Homework 5

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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:

$$-\frac{\partial f}{\partial \varepsilon} = -\frac{\partial}{\partial \varepsilon}\left(\frac{1}{e^{\frac{\varepsilon-\mu}{\tau}}+1}\right)$$

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

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

We can then evaluate:

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

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

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

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

We can then define the ensemble average occupancy:

$$\langle N\rangle = \lambda\frac{\partial}{\partial\lambda}(\ln(\mathfrak{z}))$$

$$\langle N\rangle = \frac{\lambda}{\mathfrak{z}}\left(e^{-\frac{\varepsilon}{\tau}} + 2\lambda e^{-\frac{2\varepsilon}{\tau}}\right)$$

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

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

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

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

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

$$\langle N\rangle = \lambda\frac{\partial}{\partial\lambda}(\ln(\mathfrak{z}))$$

$$\langle N\rangle = \frac{\lambda}{\mathfrak{z}}\frac{\partial}{\partial\lambda}(\mathfrak{z})$$

$$\langle N\rangle = \frac{\lambda}{\mathfrak{z}}\left(2e^{-\frac{\varepsilon}{\tau}} + 2\lambda e^{-\frac{2\varepsilon}{\tau}}\right)$$

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

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 out 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) We can begin by defining the partition function as:

$$z_1 = \sum e^{-\frac{\varepsilon}{\tau}} = \int D(\varepsilon) e^{-\frac{\varepsilon}{\tau}}\, d\varepsilon$$

In two dimensions, the energy density is:

$$D(\varepsilon)\, d\varepsilon = \frac{Ap}{2\pi\hbar^2}\, dp = \frac{A}{\pi\hbar^2}\, d\left(\frac{p^2}{2}\right) = \frac{AM}{\pi\hbar^2}\, d\left(\frac{p^2}{2M}\right) = \frac{AM}{\pi\hbar^2}\, d\left(\varepsilon\right)$$

Thus, the partition function becomes:

$$z_1 = \frac{L^2 M}{\pi\hbar^2} \int_0^{\infty} e^{-\frac{\varepsilon}{\tau}}\, d\varepsilon = \frac{L^2 M\tau}{\pi\hbar^2}$$

We can then write:

$$N = z_1\lambda$$

$$N = \frac{L^2 M\tau}{\pi\hbar^2} e^{\frac{\mu}{\tau}}$$

$$\frac{\mu}{\tau} = \ln\left(\frac{N\pi\hbar^2}{L^2 M\tau}\right)$$

$$\boxed{\mu = \tau \ln\left(\frac{N\pi\hbar^2}{L^2 M\tau}\right)}$$

(b) We can sum all of the unidimensional components to get:

$$U = \frac{1}{2}N\tau + \frac{1}{2}N\tau$$

$$\boxed{U = N\tau}$$

(c) We can begin by finding the free energy:

$$F = -\tau \ln(z)$$

We know the partition function may be written as:

$$z = \frac{z_1^N}{N!}$$

Substituting z into the free energy formula, we get:

$$F = -N\tau \ln\left(\frac{N\pi\hbar^2}{L^2 M\tau}\right) + N\tau\ln(N) - N\tau = -N\tau\left(\ln\left(\frac{N\pi\hbar^2}{L^2 M\tau}\right) + 1\right)$$

We know:

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

Which gives us:

$$\sigma = \frac{\partial}{\partial \tau}\left(N\tau\left[\ln\left(\frac{\pi N\hbar^2}{L^2 M\tau}\right)+1\right]\right)$$

$$\sigma = N\ln\left(\frac{\pi N\hbar^2}{L^2 M\tau}\right) + N - \tau\frac{\partial}{\partial \tau}\left(\ln\left(\frac{\pi N\hbar^2}{L^2 M\tau}\right)\right)$$

$$\sigma = N\ln\left(\frac{\pi N\hbar^2}{L^2 M\tau}\right) + N + \underbrace{\frac{\tau^2 M L^2}{2\pi\hbar^2}\frac{\partial}{\partial \tau}\left(\frac{\pi N\hbar^2}{L^2 M\tau}\right)}_{N}$$

We end up with an expression similar to the Sackur-Tetrode equation:

$$\boxed{\sigma = N\left[\ln\left(\frac{\pi\hbar^2}{L^2 M\tau}\right)+2\right]}$$

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

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

We know from the Gibbs sum that:

$$\mathcal{Z} = \sum_{N=0}^{\infty}\lambda^N Z_N$$

$$\mathcal{Z} = \sum_{N=0}^{\infty}\frac{\lambda^N (n_Q V)^N}{N!}$$

$$\mathcal{Z} = \sum_{N=0}^{\infty}\frac{(\lambda n_Q V)^N}{N!}$$

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

$$\boxed{\mathcal{Z} = e^{\lambda n_Q V}}$$

(b) We can write the probability as:

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

Which becomes:

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

We then need to find the average concentration:

$$\langle N \rangle = \frac{1}{3} \sum_{N=0}^{\infty} N \lambda^N Z_N$$

$$\langle N \rangle = \frac{1}{3} \sum_{N=0}^{\infty} \frac{N(\lambda n_Q V)^N}{N!}$$

$$\langle N \rangle = \frac{1}{3} \sum_{N=0}^{\infty} \frac{(\lambda n_Q V)^N}{(N-1)!}$$

$$\langle N \rangle = \frac{\lambda n_Q V}{3} \underbrace{\sum_{N=0}^{\infty} \frac{(\lambda n_Q V)^{N-1}}{(N-1)!}}_{3}$$

$$\langle N \rangle = \lambda n_Q V$$

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:

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

(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:

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

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:

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

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:

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

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:

$$T_2 = (300)\left(\frac{1}{2}\right)^{\frac{2}{3}}$$
$$\boxed{T_2 = 189[\mathrm{K}]}$$

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

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

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

$$\Delta\sigma = (6.022 \cdot 10^{23}) \ln(2)$$

This gives us:

$$\boxed{\Delta\sigma = 4.17 \cdot 10^{23}}$$