

STATISTICAL MECHANICS: ASSIGNMENT 3

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Problem 1. Return to the rubber band problem from the mid-semester assessment. We arrived at

$$dG = -SdT + Vdp + fdL.$$

- (1) Show that we can write the force as the sum of an enthalpic term and an entropic term:

$$f = \left(\frac{\partial H}{\partial L} \right)_{T,p} - T \left(\frac{\partial S}{\partial L} \right)_{T,p}$$

- (2) Using the Maxwell relation derived previously, along with the data in the graph, estimate (numerically) the fraction of the elasticity of the rubber (i.e. f) that comes from the entropic term. Because you're working with ratios, the distinction between force and modulus doesn't matter – the geometrical factors that connect them cancel out. Which term (enthalpic or entropic) dominates?
- (3) From your result, does the rubber band get warmer or colder when you stretch it? When it retracts to its original length? If you have a rubber band handy, test your conclusion empirically and report the results. (Lips are sensitive differential thermometers.)

Solution. Let's start by writing the expression

$$dG = -SdT + Vdp + fdL.$$

- (1) From that expression we have

$$f = \left(\frac{\partial G}{\partial L} \right)_{T,p},$$

and on the other hand, the definition of Gibbs free energy is given by

$$G = H - TS,$$

where H is the enthalpy, and from this definition, we have that

$$\left(\frac{\partial G}{\partial L} \right)_{T,p} = \left(\frac{\partial H}{\partial L} \right)_{T,p} - \left(\frac{\partial (TS)}{\partial L} \right)_{T,p},$$

but because we're keeping the temperature constant we have that

$$\left(\frac{\partial G}{\partial L} \right)_{T,p} = \left(\frac{\partial H}{\partial L} \right)_{T,p} - T \left(\frac{\partial S}{\partial L} \right)_{T,p},$$

and from this we can obtain the following expression for f ,

$$f = \left(\frac{\partial H}{\partial L} \right)_{T,p} - T \left(\frac{\partial S}{\partial L} \right)_{T,p},$$

and from this we can see that the force can be written in terms of an enthalpic term and an entropic term. And even more, the previous equation has the following functional form

$$f = mT + b,$$

where

$$m = - \left(\frac{\partial S}{\partial L} \right)_{T,p} \quad \& \quad b = \left(\frac{\partial H}{\partial L} \right)_{T,p},$$

but from the figure we can see that the slope is positive, this is $m > 0$, and this implies that

$$\left(\frac{\partial S}{\partial L} \right)_{T,p} < 0,$$

which means that stretching brings makes the system more ordered.

- (2) Now, we are going to calculate the contribution of the entropic term, this is $\left(\frac{\partial S}{\partial L} \right)_{T,p}$

$$m = \frac{\Delta f}{\Delta T} \approx \frac{0.22 - 0.17}{200 - 140},$$

$$\Rightarrow m \approx \frac{0.05}{60} \approx 0.00083,$$

thus we have

$$m \approx 0.00083 \frac{N}{mm^2 K},$$

and even more, from the figure we can see that the parameter b , this is, the term associated to the enthalpy is of order 10^{-2} . On the other hand, for the the entropic term we have: fixing the temperature at around 200, we have the product

$$mT \approx 0.00083 \times 200,$$

$$\approx 0.17,$$

but from the figure we can see that, $b < 0.17$, and this is if we assume that the behavior is linear for all temperatures, something that sounds weird, but at first approximation sees reasonable. And with this analysis we can see that **the entropic term dominates**.

- (3) Finally, if we stretch the rubber that means we're in some sense in high f , and this implies that the temperature should be higher, something that agrees with our everyday experience when we stretch a rubber band.

Problem 2. In this problem you will calculate analytically the vibrational contribution to the energy of a diatomic molecule as a function of temperature, and, by making suitable approximations, consider the behavior in the low- and high-temperature limits. Model the molecule quantum mechanically as a particle in a three-dimensional infinite square (i.e. cubical) well of side length L that is also able to vibrate internally at frequency ω . Represent the vibrational as a quantum harmonic oscillator. The center-of-mass and vibrational degrees of freedom are independent.

