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:

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

Solution

First we have since $y = Cx^k$

$$\mathrm{d}y = kCx^{k-1}\,\mathrm{d}x = ky\,\frac{\mathrm{d}x}{x} \qquad or \qquad \frac{\mathrm{d}y}{y} = k\frac{\mathrm{d}x}{x} \tag{8}$$

Then by the chain rule on an arbitrary function $f(x) \equiv f(y(x))$

$$x\frac{\partial f}{\partial x} = x\frac{\partial f}{\partial y}\frac{\partial y}{\partial x} = x\frac{\partial f}{\partial y} \times Ckx^{k-1} = ky\,\frac{\partial f}{\partial y} \tag{9}$$

Here f was arbitrary so

$$x\frac{\partial}{\partial x} = ky\,\frac{\partial}{\partial y} \tag{10}$$

In a more intuitive way this is clear using the previous part

$$df = x\frac{\partial f}{\partial x}\frac{\mathrm{d}x}{x} = y\frac{\partial f}{\partial y}\frac{\mathrm{d}y}{y} \tag{11}$$

Then using $dy/y = k\,\mathrm{d}x/x$ leads to the result

$$y\frac{\partial}{\partial y} = \frac{1}{k}x\frac{\partial}{\partial x} \tag{12}$$

(a) $T \propto \beta^{-1}$ so

$$T\frac{\partial}{\partial T} = -\beta\frac{\partial}{\partial \beta} \tag{13}$$

(b) $E \propto p^2$ so

$$\frac{dE}{E} = 2\frac{dp}{p} \tag{14}$$

(c) This is clear

$$\ln Z(x) = \ln Z_1 + \ln Z_2 \tag{15}$$

differentiating with respect to x leads to the quoted result.

2

Problem 2.   Basics of Partition Functions

Important!

Consider a quantum mechanical system with energy levels ϵ_i with $i = 1, 2, \ldots n$. 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

$$P_r = \frac{1}{Z(\beta)} e^{-\beta \epsilon_r} \tag{16}$$

is correctly normalized

$$\sum_i P_i = 1 \tag{17}$$

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

$$Z_1(\beta) = \int \frac{dx dp}{h} e^{-\beta \epsilon} \tag{18}$$

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

$$\langle \epsilon \rangle = -\frac{1}{Z(\beta)} \frac{\partial Z}{\partial \beta} \tag{19}$$

Show also that

$$\langle \epsilon^2 \rangle = \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) \left(-\frac{\partial}{\partial \beta} \right) Z = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \tag{20}$$

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 Δ 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 $\ln Z$

$$\langle \epsilon \rangle = -\frac{\partial \ln Z(\beta)}{\partial \beta} \tag{21}$$

$$\langle (\delta \epsilon)^2 \rangle = \frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} = -\frac{\partial \langle \epsilon \rangle}{\partial \beta} \tag{22}$$

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 Δ. 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

$$C_V = Nk \left[\frac{\langle (\delta \epsilon)^2 \rangle}{(kT)^2} \right] \tag{23}$$

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

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

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 x^2 \tag{24}$$

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?

Partition Fcn Basics

We have

$$Z = \sum_s e^{-\beta \varepsilon_s}$$

So

$$-\frac{\partial Z}{\partial \beta} = \sum_s -\frac{\partial}{\partial \beta} e^{-\beta \varepsilon_s} = \sum_s e^{-\beta \varepsilon_s} \varepsilon_s$$

This repeats

$$\left(-\frac{\partial}{\partial \beta}\right)^2 Z = -\frac{\partial}{\partial \beta}\left(\sum_s e^{-\beta \varepsilon_s} \varepsilon_s\right) = \sum_s e^{-\beta \varepsilon_s} \varepsilon_s^2$$

