2V}\right)\right] + N\left[\frac{5}{2} - \ln\left(\frac{NV_Q^B}{2V}\right)\right]\,.$$

Taking the difference we get

$$\Delta S \equiv S_f - S_i = 2N\ln(2V) - 2N\ln V = \boxed{2N\ln 2\,.}$$

This is the $\boxed{\text{entropy of mixing.}}$

If the atoms are indistinguishable, then after diffusive contact we simply have $2N$ atoms in a volume $2V$ for which the entropy is

$$S_f = 2N\left[\frac{5}{2} - \ln\left(\frac{NV_Q^A}{V}\right)\right]\,,$$

which is equal to the initial entropy, (Eq. (1) with $V_Q^B = V_Q^A$). Hence for indistinguishable particles, there is $\boxed{\text{no entropy of mixing.}}$

3. The entropy is given by

$$S(N,V) = Nk_B\left[\frac{5}{2} - \ln\left(\frac{NV_Q}{V}\right)\right].$$

The number of states is given by

$$g(N,V) = \exp(S/k_B) = \left(\frac{V}{NV_Q}\right)^N \exp(5N/2)\,. \qquad (2)$$

Now $V = 10^{-4}\,\mathrm{m}^3$, $P = 1.013 \times 10^5\,\mathrm{N\,m}^{-2}$, and so

$$N = \frac{PV}{k_BT} = \frac{1.013 \times 10^5 \times 10^{-4}}{1.38 \times 10^{23} \times 300} = 2.45 \times 10^{21}\,. \qquad (3)$$

Also

$$V_Q = \left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2} = \left(\frac{2 \times 3.142 \times (1.055 \times 10^{-34})^2}{4 \times 1.67 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300}\right)^{3/2} = 1.27 \times 10^{-31}\,\mathrm{m}^3\,. \qquad (4)$$

(a) Substituting Eqs. (3) and (4) into Eq. (2), with $V = 0.1\,\text{liters} = 10^{-4}\,\mathrm{m}^3$, gives

$$\exp\left[2.45 \times 10^{21} \times \left(2.5 + \ln\left(\frac{10^{-4}}{2.45 \times 10^{21} \times 1.27 \times 10^{-31}}\right)\right)\right] =$$

$$\exp\left(2.45 \times 10^{21} \times 15.2\right) = \exp(3.7 \times 10^{22}) = \boxed{10^{1.12\times 10^{22}}\,.}$$

(b) For $V = 0.05$ liter we get 2^{-N} times this result (where 2^N is given in Sec. (3c)), which gives

$$\boxed{10^{1.05\times 10^{22}}\,.}$$

(c) The ratio of the results with V and $V/2$ is given by

$$\frac{g(N,V)}{g(N,V/2)} = \frac{V^N}{(V/2)^N} = 2^N = \boxed{2^{2.45\times 10^{21}} = 10^{7.4\times 10^{20}}\,.}$$

(d) Total number of collisions in a year is

$$N \times 10^{10} \times 3 \times 10^7 = \boxed{7.3 \times 10^{38}\,,}$$

since there are about 3×10^7 seconds in a year.

(e) Each collision changes the state, so the number of collisions needed to get all the atoms in 1/2 of the container is estimated to be the ratio of the answer in Sec. (3c) to that in Sec. (3d). Hence the number of years is

$$\frac{10^{7.4\times 10^{20}}}{7.3 \times 10^{38}} \simeq \frac{10^{7.4\times 10^{20}}}{10^{39}} = 10^{7.4\times 10^{20} - 39} = \boxed{10^{7.4\times 10^{20}}\,,}$$

and we see that the denominator (the number of collisions) makes *negligible difference* to the power of 10 in the numerator (which is the ratio of the number of states with the larger volume to that with the smaller volume).

4. We proceed as in the handout for the classical ideal gas except that the single particle (canonical) partition is

$$\mathrm{z}^{(1)} = \frac{V}{V_Q}\, z_{\text{int}}\,,$$

where

$$z_{\text{int}} = 1 + e^{-\beta\Delta}\,,$$

is the partition function of the internal degree of freedom.

Proceeding as in the handout we get

$$\Omega = -k_B T e^{\beta\mu} \mathrm{z}^{(1)} = -k_B T e^{\beta\mu} (1 + e^{-\beta\Delta}) \frac{V}{V_Q}\,.$$

Now

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = e^{\beta\mu} \frac{V}{V_Q} (1 + e^{-\beta\Delta})\,. \tag{5}$$

It follows that

$$\Omega\,(= -PV) = -N k_B T\,. \tag{6}$$

(a) From Eq. (5) the chemical potential is given by

$$\boxed{\mu = k_B T \left[\ln(n V_Q) - \ln(1 + e^{-\beta\Delta})\right]}\,.$$

(b) Now the free energy is given by $F = \Omega + \mu N$, and so

$$\boxed{F(T, V, N) = N k_B T \left[\ln(n V_Q) - 1 - \ln(1 + e^{-\beta\Delta})\right]}\,.$$

(c) The entropy is given by $S = -(\partial F/\partial T)_{N,V}$ and so

$$\boxed{S = N k_B \left[\frac{5}{2} - \ln(n V_Q) + \frac{\Delta}{T} \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} + \ln(1 + e^{-\beta\Delta})\right]}\,,$$

(d) From Eq. (6) the pressure is given by

$$\boxed{P = \frac{N}{V} k_B T\,,}$$

i.e. we have the ideal gas law unchanged by the presence of the excited state of the atom.

(e) The energy is given by

$$U = \frac{\partial}{\partial \beta}(\beta F) = \frac{3}{2} N k_B T + N\Delta \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} = \frac{3}{2} N k_B T + N\Delta \frac{1}{e^{\beta\Delta} + 1}\,.$$

Hence the specific heat at constant volume is given by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = N k_B \left[\frac{3}{2} + \left(\frac{\Delta}{k_B T}\right)^2 \frac{e^{\beta\Delta}}{(e^{\beta\Delta} + 1)^2}\right]\,.$$

As discussed in class

$$C_P = C_V + N k_B = \boxed{N k_B \left[\frac{5}{2} + \left(\frac{\Delta}{k_B T}\right)^2 \frac{e^{\beta\Delta}}{(e^{\beta\Delta} + 1)^2}\right]}\,.$$