

## Homework 10

Due Friday, December 11th at 10pm

Finish reading [Chapter 2](#) of Schroeder's book *Thermal Physics*. You particularly want to understand sections 2.5 and 2.6 for this problem set. Review any part of our handout on [standard deviations and probabilities](#) that would be useful to you.

The goal of problems **1** to **6** on this set is to connect the two formulations of entropy that we have been discussing in class. When we first started studying entropy we introduced the thermodynamic notion of the "quality of heat":  $\Delta S = \int_a^b \frac{dQ}{T}$ . Instead the statistical notion of entropy is:  $S = k \ln \Omega$ , where  $\Omega$  is the multiplicity of the macrostate under consideration. How are these related?

In problems **1** to **6** you will show the relation explicitly for an idea gas.

**Problem 1** (Another form of Stirling's approximation)

First we need a mathematical tool. In class we discussed Stirling's approximation:

$$n! \approx \sqrt{2\pi n} e^{-n} n^n.$$

(a) Take the natural logarithm of this expression and prove that:

$$\ln n! \approx n \ln n - n + \frac{1}{2} \ln(2\pi n).$$

(b) Use Stirling's approximation to calculate:  $\ln(100!)$ ,  $\ln(10^6!)$  and  $\ln(10^{23}!)$ . Explain why we often drop the last term of your answer from part (a) and only use

$$\ln n! \approx n \ln n - n.$$

**Problem 2** (In your own words)

Read section 2.5 of Schroeder for a second time. Close your book and explain why the multiplicity  $\Omega_1$  is proportional to the volume of momentum space  $V_p$  in your own words.

**Problem 3** (Sackur-Tetrode Equation)

Using your result from Problem 1 and Schroeder's result in equation (2.40), derive the Sackur-Tetrode equation

$$S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right],$$

from the statistical definition of entropy  $S = k \ln \Omega$ . Here  $h$  is Planck's constant.

**Problem 4** (Deriving the Entropy-Heat Relation)

Using the Sackur-Tetrode equation, show that during the reversible isothermal expansion of a monatomic ideal gas, the change in entropy is related to the heat input  $Q$  by the simple formula

$$\Delta S = \frac{Q}{T}.$$

You have just derived our thermodynamic notion of entropy from our statistical notion in the special case of an ideal gas and an isothermal process.

We won't prove it in this course, but this formula is valid for any reversible process. Show, however, that it is not valid for the free expansion process that we discussed in class.

**Problem 5** (Validity)

As you know, you made several approximations in your derivation of the Sackur-Tetrode equation. In particular, according to the Sackur-Tetrode equation, the entropy of a monatomic ideal gas can become negative when its temperature (and hence its energy) is sufficiently low. Of course this is absurd.

(a) Explain why.

So, the Sackur-Tetrode equation must be invalid at very low temperatures. Suppose you start with a sample of helium at room temperature and atmospheric pressure, then lower the temperature holding the density fixed. Pretend that the helium remains a gas and does not liquefy.

(b) Below what temperature would the Sackur-Tetrode equation predict that  $S$  is negative?

The behavior of gases at very low temperatures is fascinating and led to a nobel prize for the creation of a Bose-Einstein condensate in recent years. This is one of the topics that is often studied in the Thermal Physics course.

**Problem 6** (An example)

Use the Sackur-Tetrode equation to calculate the entropy of a mole of argon gas at room temperature and atmospheric pressure. Why is the entropy greater than that of a mole of helium under the same conditions?

The rest of the problems are on different topics

**Problem 7** (Wien's Law)

In class I also stated the Wien displacement law that the most energy is emitted at a wavelength  $\lambda_{\max}$  that is inversely proportional to the temperature of the black body, that is,

$$\lambda_{\max} = \frac{\alpha}{T},$$

where the Wien constant  $\alpha$  has the empirical value  $\alpha = 2.8977 \times 10^{-3}$  K m.

(a) Using our result  $u(T, \lambda)$  write out the equation that you would need to solve in order to find  $\lambda_{\max}$ . Don't try to solve it yet, but do simplify it as much as you can. Be careful in your derivation, you will need to apply both the product rule and the chain rule multiple times.

You should find that your result from part (a) can be written very neatly in terms of the dimensionless variable  $x = \frac{hc}{\lambda kT}$ . The easiest way to find  $\lambda_{\max}$  is first to solve your equation from part (a)

for the appropriate value of  $x$  and then to plug in the definition of  $x$  and solve for  $\lambda$ . This is how we will proceed.