- (1) What are the quantum numbers that define a microstate of the molecule? What is the energy of the microstate in terms of those quantum numbers?
- (2) Calculate the partition function Z . You can assume that L is very large, so that the spacing between center-of-mass states is much smaller than $k_B T$, but do not assume that $\hbar\omega$ is small compared to $k_B T$.
- (3) Using the relation

$$\langle U \rangle = k_B T^2 \frac{\partial \ln Z}{\partial T}$$

find the average energy of the molecule at low temperature, $k_B T \ll \hbar\omega$. Compare your result to what is expected from classical equipartition.

- (4) Find the average energy of the molecule at high temperature, $k_B T \gg \hbar\omega$. Compare your result to what is expected from classical equipartition.
- (5) How does this calculation relate to the analysis we did in HW 1, Prob 5.?

Solution. Sol.

- (1) Formally, we have to solve the Schrödinger equation, and in this case we have two contributions to the energy, one is given by the particle in a box, and the other is given by the vibration modes. In the case of a particle in a box, which is the contribution for the translational degrees of freedom, we have a contribution in the energy as follows

$$E_i^{(fp)} = \frac{\hbar^2 n_i^2}{2m}, \quad i \in \{x, y, z\},$$

and the contribution for the vibrational degrees of freedom is given by

$$E_j^{(sho)} = \left(n_j + \frac{1}{2} \right) \hbar\omega, \quad j \in \{1, 2\},$$

therefore, the energy total energy is given by

$$E_{ij} = E_i^{(fp)} + E_j^{(sho)},$$

and there's a reason for the notation, which will be clear in a moment.

- (2) Once we have the energies, we can write the partition function, but there's a nice result which I want to exploit: if the total energy of a system can be decomposed in a sum of various independent contributions, then the total partition function is the product of several partition functions, this is, if

$$E_{ij} = E_i^{(a)} + E_j^{(b)},$$

then, it follows that

$$\begin{aligned} Z &= \sum_i \sum_j \exp \left[-\beta \left(E_i^{(a)} + E_j^{(b)} \right) \right], \\ &= \sum_i \exp \left[-\beta E_i^{(a)} \right] \sum_j \exp \left[-\beta E_j^{(b)} \right], \\ &= Z_a Z_b, \end{aligned}$$

and with this result at hand, we know that we usually deal with $\ln(Z)$ instead of Z itself, and in this case we have exactly that, this is

$$\begin{aligned} \ln Z &= \ln (Z_a Z_b), \\ &= \ln Z_a + \ln Z_b, \end{aligned}$$

therefore the energy will be given as follows

$$\begin{aligned} \langle U \rangle &= k_B T^2 \frac{\partial \ln Z_a Z_b}{\partial T}, \\ \Rightarrow \langle U \rangle &= k_B T^2 \left(\frac{\partial \ln Z_a}{\partial T} + \frac{\partial \ln Z_b}{\partial T} \right), \end{aligned}$$

Now, with this in mind, we have, our particular problem

$$\begin{aligned} Z &= \sum_i \sum_j \exp \left[-\beta \left(E_i^{(fp)} + E_j^{(sho)} \right) \right], \\ \Rightarrow Z &= \sum_i \exp \left[-\beta E_i^{(fp)} \right] \sum_j \exp \left[-\beta E_j^{(sho)} \right] \end{aligned}$$

and from this we have to calculate the contribution for each one this is

$$Z_{fp} \quad \& \quad Z_{sho},$$

but using the same idea we can write

$$Z_{fp} = Z_1, \quad \& \quad Z_{sho} = Z_2^2$$

where Z_1 and Z_2 are the partition functions of the particle in a box, and the simple harmonic oscillator, but in 1D, this is

$$Z_{trans} = V n_Q,$$

where n_Q is the quantum concentration, which is given by

$$n_Q = \frac{1}{h^3} \left(\frac{mk_B T}{2\pi} \right)^{3/2},$$

but let's rewrite it in a more convenient way, this is

$$\begin{aligned} Z_{trans} &= \frac{V}{h^3} \left(\frac{m}{2\pi} \right)^{3/2} (k_B T)^{3/2}, \\ Z_{trans} &= \alpha \beta^{-3/2}, \end{aligned}$$

where

$$\alpha = \frac{V}{h^3} \left(\frac{m}{2\pi} \right)^{3/2}, \quad \beta = \frac{1}{k_B T}$$

and for the simple harmonic oscillator we have

$$Z_{vib} = \frac{\exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1 - \exp(-\beta\hbar\omega)}.$$

