

Homework 5

Michael Brodskiy

Professor: A. Stepanyants

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1. First and foremost, we know the formula:

$$f = \frac{1}{e^{\frac{\varepsilon - \mu}{\tau}} + 1}$$

Thus, we can write:

$$\begin{aligned} -\frac{\partial f}{\partial \varepsilon} &= -\frac{\partial}{\partial \varepsilon} \left(\frac{1}{e^{\frac{\varepsilon - \mu}{\tau}} + 1} \right) \\ -\frac{\partial f}{\partial \varepsilon} &= - \left(-\frac{1}{\tau \left(e^{\frac{\varepsilon - \mu}{\tau}} + 1 \right)^2} \cdot e^{\frac{\varepsilon - \mu}{\tau}} \right) \\ -\frac{\partial f}{\partial \varepsilon} &= \frac{e^{\frac{\varepsilon - \mu}{\tau}}}{\tau \left(e^{\frac{\varepsilon - \mu}{\tau}} + 1 \right)^2} \end{aligned}$$

We can then evaluate:

$$f_{\varepsilon}(\varepsilon = \mu) = \frac{e^0}{\tau (e^0 + 1)^2}$$

$$f_{\varepsilon}(\varepsilon = \mu) = \frac{1}{4\tau}$$

3. (a) The partition function is given by the sum of energy values:

$$3 = 1 + \lambda e^{-\frac{\varepsilon}{\tau}} + \lambda^2 e^{-\frac{2\varepsilon}{\tau}}$$

We can write the probability of occupation of an energy level as:

$$P(N) = \frac{e^{-\frac{N\varepsilon}{\tau}}}{3}$$

We can then define the ensemble average occupancy:

$$\langle N \rangle = \frac{1}{3} (0P(0) + \lambda P(1) + 2\lambda^2 P(2))$$

$$\langle N \rangle = \frac{1}{3} (\lambda e^{-\frac{\varepsilon}{\tau}} + 2\lambda^2 e^{-\frac{2\varepsilon}{\tau}})$$

$$\boxed{\langle N \rangle = \frac{1}{1 + \lambda e^{-\frac{\varepsilon}{\tau}} + \lambda^2 e^{-\frac{2\varepsilon}{\tau}}} (\lambda e^{-\frac{\varepsilon}{\tau}} + 2\lambda^2 e^{-\frac{2\varepsilon}{\tau}})}$$

(b) In this situation, the partition function becomes:

$$3 = 1 + 2\lambda e^{-\frac{\varepsilon}{\tau}} + \lambda^2 e^{-\frac{2\varepsilon}{\tau}}$$

Just like (a), the ensemble average occupancy can be defined in a similar way:

$$\boxed{\langle N \rangle = \frac{2\lambda e^{-\frac{\varepsilon}{\tau}} + 2\lambda^2 e^{-\frac{2\varepsilon}{\tau}}}{1 + 2\lambda e^{-\frac{\varepsilon}{\tau}} + \lambda^2 e^{-\frac{2\varepsilon}{\tau}}}}$$

6. Since we know the entropy is a function of volume and temperature, we write:

$$\sigma = \sigma(V, \tau)$$

which gives us:

$$d\sigma = \left(\frac{\partial \sigma}{\partial V} \right)_{\tau} dV + \left(\frac{\partial \sigma}{\partial \tau} \right)_V d\tau$$

Furthermore, from a modification of one of Maxwell's equations, we know:

$$\left(\frac{\partial \sigma}{\partial V} \right)_{\tau} = \left(\frac{\partial P}{\partial \tau} \right)_V$$

and we also know a relation for the specific heat at constant volume:

$$\tau \left(\frac{\partial \sigma}{\partial \tau} \right)_V = C_v$$

Plugging these into our equation, we get:

$$d\sigma = \left(\frac{\partial P}{\partial \tau} \right)_V dV + \frac{C_v}{\tau} d\tau$$

Then, assuming both A and B are ideal gasses, we can write:

$$PV = N\tau$$

$$\left(\frac{\partial P}{\partial \tau}\right)_v = \frac{N}{V}$$

Returning to our equation, we obtain:

$$d\sigma = \frac{N}{V} dV + \frac{C_v}{\tau} d\tau$$

Integrating both sides, we obtain:

$$\sigma = N \ln(V) + C_v \ln(\tau)$$

We can defined these separately for each species:

$$\sigma_A = N \ln(V) + C_v^A \ln(\tau)$$

$$\sigma_B = N \ln(V) + C_v^B \ln(\tau)$$

The difference in entropy may be written as:

$$\Delta\sigma = \sigma_{A+B} - (\sigma_A + \sigma_B)$$

We know:

$$\sigma_{A+B} = 2N \ln(2V) + (C_v^A + C_v^B) \ln(\tau)$$

Which then gives:

$$\Delta\sigma = 2N \ln(2V) + \cancel{(C_v^A + C_v^B) \ln(\tau)} - 2N \ln(V) - \cancel{(C_v^A + C_v^B) \ln(\tau)}$$

$$\Delta\sigma = 2N \ln(2V) - 2N \ln(V)$$

$$\boxed{\Delta\sigma = 2N \ln(2)}$$

Assuming the two are the same species, the volume occupied would become $2V$, since each is indistinguishable. Bringing us to the last step, we find:

$$\Delta\sigma = 2N \ln(2V) - 2N \ln(2V)$$

And, thus:

$$\boxed{\Delta\sigma_{A \equiv B} = 0}$$

12. (a)
- (b)
- (c)

