

## Problem 1. Logarithmic Derivatives

The percent change in  $x$  is  $dx/x$ . Thus it is common to see

$$x \frac{dy}{dx} \tag{1}$$

which is the change in  $y$  per *percent* change in  $x$ . This is known as a logarithmic derivative with respect to  $x$  since

$$x \frac{dy}{dx} = \frac{dy}{d \ln x} \tag{2}$$

Similarly the *percent* change in  $y$  per change in  $x$  is

$$\frac{1}{y} \frac{dy}{dx} = \frac{d \ln y}{dx} \tag{3}$$

Logarithmic derivatives appear frequently in the course and recognizing this can help.

Let  $y \propto x^k$  with  $k$  a real number. Show that the percent change in  $y$  is proportional to the percent change in  $x$

$$\frac{dy}{y} = k \frac{dx}{x} \tag{4}$$

Show also

$$x \frac{\partial}{\partial x} = k y \frac{\partial}{\partial y} \tag{5}$$

Briefly answer:

(i) With  $\beta = 1/kT$ , relate

$$T \frac{\partial}{\partial T} \quad \text{and} \quad \beta \frac{\partial}{\partial \beta} \tag{6}$$

(ii) If  $E = p^2/2m$ , how is  $dE/E$  related to  $dp/p$ ?

(iii) Show that if  $Z(x) = Z_1(x)Z_2(x)$  then the percent change in  $Z$  with  $x$  is a sum of the percent changes:

$$\frac{1}{Z} \frac{dZ}{dx} = \frac{1}{Z_1} \frac{dZ_1}{dx} + \frac{1}{Z_2} \frac{dZ_2}{dx} \tag{7}$$

## Problem 2. Basics of Partition Functions

### Important!

Consider a quantum mechanical system with energy levels  $\epsilon_i$  with  $i = 1, 2, \dots, n$ . Recall the definition of the partition function

$$Z(\beta) = \sum_i e^{-\beta\epsilon_i}$$

$Z$  is a the normalization constant so that the probability of being in the  $r$ -th state

$$P_r = \frac{1}{Z(\beta)} e^{-\beta\epsilon_r} \quad (8)$$

is correctly normalized

$$\sum_i P_i = 1 \quad (9)$$

The results of this problem also apply to a classical particle where (in 1D for simplicity) the single particle partition function reads

$$Z_1(\beta) = \int \frac{dx dp}{h} e^{-\beta\epsilon} \quad (10)$$

- (a) Show that the mean energy can be found if you know  $Z(\beta)$  via the formula:

$$\langle \epsilon \rangle = - \frac{1}{Z(\beta)} \frac{\partial Z}{\partial \beta} \quad (11)$$

Show also that

$$\langle \epsilon^2 \rangle = \frac{1}{Z} \left( - \frac{\partial}{\partial \beta} \right) \left( - \frac{\partial}{\partial \beta} \right) Z = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad (12)$$

What is  $\langle \epsilon^m \rangle$  in terms of the derivatives of  $Z(\beta)$ ?

From this exercise you should realize that the partition function is essentially the generating function for the probability distribution in Eq. (8). Indeed, the partition function “generates” averages of the form,  $\langle \epsilon^m \rangle$ , by differentiating  $m$  times with respect to the parameter  $-\beta$ .

- (b) Consider the two state system with energy 0 and  $\Delta$  discussed two homeworks ago. Compute the partition function, and then compute  $\langle \epsilon \rangle$  and  $\langle \epsilon^2 \rangle$  using the methods of this problem, and compare with the methods of the previous homework.
- (c) Although it is not obvious at this level, it is generally better to work with the logarithm of  $Z(\beta)$ , i.e.  $\ln Z(\beta)$ . Show that the mean and variance of the energy are determined by the derivatives of  $\ln Z$

$$\langle \epsilon \rangle = - \frac{\partial \ln Z(\beta)}{\partial \beta} \quad (13)$$

$$\langle (\delta\epsilon)^2 \rangle = \frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} = - \frac{\partial \langle \epsilon \rangle}{\partial \beta} \quad (14)$$

In particular note, that the mean  $\langle \epsilon \rangle$  determines the variance.

