Second Exam, PY541, Solutions

1) At room temperature, T is much greater than the rotational temperature but much less than the vibrational temperature. From the equipartition theorem, C_V gets a contribution of (3/2)k from center of mass translational kinetic energy and k from rotational energy. (Recall that, for a diatomic molecule there are only 2 rotation modes.) So $C_V/N = 5k/2$ at room temperature. At T=20,000K we are well above the vibrational temperature so vibrational modes contribute an additional k to the heat capacity: $c_V/N \approx 7k/2$.

2)

$$Z_{in} = 1 + 3e^{-\Delta/kT}. \tag{1}$$

Note that factor of 3=(2J+1) due to the degeneracy of the J=1 states. The general formula for the heat capacity from internal degrees of freedom for an ideal gas is:

$$C_V/N = -T\frac{d^2A_{in}}{dT^2} = k\frac{d}{dT}\left[T^2\frac{d}{dT}\ln Z_{in}\right]. \tag{2}$$

In this case:

$$\frac{d}{dT}\ln Z_{in} = \frac{3\Delta}{kT^2}\frac{1}{e^{\Delta/kT}+3} \tag{3}$$

and hence:

$$C_V/N = \frac{3\Delta^2}{kT^2}\frac{e^{\Delta/kT}}{(e^{\Delta/kT}+3)^2}. \tag{4}$$

This vanishes as $3(\Delta^2/kT^2)e^{-\Delta/kT}$ for $kT << \Delta$ and as $3\Delta^2/16kT^2$ for $kT >> \Delta$. N.B. This is the internal heat capacity only. There is an additional contribution from center of mass motion of $(3/2)k$ per atom.

3a) Using the general formula for the average number of particles for $\mu = 0$,

$$N = \sum_i \frac{1}{e^{\beta\epsilon_i} - 1}, \tag{5}$$

now summing over both sets of single particle states with energies $p^2/2m$ and $p^2/2m + \Delta$ and replacing the sums by integrals, I obtain:

$$N/V = \int \frac{d^3p}{(2\pi\hbar)^3}\left[\frac{1}{e^{\beta p^2/2m}-1} + \frac{1}{e^{\beta(p^2/2m+\Delta)}-1}\right]. \tag{6}$$

b) T_c is simply obtained from Eq. (6) by setting $T = T_c$, since T_c is the temperature at which the density that will fit into the system without macroscopic occupation of the groundstate equals the actual density. We must solve this equation for T_c as a function of $N/V = n$. This is difficult to do in general but it simplifies when $kT_c << \Delta$. The first term in Eq. (6) has the value given in the exam. The second term can be approximated by dropping the (-1) term in the denominator since the exponential term is very large. The p-integral then becomes a familiar Gaussian:

$$n \approx 2.315(2mkT)^{3/2}/4\pi^2\hbar^3 + e^{-\Delta/kT}(mkT)^{3/2}/[(2\pi)^{3/2}\hbar^3]. \tag{7}$$

Since the second term in this equation is already small, we may use the lowest order approximation for T_c in it. This gives:

$$n \approx 2.315[(2mkT)^{3/2}/4\pi^2\hbar^3]\left[1 + e^{-\Delta/kT_{c0}}\frac{4\pi^2}{2^{3/2}(2\pi)^{3/2}2.315}\right] = 2.315[(2mkT)^{3/2}/4\pi^2\hbar^3]\left[1 + .383e^{-\Delta/kT_{c0}}\right] \tag{8}$$

Now solving for T gives:

$$T_c \approx T_{c0}\left[1 + .383e^{-\Delta/kT_{c0}}\right]^{-2/3} \approx T_{C0}[1 - .255e^{-\Delta/kT_{c0}}]. \tag{9}$$