- (3) On the other hand, for this kind of calculations it's easier to take derivatives with respect to β , or at least for the energy it's quite convenient, this using the chain rule we have

$$\begin{aligned} U &= k_B T^2 \frac{\partial \ln Z}{\partial T} = -\frac{d}{d\beta} \ln Z, \\ \implies U &= -\frac{d}{d\beta} \ln Z, \end{aligned}$$

but as stated before the partition function is the product of two independent contributions, thus

$$\begin{aligned} U &= U_{trans} + U_{vib}, \\ &= -\left[\frac{d}{d\beta} \ln Z_{trans} + -\frac{d}{d\beta} \ln Z_{vib} \right], \end{aligned}$$

thus for U_{trans} we have

$$\begin{aligned} U_{trans} &= -\frac{d}{d\beta} \ln Z_{trans} \\ &= -\frac{d}{d\beta} \left[\ln \left(\alpha \beta^{-3/2} \right) \right], \\ &= -\frac{d}{d\beta} \left[\ln \alpha - \frac{3}{2} \ln \beta \right], \end{aligned}$$

and from this we have

$$\begin{aligned} U_{trans} &= \frac{3}{2} \frac{d}{d\beta} \ln \beta, \\ \implies U_{trans} &= \frac{3}{2} \frac{1}{\beta} \end{aligned}$$

therefore

$$U_{trans} = \frac{3}{2} k_B T.$$

On the other hand, for U_{vib} we have

$$\begin{aligned}
 U_{vib} &= -\frac{d}{d\beta} \left[\ln \left(\frac{\exp \left(-\frac{1}{2}\beta\hbar\omega \right)}{1 - \exp(-\beta\hbar\omega)} \right) \right], \\
 &= -\frac{d}{d\beta} \left[\ln \left(\exp \left(-\frac{1}{2}\beta\hbar\omega \right) \right) - \ln(1 - \exp(-\beta\hbar\omega)) \right], \\
 &= -\frac{d}{d\beta} \left[-\frac{1}{2}\beta\hbar\omega - \ln(1 - \exp(-\beta\hbar\omega)) \right], \\
 &= \frac{1}{2}\hbar\omega + \frac{\hbar\omega \exp(-\beta\hbar\omega)}{1 - \exp(-\beta\hbar\omega)}, \\
 &= \hbar\omega \left(\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1} \right),
 \end{aligned}$$

therefore

$$U_{vib} = \hbar\omega \left(\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1} \right),$$

and the total contribution is given by

$$U = \frac{3}{2}k_B T + \hbar\omega \left(\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1} \right),$$

now, in the limit given

$$k_B T \ll \hbar\omega \implies 1 \ll \beta\hbar\omega,$$

the term with the exponential goes to infinity and the denominator goes to 0, and the other factor is just a constant, thus we end up with the result

$$U \approx \frac{3}{2}k_B T,$$

which matches with the classical result.

- (4) Now, in the case of high temperature, we have $k_B T \gg \hbar\omega$, and this implies that we can Taylor expand the term with the exponential as follows

$$\frac{1}{\exp(\beta\hbar\omega) - 1} \approx \frac{1}{\beta\hbar\omega},$$

thus

$$\begin{aligned}
 U &\approx \frac{3}{2}k_B T + \hbar\omega \left(\frac{1}{2} + \frac{1}{\beta\hbar\omega} \right), \\
 &\approx \frac{3}{2}k_B T + \frac{\hbar\omega}{2} + \frac{1}{\beta},
 \end{aligned}$$

and from this we can see that

$$U \approx \frac{3}{2}k_B T + k_B T,$$

this is

$$U \approx \frac{5}{2}k_B T,$$

which again, matches with the equipartition theorem.

- (5) This result is in agreement with the analysis presented in the HW 1, in which we found the following: “the spacings between vibrational levels and between rotational levels about the molecular axis are much larger than $k_B T$, which implies that classical thermodynamics, including the equipartition theorem, do not apply”. And even more “..for rotations about the two axes perpendicular to the molecular axis, however, the spacings between energy levels are much smaller than $k_B T$, so equipartition does apply.”

Problem 3. The molar concentration of carbon dioxide in the Earth's atmosphere is currently about 420 ppm (0.042), and rising. Even if we were to stop adding CO_2 , it will take hundreds of years for what is already there to be removed by natural processes. It has therefore been proposed that we actively remove CO_2 from the atmosphere, liquify it, and inject it deep underground or deep into the ocean, where the pressure is sufficient to keep it liquid and, hopefully, in place for geological times. In this problem, you will examine the minimum energy cost of such an approach set by fundamental principles of thermodynamics. (Practical technologies will probably require at least twice that much energy.)