- (d) Now consider a hunk of material consisting of  $N$  two level atoms with energy levels 0 and  $\Delta$ . Find the total energy  $U(T)$  of the system at temperature  $T$ . Use the results of this problem to show quite generally that the specific heat  $C_V$  of the material is related to the variance in the energy of an individual atom

$$C_V = Nk \left[ \frac{\langle(\delta\epsilon)^2\rangle}{(kT)^2} \right] \quad (15)$$

Sketch  $C_V/R$  for one mole of substance, versus  $\Delta/kT$  and comment in comparison to last weeks homework.

- (e) Finally consider a classical particle in a harmonic potential from last week.

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \quad (16)$$

Compute the partition function recognizing the similarities with part (a) of the problem from last week. Compute the average energy  $\langle\epsilon\rangle$  using Eq. (13). Does your answer agree with last week's Homework and the equipartition theorem?

### Problem 3. Probability distribution of a Quantum Harmonic Oscillator

Consider a quantum harmonic oscillator in one dimension interacting with a thermal environment. This could be, for example, a single atom attached via a spring-like bond to a large stationary molecule. The vibrational frequency of the oscillator is  $\omega_0 = \sqrt{k_{\text{sp}}/m}$ .

Recall that the energy levels of a quantum harmonic oscillator are

$$\epsilon_n = \left(n + \frac{1}{2}\right) \hbar\omega_0 \quad (17)$$

with  $n = 0, 1, 2, \dots, \infty$ . Here  $\hbar\omega_0$  is one discrete unit of quantized vibrational energy. The integer  $n$  is known as the *vibrational* quantum number – the larger is  $n$ , the larger is the energy (in units of  $\hbar\omega_0$ ), and the more the atom is vibrating. For large  $n$  the energy is nearly continuous and the motion can be treated classically. A plot of the energy levels and the wave-functions are shown in Fig. 1.

Since only differences in energies are physically important, we can shift what we call “zero energy” downward by  $\frac{1}{2}\hbar\omega_0$  and write the energy levels as

$$\epsilon_n = n\hbar\omega_0 \quad (18)$$

The probability to find the oscillator in the  $n$ -th vibrational state is

$$P_n = \frac{1}{Z} e^{-\epsilon_n/kT} = \frac{1}{Z} e^{-n\hbar\omega_0/kT} \quad (19)$$

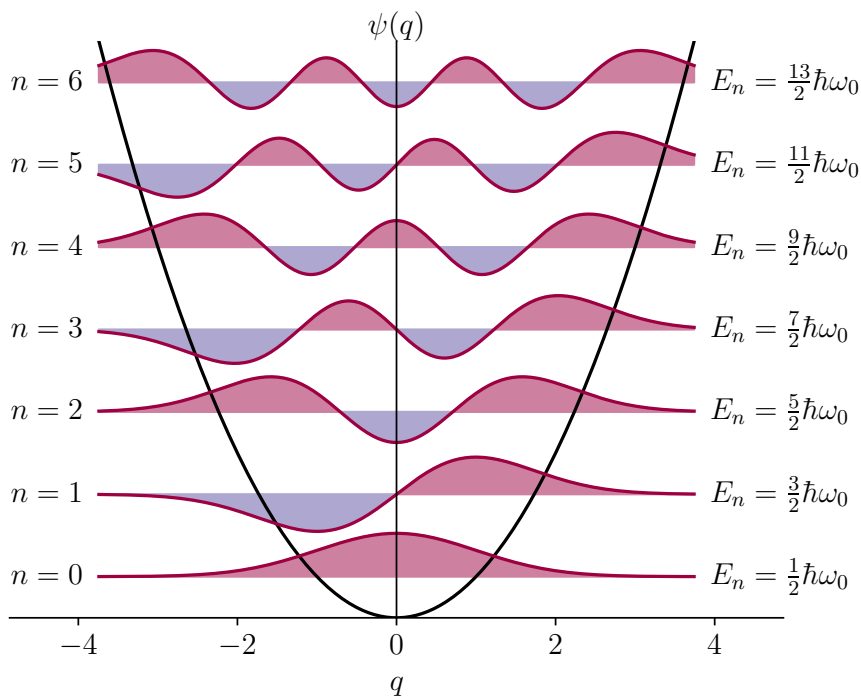


Figure 1: Energy levels  $\epsilon_n \equiv E_n = (n + \frac{1}{2})\hbar\omega_0$  and wave functions for the first six levels of the quantum harmonic oscillator.