So

$$\boxed{\langle \varepsilon \rangle = \frac{\sum_s e^{-\beta \varepsilon_s} \varepsilon_s}{\sum_s e^{-\beta \varepsilon_s}} = \frac{1}{Z}\frac{-\partial Z}{\partial \beta}}$$

and

$$\boxed{\langle \varepsilon^2 \rangle = \frac{\sum_s e^{-\beta \varepsilon_s} \varepsilon_s^2}{\sum_s e^{-\beta \varepsilon_s}} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}}$$

b) We had $Z(\beta) = \sum_s e^{-\beta \varepsilon_s} = e^{-\beta 0} + e^{-\beta \Delta} = 1 + e^{-\beta \Delta}$

Then $\langle \varepsilon \rangle = \frac{-\partial Z}{Z \, \partial \beta} = \frac{1}{(1+e^{-\beta \Delta})} \Delta e^{-\beta \Delta}$ ✓

Similarly

$$\langle \varepsilon^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{(1+e^{-\beta\Delta})} \Delta^2 e^{-\beta\Delta} \quad \checkmark$$

c) $\boxed{\langle \varepsilon \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{Z}\left(-\frac{\partial Z}{\partial \beta}\right) = \text{same as before}}$

Similarly

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial}{\partial \beta}\left(\frac{1}{Z} -\frac{\partial Z}{\partial \beta}\right) = \underbrace{\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}}_{} - \underbrace{\frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2}_{}$$

$$= \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \langle \delta \varepsilon^2 \rangle$$

We note that

$$\boxed{\langle \delta \varepsilon^2 \rangle = -\frac{\partial}{\partial \beta}\langle \varepsilon \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2}}$$

d) Then

$$U(T) = N \langle \varepsilon \rangle$$

Now recall since at fixed volume $dU_v = dQ_v = C_v \, dT$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_v = N \frac{\partial}{\partial T}\langle \varepsilon \rangle = \frac{N}{T} T\frac{\partial \langle \varepsilon \rangle}{\partial T} = \frac{N}{T} -\beta \frac{\partial}{\partial \beta}\langle \varepsilon \rangle$$

use $T\frac{\partial}{\partial T} = -\beta\frac{\partial}{\partial \beta}$

see problem on log derivs

So

$$C_V = Nk \beta^2 \left(-\frac{\partial \langle \varepsilon \rangle}{\partial \beta} \right) = Nk \beta^2 \langle \delta \varepsilon^2 \rangle$$

use previous item

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

Now we find

$$\langle \delta \varepsilon^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{-\partial}{\partial \beta} \frac{\Delta e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})} = \frac{-\partial}{\partial \beta} \frac{\Delta}{(e^{\beta \Delta} + 1)}$$
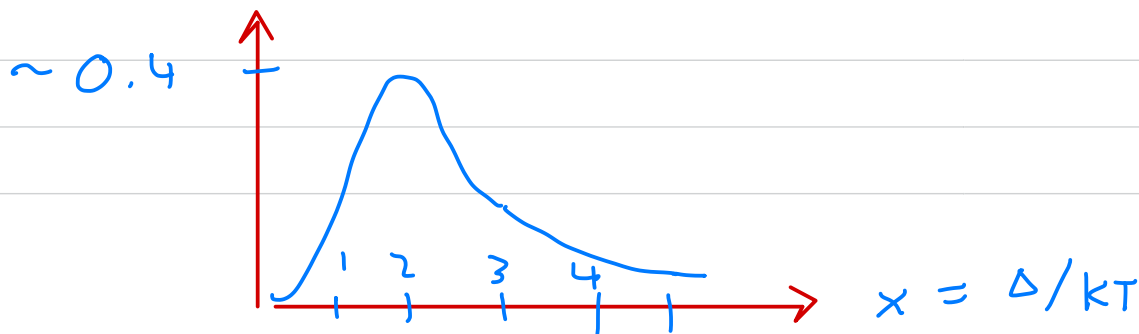
$$= \Delta^2 \frac{e^{\beta \Delta}}{(e^{\beta \Delta} + 1)^2} = \frac{\Delta^2 e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})^2}$$

So

$$\boxed{\frac{C_V}{Nk} = \beta^2 \langle \delta \varepsilon^2 \rangle = (\beta \Delta)^2 \frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})^2}}$$