- (1) Let's suppose we want to isolate and liquify 1 kg of CO_2 . What is the volume of air that contains that much CO_2 ? How many moles of CO_2 does it contain? How many moles of air?
- (2) Separating the CO_2 means going from a state of volume V_0 containing the mixed gas, to a state in which there is a volume V_{CO_2} that contains just CO_2 , and a volume $(V_0 - V_{\text{CO}_2})$ that contains just air. Assume that the temperature and pressure remain constant. What is the change in entropy of the CO_2 in this process? What is the change in entropy of the air?
- (3) What is the minimum energy input required to effect this separation? Give an answer in J/kg
- (4) At room temperature, CO_2 liquifies at a pressure of about 56 atm. How much work is required to compress the separated CO_2 isothermally to that pressure? Give an answer in J/kg
- (5) To put these numbers in some perspective, compare the energy required to separate and liquify the CO_2 released annually in the US to the country's annual electricity consumption.

Solution. Let's start with the solution:

- (1) The ppm of CO_2 in the atmosphere is given by 421, which is around 0.04% of the gases in the atmosphere, therefore if we assume that we can model the CO_2 as an ideal gas, this is

$$pV = nRT,$$

thus using the fact that the molar mass of the CO_2 is also given by 44.01 we have that

$$V = n \frac{RT}{p}.$$

But we need to convert the CO_2 mass to moles, and for that we are going to use using its molar mass as follows:

$$\begin{aligned} \text{moles of } \text{CO}_2 &= \frac{\text{mass of } \text{CO}_2}{\text{molar mass of } \text{CO}_2} \\ \text{moles of } \text{CO}_2 &= 0.0226 \text{ mol}, \end{aligned}$$

on the other hand the molar mass of air, on average is given by 28.97g/mol, and after plug those quantities in the ideal gas equation we have that the volume occupied by 1 kg of CO_2 is given by approximately

$$V = 86296.17 \text{ L}.$$

- (2) For the change in entropy let's model this as an isobaric compression, and for this we know that

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right),$$

thus, for the CO₂, we have that

$$\Delta S_{\text{CO}_2} = nR \ln \left(\frac{V_{\text{CO}_2}}{V_0} \right),$$

and in the same way, for the air, we have

$$\Delta S_{\text{air}} = nR \ln \left(\frac{V_0 - V_{\text{CO}_2}}{V_0} \right).$$

- (3) -

- (4) For this process we're going to model it as an isothermal compression, thus we have that

$$W =$$

To calculate the work required to compress the separated CO₂ isothermally to a pressure of 56 atm, we can use the formula for the work done during an isothermal compression of a gas:

$$W = - \int_{V_i}^{V_f} P dV,$$

but because the compression is isothermal, the pressure and temperature remain constant, thus we have

$$W = -P \int_{V_i}^{V_f} dV,$$

but again, the compression is isothermal, we can use the ideal gas law to relate the initial and final volumes as follows

$$p_i V_i = p_f V_f = \text{constant},$$

and if assume that the initial pressure is $p_i = 1$ atm, and the final is $p_f = 56$ atm, we have that

$$V_i = 56V_f,$$

and from this we have

$$W = -P \int_{V_i}^{V_f} dV,$$

$$W = 55pV_f,$$

now using the fact that the work done per unit mass is equal to W divided by the mass of CO₂, we have

$$W = \frac{55pV}{m_{\text{CO}_2}},$$

and now, in order to find V_f we can use the fact that at room temperature, the volume occupied by 1 kg of liquid CO₂ at 56 atm pressure would be the reciprocal of its density at that pressure. The density of liquid CO₂ at 56 atm is approximately 0.881 kg/L, thus if we put the

numbers, this will be

$$W \approx 3469.38 \left[\frac{J}{kg} \right]$$

- (5) The energy required to compress CO₂ to a pressure of 56 atm, which is approximately 3469.38 J/kg. And we're going to consider that the annual CO₂ emissions in the US is around 5×10^{12} kg, and finally According to the U.S. Energy Information Administration (EIA), the annual electricity consumption in the US is around 3.5 to 4 trillion kilowatt-hours (kWh), and let's use former as an upper bound, thus we have that the total Energy for CO₂ separation is equal to the energy required per kg times the total of CO₂ emissions, and using the previous result we have that total energy for CO₂ separation is