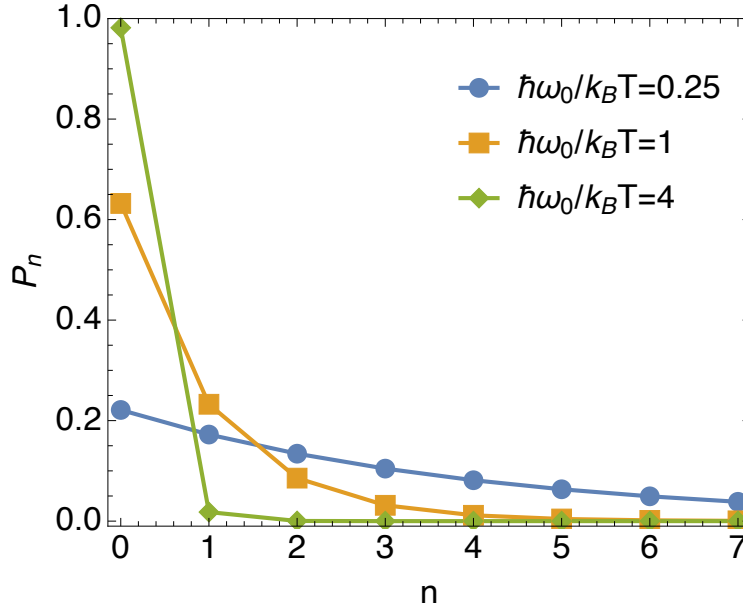


Figure 2: Probability for the oscillator to have  $n$  quanta of vibrational energy  $\hbar\omega_0$  for different values  $\hbar\omega_0/k_B T$ .

where  $Z$  is a normalizing constant.  $Z$  is known as the partition function in English, and the letter  $Z$  is short for **Zustandsumme** in German (meaning “sum over states”).

- By normalizing the probability  $P_n$ , show that  $Z = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_0}$ . I find the German name descriptive, because, as you see, it is a “sum over states”.
- Noting that  $e^{-n\hbar\omega_0/k_B T} = u^n$  with  $u = e^{-\hbar\omega_0/k_B T}$ , evaluate the sum, and determine the explicit form for  $Z$  and  $P_n$ . A plot of  $P_n$  for a variety of  $\hbar\omega_0$  is shown in Fig. 2. Describe qualitatively what this plot is telling you physically. For each of the three curves in Fig. 2, give a rough graphical estimate for the mean vibrational quantum number.

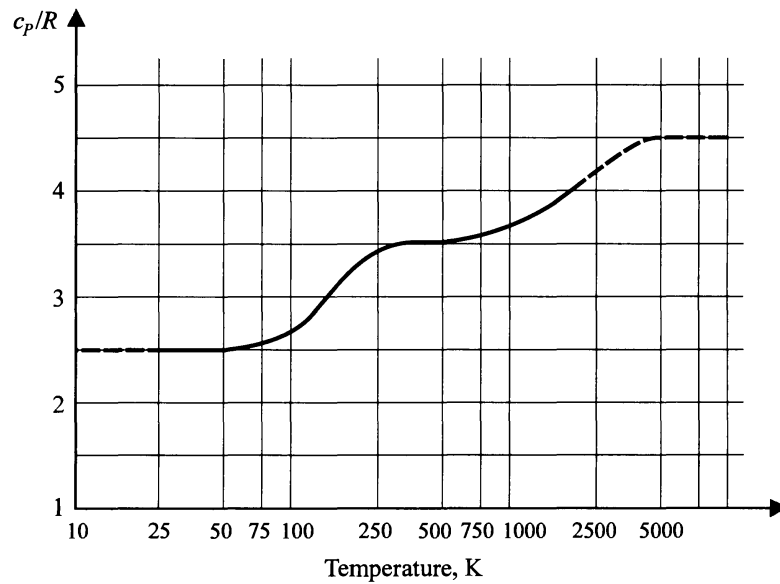
You should find

$$P_n = e^{-n\hbar\omega_0/k_B T} (1 - e^{-\hbar\omega_0/k_B T}) \quad (20)$$

- The first vibrational excited state ( $n = 1$ ) of diatomic hydrogen  $H_2$  is excited from the ground state ( $n = 0$ ) by a photon of wavelength of  $\lambda_0 = 2270$  nm. This wavelength is typical of molecular vibrations – is the photon, infrared, visible, or uv? Express the vibrational unit of energy  $\hbar\omega_0$  in eV. By looking at Fig. 2, give a rough estimate for the temperature when the mean number of vibrational quanta of energy in the oscillations of  $H_2$  becomes of order unity.