(b) Express your result from part (a) in terms of  $x$ . The resulting equation is transcendental and cannot be solved exactly in a straightforward manner. However, by properly organizing your equation you should be able to drop an exponentially small term and arrive at a very simple approximate value for  $x$ . Do this.

(c) Use your result from part (b) to find an equation for  $\lambda_{\max}$ . Does your result scale properly with  $T$ ?

(d) Find a formula and value for the Wien constant  $\alpha$  using your approximation from (b). By what percentage does it differ from the empirical value?

(e) Find a better value for the Wien constant by using python. You can do this as follows: Start a new jupyter notebook, import the math package, and use the command `from scipy.optimize import fsolve` to import the fsolve command. The fsolve command allows you to numerically find where a function vanishes near a given starting point. Use your result from part (b) to define a function in python, call it `fMax(x)`, that when it is set equal to zero will be an equation for the desired value of  $x$ . Then use the python command `fsolve(fMax, InitGuess)` to find the desired value of  $x$ . Here `InitGuess` is the value of your initial guess and it makes sense to use your approximate value for the solution from (b). [Hint: If you start with an equation of the form  $g(x) = 5$ , then you will want your `fMax` function to be defined by  $fMax(x) = g(x) - 5$  since fsolve looks for **zeroes** of the function.]

Find a new value for the Wien constant using your new value for  $x$ . How does this new value compare to the empirical value?

For the last four problems read [Chapter 1](#) and [pp 24-40 of Chapter 2](#) from Griffiths' *Introduction to Quantum Mechanics*.

**Problem 8** (Occupation of states)

(a) Based on Boltzmann's probability for occupying states and the Bohr model, in a gas of hydrogen at room temperature how many times more atoms have their electrons in the lowest energy orbit (known as the "ground state") than in the next lowest orbit (known as the "first excited state")? [Hint: You do not need to calculate the partition function  $Z$  in order to answer this question.]

(b) What temperature would the gas have to be at for there to be 100 times as many atoms with electrons in the ground state as in the first excited state?

**Problem 9** (Characterizing a wave function)

Consider the wave function

$$\Psi(x, t) = Ae^{-\lambda|x|}e^{-i\omega t},$$

where  $A$ ,  $\lambda$ , and  $\omega$  are positive real constants.

- (a) Normalize  $\Psi$ .
- (b) Determine the expectation values of  $x$  and  $x^2$ .
- (c) Find the standard deviation of  $x$ . Sketch the graph of  $|\Psi|^2$ , as a function of  $x$ , and mark the points  $(\langle x \rangle + \sigma)$  and  $(\langle x \rangle - \sigma)$ , to illustrate the sense in which  $\sigma$  represents the “spread” in  $x$ . What is the probability that the particle would be found outside this range?

**Problem 10** (Square well practice)

Calculate  $\langle x \rangle$ ,  $\langle x^2 \rangle$ ,  $\langle p \rangle$ ,  $\langle p^2 \rangle$ ,  $\sigma_x$  and  $\sigma_p$ , for the  $n$ th stationary state of the infinite square well. Check that the uncertainty principle is satisfied. Which state comes closest to the uncertainty limit?

**Problem 11** (Superpositions) A particle in the infinite square well has as its initial wave function an even mixture of the first two states:

$$\Psi(x, 0) = A[\psi_1(x) + \psi_2(x)].$$

- (a) Normalize  $\Psi(x, 0)$ . (That is, find  $A$ . This is very easy, if you exploit the orthonormality of  $\psi_1$  and  $\psi_2$ . Recall that, having normalized  $\Psi$  at  $t = 0$ , you can rest assured that it *stays* normalized—if you doubt this, check it explicitly after doing part (b).)
- (b) Find  $\Psi(x, t)$  and  $|\Psi(x, t)|^2$ . Express the latter as a sinusoidal function of time, as in Example 2.1 in the text. To simplify the result, let  $\omega \equiv \pi^2 \hbar / 2mL^2$ , where  $L$  is the width of the well.
- (c) Compute  $\langle x \rangle$ . Notice that it oscillates in time. What is the angular frequency of the oscillation? What is the amplitude of the oscillation? (If your amplitude is greater than  $L/2$ , go directly to jail.)
- (d) Compute  $\langle p \rangle$ . (As Peter Lorre would say, “Do it ze *kveek* vay, Johnny!”)
- (e) if you measured the energy of this particle, what values might you get, and what is the probability of getting each of them? Find the expectation value of  $H$ . How does it compare with  $E_1$  and  $E_2$ ?