$$3469.38 \times (5 \times 10^{12}) \left[\frac{Jkg}{kg} \right],$$

thus the total energy of separation is given by

$$1.73469 \times 10^{16} J,$$

and on the other hand, the electricity consumption is given by

$$4 \times 10^{12} (3.6 \times 10^6) \left[kWh \frac{J}{kWh} \right],$$

which is equal to

$$1.44 \times 10^{19} J,$$

thus comparing the previous results we can see that the energy required to separate and liquefy the CO₂ emitted annually in the US is smaller by three orders of magnitude compared to the country's annual electricity consumption. I think this suggest that it's worthwhile to think in the CO₂, I mean, it's still quite expensive, but small compared to the overall energy consumption of the nation.

Problem 4. In class, we showed that the Planck blackbody radiation formula has the form

$$P(\omega) = A \left(\frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \right),$$

where A is a constant with no dependence on ω or T , and $dP(\omega)$ represents the intensity in a frequency interval of width $d\omega$ at frequency ω .

- (1) The sun is well modeled as a blackbody with an effective temperature of about 5800 K. Using that model, find the frequency at which the sun's radiation has its maximum intensity. What is the wavelength corresponding to that frequency? Give a numerical value. What part of the electromagnetic spectrum does that frequency/wavelength fall in?
- (2) Wien's displacement law is a convenient way to find the wavelength at the peak of the blackbody spectrum. It is generally written

$$\lambda_{peak} = \frac{b}{T}, \quad b = 2.898 \times 10^{-3} \text{ mK}.$$

Does your analysis agree with an expression of this form; that is, that the peak wavelength should depend inversely on the temperature?

- (3) Use the Wien displacement law, with the given value of b , to find the peak wavelength for the Sun's spectrum. Again, give a numerical value. Compare the result with your answer in 1.
- (4) Your answers in 1 and 3 should not agree. See if you can figure out where the discrepancy comes from. You will likely need to look up the derivation of the Wien displacement expression.

Solution. Let's begin:

- (1) By definition ω is the angular frequency, and in order to not deal of factors of 2π , let's work with

$$\omega = 2\pi\nu,$$

and with this $P(\omega)$ can be written as

$$P(\nu) = \frac{A(2\pi\nu)^3}{\exp[\beta\hbar(2\pi\nu)] - 1},$$

where $\beta = 1/k_B T$, and because $\hbar = h/2\pi$ we have

$$P(\nu) = \frac{8\pi^3 A \nu^3}{\exp[\beta h \nu] - 1},$$

now, going even further, let's make the following change of variables

$$x = \beta h \omega,$$

and with this we have

$$P(x) = \frac{8\pi^3 A}{\beta^3 \hbar^3} \left(\frac{x^3}{\exp(x) - 1} \right),$$

and let's rename

$$A' = \frac{8\pi^3 A}{\beta^3 \hbar^3},$$

then it follows that

$$P(x) = A' \left(\frac{x^3}{\exp(x) - 1} \right),$$

and from this we have the derivative

$$\frac{dP}{dx} = A' \left(\frac{3x^2}{\exp(x) - 1} - \frac{x^3 \exp(x)}{(\exp(x) - 1)^2} \right),$$