A sketch is shown below, we are plotting

$$\frac{x^2 e^{-x}}{(1 + e^{-x})^2} \quad \text{with} \quad x = \beta \Delta = \Delta/kT$$

e)

$$Z = \int \frac{dx\,dp}{h}\, e^{-\beta\left(p^2/2m + \frac{1}{2}mw_0^2 x^2\right)}$$

The integrals factorize and are gaussians

$$Z = \frac{1}{h}\int dx\, e^{-\frac{1}{2}x^2/\sigma_x^2} \cdot \int dp\, e^{-p^2/2\sigma_p^2}$$

where

$$\sigma_x^2 \equiv \frac{1}{\beta m w_0^2} \quad \text{and} \quad \sigma_p^2 \equiv \frac{m}{\beta}$$

So

$$Z = \frac{(2\pi \sigma_x^2)^{1/2}(2\pi \sigma_p^2)^{1/2}}{h} = \frac{2\pi}{h}\left(\frac{1}{\beta m w_0^2}\frac{m}{\beta}\right)^{1/2} = \frac{2\pi}{\beta h w_0} = \frac{1}{\beta \hbar w_0}$$

$$\boxed{Z = \frac{1}{\beta \hbar w_0}} \quad \propto \frac{1}{\beta} \quad \Longleftarrow$$

Note we will differentiate $\ln Z$ with β. Follow this algebra the constants don't matter, just $Z \propto \beta^{-1}$!

Now

$$\langle \varepsilon \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{-\partial}{\partial \beta}\left(\ln \frac{1}{\beta \hbar w_0}\right) = -\frac{\partial}{\partial \beta}\left[\ln \frac{1}{\beta} + \text{const}\right]$$

$$= \frac{\partial}{\partial \beta} \ln \beta = \frac{1}{\beta} = kT$$

See how constants don't matter. This greatly simplifies algebra going forward.

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 $\omega_0 = \sqrt{k_{\mathrm{sp}}/m}$.

Recall that the energy levels of a quantum harmonic oscillator are

$$\epsilon_n = \left(n + \tfrac{1}{2}\right)\hbar\omega_0 \tag{25}$$

with $n = 0, 1, 2, \ldots \infty$. 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

$$\epsilon_n = n\hbar\omega_0 \tag{26}$$

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

$$P_n = \frac{1}{Z}e^{-\epsilon_n/kT} = \frac{1}{Z}e^{-n\hbar\omega_0/kT} \tag{27}$$
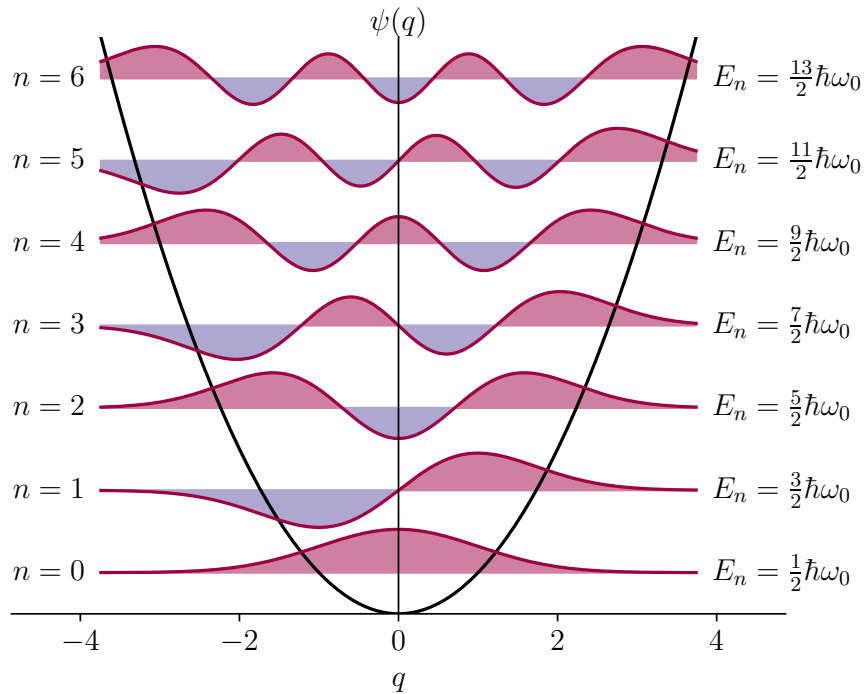

