

Homework 5 - Solutions

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Problem 1

(a) The partition function is

$$Z = \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1) \frac{\hbar^2}{2I\tau}}$$

By assumption $\frac{\hbar^2}{2I\tau} \ll 1$. In that case the integrand is slowly varying and we can replace it by integral

$$Z = \int_0^{\infty} (2l+1) e^{-l(l+1) \frac{\hbar^2}{2I\tau}} dl$$

Now make substitution $x = l(l+1) \frac{\hbar^2}{2I\tau}$. Then

$$Z = \frac{2I\tau}{\hbar^2} \int_0^{\infty} x e^{-x} dx = \frac{2I\tau}{\hbar^2}$$

For the thermodynamic variables we have

$$F = -\tau \log Z = -\tau \log \frac{2I\tau}{\hbar^2}$$

$$U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \tau$$

$$\sigma = \frac{U - F}{\tau} = 1 + \log \frac{2I\tau}{\hbar^2}$$

(b) In this case $a \gg 1$ and

$$Z = 1 + 3e^{-2a} + 5e^{-6a} + \dots \approx 1 + 3e^{-2a} = 1 + 3e^{-\frac{\hbar^2}{I\tau}}$$

Set $\epsilon = \hbar^2/I$. We have

$$U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \frac{\epsilon}{e^{\epsilon/\tau} + 3} \approx \epsilon e^{-\epsilon/\tau}$$

$$F = -\tau \log Z = -\tau \log(1 + 3e^{-\epsilon/\tau}) \approx -\tau 3e^{-\epsilon/\tau} \ll U$$

$$\sigma = (U - F)/\tau \approx U/\tau = \frac{\epsilon/\tau}{e^{\epsilon/\tau} + 3} \approx \epsilon e^{-\epsilon/\tau}$$

(c) The temperature that divides the two regimes is $\hbar^2/2I$. We can estimate $R \sim 10^{-10}m$, $M \sim 28 \times m_{proton}$, $I \sim MR^2$. From this:

$$\begin{aligned} \Theta_R(\text{in K}) &= \frac{\hbar^2}{2Ik_B} = \frac{(1.05 \times 10^{-34})^2}{2(28 \times 1.67 \times 10^{27})(10^{-10})^2(1.38 \times 10^{-23})} \\ &\approx 0.86\text{K} \end{aligned}$$

Thus at the room temperature, the rotational modes are excited and the heat capacity is $\frac{5}{2}Nk$.

Problem 2

$$\frac{\partial f}{\partial \epsilon} = \frac{\partial}{\partial \epsilon} \frac{1}{e^{(\epsilon-\mu)/\tau} + 1} = \frac{e^{(\epsilon-\mu)/\tau}}{(e^{(\epsilon-\mu)/\tau} + 1)^2} = \frac{1}{4\tau^2}$$

Where the last equality holds at $\epsilon = \tau$.

Problem 3

We use

$$\langle N \rangle = \frac{\sum N e^{(N\mu-E)/\tau}}{\sum e^{(N\mu-E)/\tau}}$$

(a)

$$\langle N \rangle = \frac{e^{(\mu-\epsilon)/\tau} + 2e^{(2\mu-2\epsilon)/\tau}}{1 + e^{(\mu-\epsilon)/\tau} + e^{2(\mu-\epsilon)/\tau}}$$

(b)

$$\langle N \rangle = \frac{2e^{(\mu-\epsilon)/\tau} + 2e^{2(\mu-\epsilon)/\tau}}{1 + e^{(\mu-\epsilon)/\tau} + e^{(\mu-\epsilon)/\tau} + e^{2(\mu-\epsilon)/\tau}} = 2 \frac{e^{(\mu-\epsilon)/\tau}}{1 + e^{(\mu-\epsilon)/\tau}}$$

We see that in the second case, the levels are independent and we get the result of one level multiplied by 2.

Problem 4

The energy of a state is $E = pc$. The probability of such state is $\sim e^{-pc/\tau}$.

Thus

$$\langle E \rangle = \langle pc \rangle = \frac{\int d^3p \, pc \, e^{-pc/\tau}}{\int d^3p \, e^{-pc/\tau}} = \tau \frac{\int d^3x \, x e^{-x}}{\int d^3x \, e^{-x}} = \tau \frac{\int dx \, x^3 e^{-x}}{\int dx \, x^2 e^{-x}} = \tau \frac{3!}{2!} = 3\tau$$

where we have made substitution $x = pc/\tau$.