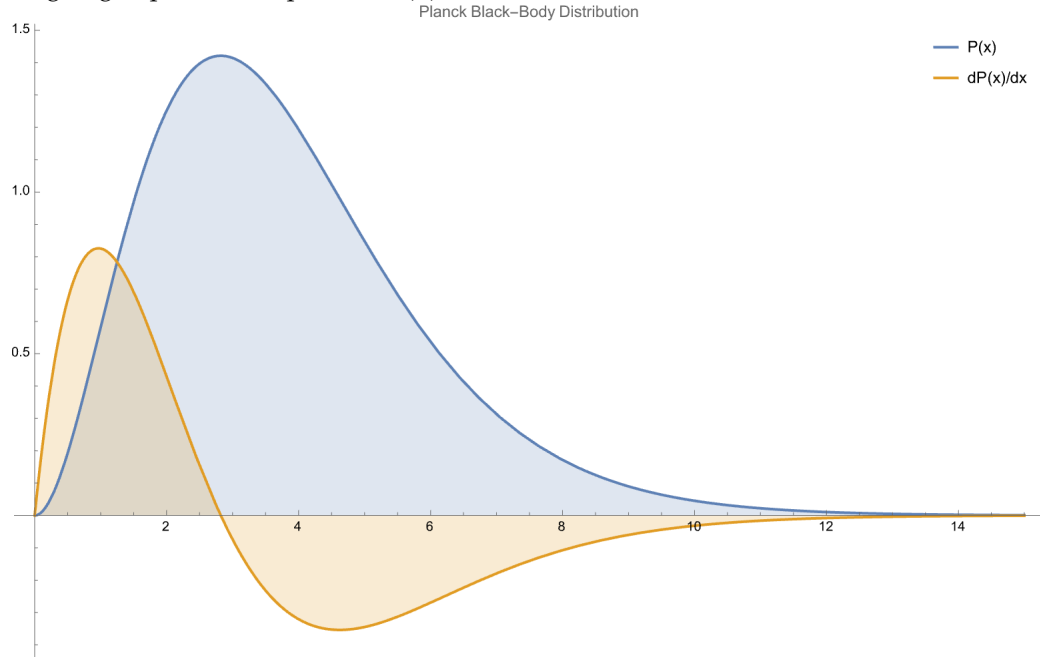
and in order to obtain the maximum we need to solve

$$\frac{3x^2}{\exp(x) - 1} - \frac{x^3 \exp(x)}{(\exp(x) - 1)^2} = 0 \iff \frac{x^2}{\exp(x) - 1} \left(3 - \frac{x \exp(x)}{\exp(x) - 1} \right),$$

and from that we have two options, one is $x = 0$, and the other one is given by the condition

$$3 - \frac{x \exp(x)}{\exp(x) - 1} = 0 \iff x = 3(1 - \exp(x)),$$

but the previous equation is a transcendental equation, and in general is hard to find an analytical solution, or impossible in some cases. After plotting and exploring the behavior of the function and its derivative I decided to solve the equation it using Newton's method, and after my initial guess was $x_0 = 2$, let's me elaborate a little more on the reason for that, but first, I'm going to present the plots of $P(x)$ and its derivative dP/dx :



As we can see, the maximum is located around $x = 3$, but with the condition $x < 3$, that's why I choose the initial guess $x = 2$. Now, the numerical result is given by

$$x_{max} = 2.82144,$$

but we know that

$$x = \beta h\nu, \quad \beta = \frac{1}{k_B T},$$

thus, we have that

$$\frac{h\nu_{max}}{k_B T} = 2.82144$$

thus

$$\nu_{max} = 2.82144 \frac{k_B T}{h}.$$

Now if we consider $T = 5800$ K, and

$$h = 6.62607015 \times 10^{-34} \text{ [Js]}, k_B = 1.380649 \times 10^{-23} \text{ [J/K]}$$

we have that

$$\nu_{max} = 2.82144 \left[\frac{(1.380649 \times 10^{-23}) (5800)}{6.62607015 \times 10^{-34}} \right] \left[\frac{\frac{J}{K} K}{Js} \right],$$

and if we use

$$c = \nu \lambda,$$

we have

$$\begin{aligned} \lambda_{max} &= \frac{c}{\nu_{max}}, \\ \implies \lambda_{max} &= 8.76303 \times 10^{-7} \text{ m}, \end{aligned}$$

and from that we have

$$\lambda_{max} = 876.303 \text{ nm}.$$

For b), yes my analysis shows a functional dependence of $1/T$ in the peak, and this comes from the fact of making that change of variables which at the end, will give us the functional dependence showed in Wien's law.

c) Using the Wien's law with the temperature $T = 5800$ K, we have

$$\begin{aligned} \lambda &= \frac{2.898 \times 10^{-3}}{5800} \left[\frac{mK}{K} \right], \\ \implies \lambda &= 4.99655 \times 10^{-7} \text{ m} \\ \therefore \lambda &= 499.655 \text{ nm}, \end{aligned}$$

and as we can see the peak do not match.

d) I have some thoughts on why the values of the peak do not coincide, one of them is because if we write the distribution in terms of λ since the beginning, the functional form will be different, and that will move the peak, this is because of the relation between those variables, this is

$$c = \lambda \nu \implies d\nu = -\frac{c}{\lambda^2} d\lambda,$$

and the full distribution will be

$$P(\lambda) = \frac{8\pi hc}{\lambda^5} \left(\frac{A}{\exp\left(\frac{\beta hc}{\lambda}\right) - 1} \right),$$

which as we can see have a different functional form.