Please do *not* use constants like  $\hbar = 1.05 \times 10^{-34}$  J s and  $k_B = 1.38 \times 10^{-23}$  J/°K<sup>-1</sup>, but rather try to put it in physical terms. For instance use  $\hbar c = 197$  eV nm, and  $k_B T \simeq 1/44$  eV at freezing 273 °K. A summary of constants you will need for the course are given [on the website](#).

**Discussion:** I find  $T \simeq 6000^\circ\text{K}$ . Indeed this is about right. At room temperatures ( $T = 300^\circ\text{K}$ ) diatomic molecules translate and rotate but do not vibrate significantly. And so<sup>1</sup>,  $\langle \epsilon \rangle = \frac{5}{2}kT$  and  $C_p^{\text{1ml}} = \frac{7}{2}R$  as seen in the figure below for the specific heat of  $H_2$ . At higher temperatures (at around  $1000^\circ\text{K}$ ) they begin to vibrate, and the  $\frac{5}{2}kT$  estimate for the molecule's energy is no longer valid. Much above this temperature the molecule begins to break apart as the number of vibrational quanta gets too large (the dashed line). The following figure shows the specific heat of  $H_2$  gas. As we will discuss fully later, the increase starting at around  $1000^\circ\text{K}$  reflects the fact vibrational degrees of freedom becoming "active", i.e. this means that the average  $n$  is becoming significantly larger than zero.



<sup>1</sup>You should be able to explain the rest of this sentence. Ask me or look in the course notes if you can't!

## Problem 4. Working with the speed distribution

Consider the Maxwell speed distribution,  $d\mathcal{P}_v = P(v)dv$ .

- (a) In three dimensions, evaluate the most probable speed  $v_*$ . You should find  $v_* = (2kT/m)^{1/2}$ .
- (b) Determine the normalized speed distributions  $d\mathcal{P}_v = P(v)dv$  in two spatial dimensions, and sketch it. Then repeat part (a) in two dimensions. You should find  $v_* = (kT/m)^{1/2}$ .

*Hint:* Go through the derivation of the velocity distribution  $d\mathcal{P}_{v_x, v_y, v_z}$  in three dimensions and generalize it to two dimensions. Then go through the steps to get from the velocity distribution to the speed distribution  $d\mathcal{P}_v$  and generalize these steps to two dimensions.

- (c) Return to three dimensions, determine the probability of having  $v < v_*$ . Follow the following steps:
  - (i) Write down the appropriate integral.
  - (ii) Change variables to an appropriate dimensionless speed  $u$ , writing the probability as a dimensionless integral to be done numerically.
  - (iii) Write a short program (in any language) to evaluate the dimensionless integral, by (for example) dividing up the interval into 200 bins, and evaluates the integral with Riemann sums. You should find

$$\mathcal{P} \simeq 0.428 \tag{21}$$

## Problem 5. Distribution of DeBroglie Wavelengths

(a) Show that

$$\int_{-\infty}^{\infty} dx f(x) = \int_{-\infty}^{\infty} du f(-u) \quad (22)$$

with  $u = -x$ .

(b) Consider the de Broglie wavelength  $\lambda \equiv h/p$ . Recall that we defined a *typical* thermal de Broglie wavelength of a non-relativistic particle as<sup>2</sup>

$$\lambda_{\text{th}} \equiv \frac{h}{\sqrt{2\pi mkT}}, \quad (23)$$

with the  $\sqrt{2\pi}$  business a matter of convention.

(i) Ignoring all numerical factors, explain qualitatively why a typical de Broglie wavelength is of order  $\lambda \sim h/\sqrt{mkT}$ . Give a similar parametric estimate<sup>3</sup> for the typical thermal wavelength of a gas of photons at temperature  $T$ ? Note the energy of a photon is related to its momentum,  $\epsilon \equiv cp$ .