Problem 5

Things are easiest to see in the canonical ensemble. The internal and motional (center of mass) degrees of freedom are independent. We can see that the partition function for one particle can be written as

$$Z_1 = \sum_{cI} e^{-(\epsilon_c + \epsilon_I)/\tau} = \sum_c e^{-\epsilon_c/\tau} \sum e^{-\epsilon_I/\tau} = Z_c Z_I$$

Where c refers to center of mass degrees of freedom and I to internal ones. The total partition function is

$$Z = Z_1^N / N!$$

And obviously

$$Z_I = 1 + e^{-\Delta/\tau}$$

Thus:

$$F = -\tau \log Z = -\tau \log Z_c^N Z_I^N / N! = -\tau \log Z_c^N / N! - \tau \log Z_I^N = F_c - N\tau \log Z_I$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,\tau} = \mu_c - \tau \log Z_I$$

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_{V,N} = \sigma_c + N \log Z_I + N\tau \frac{\partial}{\partial \tau} \Big|_{N,V} \log Z_I = \sigma_c + N \log Z_I + \frac{\Delta/\tau}{e^{\Delta/\tau} + 1}$$

$$p = - \left(\frac{\partial F}{\partial V} \right)_{\tau,N} = p_c$$

$$C_p = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_{p,N}$$

The first part is the derivative of σ_c and gives the same answer as for simple ideal gas. For the second part, we have to eliminate V in favor of p . However, in σ_I there is no V and so the derivative with τ is just the simple derivative with τ . Thus

$$\begin{aligned} C_p &= (C_p)_c + \tau \frac{\partial}{\partial \tau} \left(N \log(1 + e^{-\Delta/\tau}) + N \frac{\Delta}{\tau} \frac{1}{e^{\Delta/\tau} + 1} \right) \\ &= (C_p)_c + N \left(\frac{\Delta}{\tau} \right)^2 \frac{e^{\Delta/\tau}}{(e^{\Delta/\tau} + 1)^2} \end{aligned}$$

Problem 6

First notice that for process at constant pressure

$$C_p = \tau \frac{d\sigma}{d\tau} = \frac{dU}{dT} + p \frac{dV}{dT} = C_V + \frac{d(pV)}{dT} - v \frac{dp}{dT} = C_V + nR$$

Now consider isentropic process $d\sigma = 0$. From $dU = \tau d\sigma - pdV$ and $dU = C_V dT$ we have

$$pdV = -C_V dT$$

From $pV = nRT$ and $C_P = C_V + nR$ we have

$$pV = (C_P - C_V)T$$

Now we combine them

$$C_V dT = \frac{C_P - C_V}{V} dVT$$

so

$$\frac{dT}{T} = (\gamma - 1) \frac{dV}{V}$$

Next

$$C_P dT = C_V dT + d(pV) = V dp = \frac{(C_P - C_V)T}{p} dp$$

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{d\tau}{\tau}$$

Dividing those two formulas we get

$$\frac{dp}{p} = -\gamma \frac{dV}{V}$$

(b) Since the above formulas are for constant entropy process we have directly from relation between dp and dV :

$$B_\sigma = -V \left(\frac{\partial p}{\partial V} \right)_\sigma = V \gamma \frac{p}{V} = \gamma p$$

For B_τ we use the ideal gas law $p = NkT/V$ to get

$$B_\tau = -V \left(\frac{\partial p}{\partial V} \right)_\tau = -V \left(\frac{\partial}{\partial V} \right)_\tau \frac{NkT}{V} = \frac{NkT}{V} = p$$

Problem 7

Consider a thin layer of atmosphere of thickness dz . The difference in the pressures dp between the top and the bottom is $\rho g dz$. Thus

$$\frac{dp}{dz} = \rho g = \frac{m}{V} g = Mg \frac{n}{V} = Mg \frac{p}{RT}$$

where M is the molecular mass of the gas. Using relation between dp and dT from the previous problem we see that

$$\frac{dT}{dz} = \frac{\gamma - 1}{\gamma} \frac{Mg}{R}$$

which is a constant. Numerically:

$$\frac{dT}{dz} \approx -\frac{0.428 \times 1.67 \times 10^{-27} \times 9.8}{1.4 \times 1.38 \times 10^{-23}} \approx -10^{-2} \frac{\text{K}}{\text{m}} = -10 \frac{\text{K}}{\text{km}}$$

(c) Consider given amount of molecules with mass m . At different heights they occupy different volume V . Their density is $\rho = m/V$. This volume changes according to $pV^\gamma = \text{const}$. Thus $p = \rho^\gamma$.

Problem 8

We have isentropic relation

$$TV^{\gamma-1} = \text{const}$$

(This one gets for example from integrating the relation between dT and dV in problem 6.) Thus

$$T_2 = T_1 \left(\frac{V_2}{V_1} \right)^{1-\gamma} = 300(\text{K})(15)^{0.4} = 886\text{K}$$