Problem 5. In this problem you will apply the idea of chemical potential to two very different real-world contexts.

- (1) Centrifugal isotope separation. Gas centrifuges are used to separate isotopes of uranium to produce fuel that is sufficiently enriched for fission applications.
 - (a) Consider a cylinder of gas, of radius R , rotating at angular velocity ω . In order to move a particle inward by an amount $-dr$, one must exert an inward force equal to the centripetal force at that radius, doing work on the particle. Use this fact to write an expression for the total chemical potential as a function of r .
 - (b) Use your result in (1a) to determine the ratio of the gas density at radius R to the density at $r = 0$.
 - (c) In uranium enrichment, the goal is to increase the concentration of the fissile isotope ^{235}U , which is naturally only 0.7%, with the remainder being almost entirely non-fissile ^{238}U . Because uranium is not normally a gas, it is first reacted with fluorine to make UF_6 . A typical enrichment centrifuge may have a radius of 0.2 m and rotate at a speed of 1500 revolutions per second. At the perimeter of the centrifuge, will the concentration of ^{235}U be enhanced or reduced? What will be the new concentration at that point?
- (2) Sap in trees. Giant sequoias are among the tallest trees in the world, reaching heights of 100 m. This raises an interesting question: how does sap get to the top of the tree? Atmospheric pressure cannot support a column of water higher than about 10 m.
 - (a) Consider a very simplified model of sap in the tree as represented by a thin vertical tube filled with liquid water. The bottom is immersed in a pool of water, and the density of water vapor in the air just above the water is n_0 . The top is at height h , where the relative humidity is $r = n(h)/n_0$. Assume that the water in the tube is in diffusive equilibrium with the water vapor in the air at both the top and bottom of the tube. If that is the case, what is the difference in internal chemical potential $\Delta\mu_{\text{int}}$ between the top and the bottom?
 - (b) In addition, there is an external chemical potential difference due to the change in gravitational potential energy. Taking this into account, what is the total chemical potential difference (internal + external) between the top and the bottom?
 - (c) If $\mu_{\text{tot}}(h) < \mu_{\text{tot}}(0)$, then water will flow upwards in the tube, feeding the top of the tree. Once $\mu_{\text{tot}}(h) \geq \mu_{\text{tot}}(0)$, upward flow will stop. Using this principle, find the maximum height h_{max} to which the tree can move sap, as a function of the relative humidity r . Find the numerical value for $r = 90\%$. Is your answer consistent with the existence of giant sequoias?

Solution. Before doing any calculation I would like to write some definitions that are useful for the following discussion: let's suppose we have two systems S_1 and S_2 , each one with its own thermodynamical parameters, if we put the system in thermal contact and let them exchange particles, after some time, we will reach equilibrium, assuming the connected system are closed. Thus the condition

for diffusive equilibrium can be expressed as

$$\mu_1 = \mu_2 = \mu_0,$$

where μ_0 represents the chemical potential of the system at some “point of reference”. Having said that, we know that particles flow from high chemical potential to lower chemical potential, in the same way as we observe heat flow, thus a difference in chemical potential acts in some sense as a driving force for the transfer of particles. And even more, we know that only differences in chemical potential have physical meaning, and we’re also free to choose our “zero” potential reference. Now, with this in mind, we know that when a potential is present, we can express the total chemical potential as the sum of the internal chemical potential and the external chemical potential, and the former is defined as the potential energy per particle in the external potential, this is

$$\Delta\mu_{tot} = \Delta\mu_{int} + \Delta\mu_{ext}.$$

Now, in the following two problems I’m going to model the system as an ideal gas, I know this is not very accurate, in particular for the tree problem, but still, it’ll give us a good feeling of the system, and for this reason I think it’s important to write the chemical potential for an ideal gas, this is

$$\mu = k_B T \ln \left(n \lambda_{th}^3 \right),$$

but we also know that

$$n_Q^{-1/3} = \lambda_{th},$$

thus, we can write

$$\mu = k_B T \ln \left(\frac{n}{n_Q} \right).$$

(1) Centrifugal Isotope Separation:

