PH441, MIDTERM, February 8, 2010

Note: calculations in thermodynamics can be done different ways, and sometimes a path taken, even though correct, can be tedious. Hence always indicate what you try to do, even if you are not able to finish the actual work.

Problem 1: A system can be in three different states, with energy $-\epsilon, 0, \epsilon$, where $\epsilon > 0$. The probabilities of being in these states are $P_{-\epsilon}$, P_0 , and P_ϵ. These values of these probabilities depend on the temperature of the system.

1. What is the smallest value of P_0? Explain your answer!
2. What is the largest value of P_0? Explain your answer!
3. Find the temperature for which P_0 is exactly half that of $P_{-\epsilon}$.

Probabilities are numbers between zero and one. At very low temperature the system will be in the lowest energy state, and hence $P_0 = 0$. At very high temperatures, all states are equally probable, and hence $P_0 = \frac{1}{3}$. For other temperatures the value of P_0 is in between. In general we have

$$P_{-\epsilon} = \frac{1}{\mathcal{Z}} e^{\beta\epsilon}$$

$$P_0 = \frac{1}{\mathcal{Z}}$$

$$\mathcal{Z} = e^{\beta\epsilon} + 1 + e^{-\beta\epsilon}$$

The requirement $P_{-\epsilon} = 2P_0$ gives

$$\frac{1}{\mathcal{Z}} e^{\beta\epsilon} = 2\frac{1}{\mathcal{Z}}$$

or

$$e^{\beta\epsilon} = 2 \quad \Rightarrow \quad \beta\epsilon = \ln(2)$$

which gives

$$T = \frac{\epsilon}{k_B \ln(2)}$$

Problem 2: The partition function of an ideal gas with N particles and volume V is given by $\mathcal{Z} = \frac{1}{N!}\left(n_Q V\right)^N$, where $n_Q = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}$.

1. A certain free energy follows directly from the partition function, without the need for derivatives. Give the formula for this free energy, relating it to the internal energy.
2. What is the first law in terms of that energy?
3. Based on the expression given above for the partition function, calculate the entropy of the system. Show all steps you take.
4. How does the volume V change as a function of temperature T for an ideal gas in an adiabatic process where the number of particles is conserved?

The Helmholtz free energy $F = U - TS$ follows directly from the partition function, $F = -k_BT\ln(\mathcal{Z})$. In that case we have $dF = -SdT - pdV + \mu dN$ and hence

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \left(\frac{\partial}{\partial T}\right)_{V,N} k_BT\left(N\ln(n_Q) + N\ln(V) - \ln(N!)\right) =$$

$$k_B\left(N\ln(n_Q) + N\ln(V) - \ln(N!)\right) + k_BT\frac{1}{n_Q}\left(\frac{\partial n_Q}{\partial T}\right)_{V,N} =$$

$$Nk_B\ln(Vn_Q) - k_B\ln(N!)) + \frac{3}{2}k_B$$

If N and S are constant, we need n_QV to be a constant, or

$$V \propto T^{-\frac{3}{2}}$$

Problem 3: According to an extension of the Debye model of a solid, the heat capacity at low temperatures is given by

$$C_V = c_0V\left(\frac{T}{\Theta_D(n)}\right)^3$$

where c_0 is a constant, and the Debye temperature $\Theta_D(n)$ is a function of the density $n = \frac{N}{V}$. The free energy that uses temperature is the Helmholtz free energy, $F = U - TS$ and the first law in that case is $dF = -SdT - pdV + \mu dN$.

1. Calculate the entropy at low temperature based on the heat capacity.
2. Using a Maxwell relation, find how the pressure changes with temperature. In other words, calculate $\left(\frac{\partial p}{\partial T}\right)_{V,N}$.

We know that

$$S = \int_0^T \frac{C_V}{T'} dT' = \int_0^T \frac{1}{T'} c_0 V \left(\frac{T'}{\Theta_D(n)}\right)^3 dT'$$

which leads to

$$S = \frac{1}{3} c_0 V \left(\frac{T}{\Theta_D(n)}\right)^3$$

We know from Mr. Maxwell:

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = -\left(\frac{\partial^2 F}{\partial V^2}\right)_T N = \left(\frac{\partial S}{\partial V}\right)_{T,N}$$

and hence

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{1}{3} c_0 \left(\frac{T}{\Theta_D(n)}\right)^3 - 3\frac{1}{3} c_0 V \frac{T^3}{\Theta_D^4(n)} \Theta_D'(n) \frac{-N}{V^2}$$

We can simplify if we want:

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{S}{V}\left(1 + 3\frac{\Theta_D'(n)}{\Theta_D(n)} \frac{N}{V}\right)$$

but that was not asked for.