13. (a) We know the canonical partition function is:

$$Z_N = \frac{(n_Q V)^N}{N!}$$

We know from the Gibbs sum that:

$$\begin{aligned} 3 &= \sum_{N=0}^{\infty} \lambda^N Z_N \\ 3 &= \sum_{N=0}^{\infty} \frac{\lambda^N (n_Q V)^N}{N!} \\ 3 &= \sum_{N=0}^{\infty} \frac{(\lambda n_Q V)^N}{N!} \end{aligned}$$

Since this sum is of a known form, we can rewrite it as:

$$\boxed{3 = e^{\lambda n_Q V}}$$

- (b) We can write the probability as:

$$P(N) = \frac{\lambda^N Z_N}{3}$$

Which becomes:

$$P(N) = \frac{(\lambda n_Q V)^N}{N! e^{\lambda n_Q V}}$$

We then need to find the average concentration:

$$\begin{aligned} \langle N \rangle &= \frac{1}{3} \sum_{N=0}^{\infty} N \lambda^N Z_N \\ \langle N \rangle &= \frac{1}{3} \sum_{N=0}^{\infty} \frac{N (\lambda n_Q V)^N}{N!} \\ \langle N \rangle &= \frac{1}{3} \sum_{N=0}^{\infty} \frac{(\lambda n_Q V)^N}{(N-1)!} \\ \langle N \rangle &= \frac{\lambda n_Q V}{3} \underbrace{\sum_{N=0}^{\infty} \frac{(\lambda n_Q V)^{N-1}}{(N-1)!}}_3 \\ \langle N \rangle &= \lambda n_Q V \end{aligned}$$

Now returning to our expression for probability, we can write it as:

$$P(N) = \frac{\langle N \rangle^N}{N! e^{\langle N \rangle}}$$

Bringing the exponential up, we get:

$$P(N) = \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!}$$

(c) We can write the first summation as:

$$\sum_{N=0}^{\infty} \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!}$$

This can also be written as:

$$e^{-\langle N \rangle} \underbrace{\sum_{N=0}^{\infty} \frac{\langle N \rangle^N}{N!}}_{e^{\langle N \rangle}}$$

Which becomes:

$$\sum_N P(N) = e^{-\langle N \rangle} e^{\langle N \rangle} = 1$$

We can write the second summation as:

$$\sum_{N=0}^{\infty} \frac{N \langle N \rangle^N e^{-\langle N \rangle}}{N!}$$

This can be written as:

$$\sum_{N=0}^{\infty} \frac{\langle N \rangle^N e^{-\langle N \rangle}}{(N-1)!}$$

$$\langle N \rangle e^{-\langle N \rangle} \sum_{N=0}^{\infty} \frac{\langle N \rangle^{N-1}}{(N-1)!}$$

This then becomes:

$$\sum_N N P(N) = \langle N \rangle e^{-\langle N \rangle} e^{\langle N \rangle} = \langle N \rangle$$

14. (a) For this problem, we can simply use a formula:

$$Q = N\tau \ln \left(\frac{V_2}{V_1} \right)$$

This becomes:

$$Q = Nk_B T \ln \left(\frac{V_2}{V_1} \right)$$
$$Q = (1)(8.314)(300) \ln(2)$$

Which is:

$$\boxed{Q = 1.729[\text{kJ}]}$$

For the second process, since the gas expands isentropically, there is no heat transfer between the gas and its surroundings.

(b) We can write the ratio of temperatures as:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

With volumes:

$$V_1 = 2V_o$$

$$V_2 = 4V_o$$

γ is the ratio of specific heats. We assume $\gamma = 1.6\bar{6}$, as we are dealing with a monatomic gas, which yields:

$$T_2 = (300) \left(\frac{1}{2} \right)^{\frac{2}{3}}$$

$$\boxed{T_2 = 189[\text{K}]}$$

(c) We know that the change in entropy may be written as:

$$\Delta\sigma = nk_B \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta\sigma = nk_B \ln(2)$$

This gives us:

$$\boxed{\Delta\sigma = 5.76 \left[\frac{\text{J}}{\text{K}} \right]}$$