(a) In this case the external potential is given by the centripetal force, which is given by the following expression

$$f_c = ma_c,$$

where we know $a_c = \omega^2 r$, where ω is the angular velocity. Thus from this we have

$$f_c = m\omega^2 r,$$

but as stated in the problem, in order to move a particle inward by an amount $-dr$, one must exert an inward force equal to the centripetal force at that radius, doing work on the particle, this is

$$-m\omega^2 r dr,$$

but, on the other hand, by definition we know that the chemical potential is the amount of energy we need in order to add one particle to the system, thus we have

$$\begin{aligned} \mu &= -m\omega^2 \int r dr, \\ \implies \mu &= -\frac{m}{2} \omega^2 r^2. \end{aligned}$$

Now, with this we have that the total chemical potential is given by

$$\mu_{tot} = k_B T \ln \left(\frac{n(r)}{n_Q} \right) - \frac{m}{2} \omega^2 r^2.$$

(b) Now, if we imposing the condition of diffusive equilibrium, this is

$$\mu_{tot} = \mu_0,$$

and even more assuming an ideal gas, we have

$$\mu_{tot} = k_B T \ln \left(\frac{n(r)}{n_Q} \right) - \frac{m}{2} \omega^2 r^2 = \mu_0,$$

and in this case we choose our reference potential such that

$$\mu_0 = k_B T \ln \left(\frac{n_0}{n_Q} \right),$$

where $n_0 = n(0)$, we have that

$$\begin{aligned} k_B T \ln \left(\frac{n(r)}{n_Q} \right) - \frac{m}{2} \omega^2 r^2 &= k_B T \ln \left(\frac{n_0}{n_Q} \right), \\ \Rightarrow \ln \left(\frac{n(r)}{n_Q} \frac{n_Q}{n_0} \right) &= \frac{m}{2k_B T} \omega^2 r^2, \end{aligned}$$

thus

$$n(r) = n_0 \exp \left(\frac{m \omega^2 r^2}{2k_B T} \right)$$

(2) Tree:

(a) As above, if we assume that the system is in diffusive equilibrium, and there are no external fields in the system, and even more, approximating the problem as an ideal gas,

$$\Delta \mu_{int} = k_B T \ln \left(\frac{n}{n_Q} \right),$$

where $n = n_0 r$.

(b) Now, with the previous result and assuming an external potential due to the gravitational field we have

$$\Delta \mu_{ext} = mgh,$$

and even more, assuming again, diffusive equilibrium

$$\mu_{tot} = \mu_0,$$

such that our reference point is given by

$$k_B T \ln \left(\frac{n_0}{n_Q} \right),$$

then we have

$$k_B T \ln \left(\frac{n}{n_Q} \right) + mgh = k_B T \ln \left(\frac{n_0}{n_Q} \right),$$

thus

$$mgh = -k_B T \ln \left(\frac{n}{n_Q} \frac{n_Q}{n_0} \right),$$

and from this we have

$$h = \frac{k_B T}{mg} \ln \left(\frac{n_0}{n} \right),$$

but we know that

$$\frac{n}{n_0} = r,$$

thus

$$h = \frac{k_B T}{mg} \ln \left(\frac{1}{r} \right).$$

- (c) Finally, if we consider the humidity as $n(r)/n_0 = 0.9$, $T = 300$ K, and the mass of water as $m = 18$ g, then, then numerical value, after the corresponding conversions will be

$$h = 1490.04 \text{ m},$$

which is a really high number, consistent in some sense with the giant sequoias, but I not expect to have a good map with a real tree, because I'm not sure if the sap of a tree can be well modeled by an ideal, gas, I suspect that this is not the case, however, this give us some insight into the physical mechanism.

Resources. List any resources, aside from course materials, that you consulted in doing this assignment, and describe how you used them and for which problem(s). This could include web sites, videos, computational tools (e.g. Desmos), or AI tools (e.g. ChatGPT). If you didn't use any such resources, write "None."

- I used the following books to check the theory and useful identities:
 - Blundell, Stephen J., and Katherine M. Blundell. Concepts in thermal physics. Oup Oxford, 2010.
 - Kittel, Charles, and Herbert Kroemer. "Thermal physics." American Journal of Physics 39, no. 1 (1971): 126-127.
 - Young, Hugh D. Sears y Zemansky, Física universitaria." (2013).
- On the part of AI tools, I sed ChatGPT to guide in the unit conversions and to obtain data, in particular for problem 3 for the annual energy consumption in the USA.