(ii) Evaluate  $\lambda_{\text{th}}$  defined in Eq. (23) numerically for He gas at room temperature  $T = 300^\circ\text{K}$ , and show that

$$\lambda_{\text{th}} = 0.50 \text{ \AA} \left( \frac{4m_p}{m} \right)^{1/2} \left( \frac{300^\circ\text{K}}{T} \right)^{1/2} \quad (24)$$

where  $m_p$  is the proton mass. Use the scaling in Eq. (24) to evaluate  $\lambda_{\text{th}}$  for Ne at  $100^\circ\text{K}$

As always try to use interpretable constants that you can remember and avoid using things like  $\hbar = 1.05 \times 10^{-34} \text{ J s}$  and  $k_B = 1.38 \times 10^{-23} \text{ J/}^\circ\text{K}^{-1}$ .

(c) The particles in the gas have a range of momenta and velocities, and hence a range of de Broglie wavelengths. By a change of variables, show that the probability to have a particle with de Broglie wavelength between  $\lambda$  and  $\lambda + d\lambda$  is

$$d\mathcal{P} = \frac{1}{\lambda_{\text{th}}} \left( \frac{\lambda_{\text{th}}}{\lambda} \right)^4 e^{-\pi(\lambda_{\text{th}}/\lambda)^2} 4\pi d\lambda. \quad (25)$$

The figure below shows the probability density  $P(\lambda)$  (i.e. the formula above without the  $d\lambda$ ). From the figure, determine graphically the ratio between the most probable de Broglie wavelength and  $\lambda_{\text{th}}$ . Also make a rough graphical estimate for the ratio between mean wavelength and  $\lambda_{\text{th}}$ , and the ratio between the standard deviation  $\sqrt{\langle \delta\lambda^2 \rangle}$  and  $\lambda_{\text{th}}$ . Hopefully the meaning and utility of “typical” is becoming clear.

<sup>2</sup>Our textbook uses the word “quantum length”,  $\ell_Q \equiv \lambda_{\text{th}}$  for  $\lambda_{\text{th}}$ .

<sup>3</sup>By a “parametric estimate” we mean an estimate that shows how a typical  $\lambda$  depends on the parameters of the problem,  $h$ ,  $m$ ,  $T$ , and  $k_B$  in this case, and not an actual number. I will use “numerical estimate” when I want an actual number. In the non-relativistic case we made a parametric estimate that the *typical* wavelength is of order,  $\lambda \sim h/\sqrt{mk_B T}$ . I want something similar here  $\lambda_{\text{typ}} \sim$  some function of  $T, h, c, k_B$ .



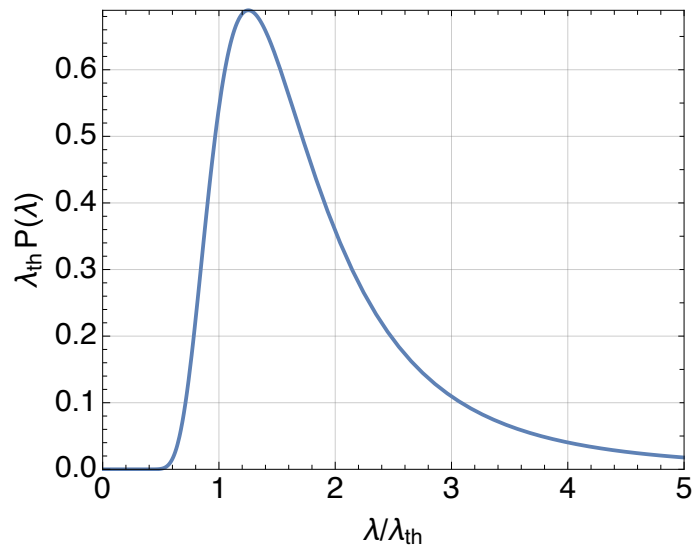


Figure 3: Probability density  $P(\lambda) \equiv d\mathcal{P}/d\lambda$  times a constant  $\lambda_{\text{th}}$ . Note that  $\lambda_{\text{th}}P(\lambda) = \lambda_{\text{th}}d\mathcal{P}/d\lambda$  is the probability per  $d\lambda/\lambda_{\text{th}}$ . The integral under the curve shown above is unity.