Figure 1: Energy levels $\epsilon_n \equiv E_n = (n + \tfrac{1}{2})\hbar\omega_0$ and wave functions for the first six levels of the quantum harmonic oscillator.
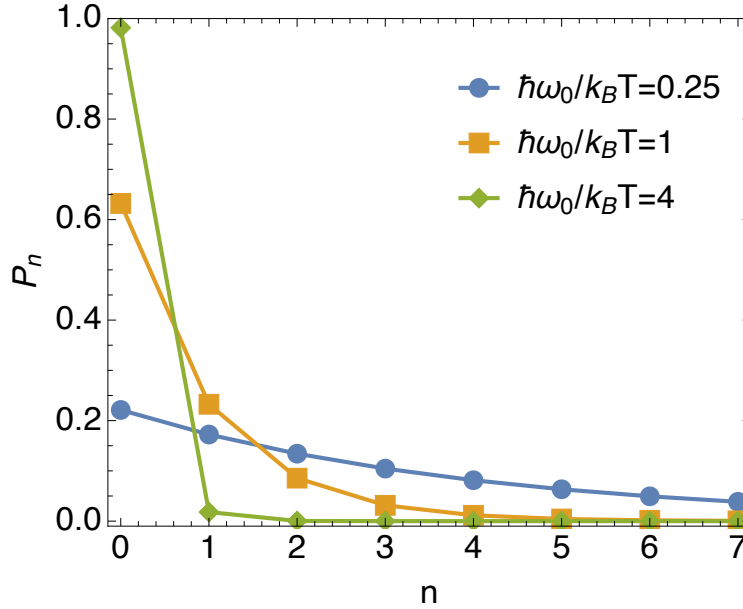
Figure 2: Probability for the oscillator to have n quanta of vibrational energy $\hbar\omega_0$ for different values $\hbar\omega_0/kT$.

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").

(a) 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".

(b) Noting that $e^{-n\hbar\omega_0/kT} = u^n$ with $u = e^{-\hbar\omega_0/kT}$, 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.
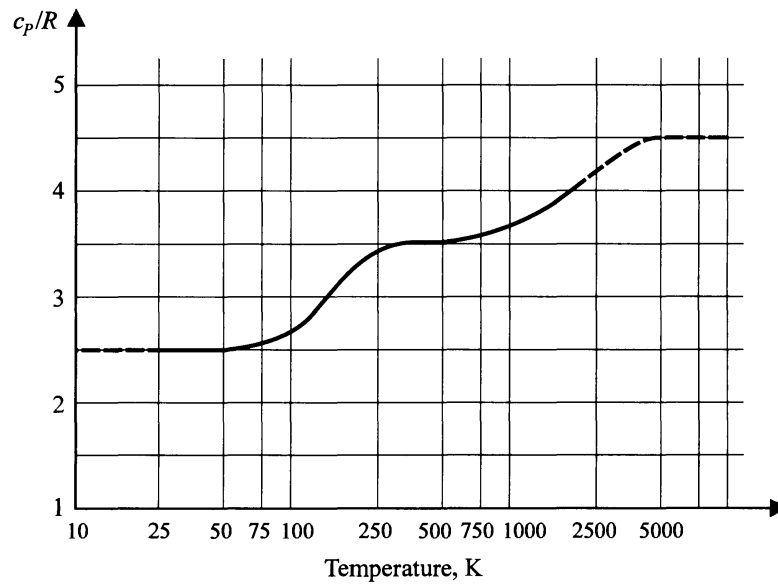
You should find

$$P_n = e^{-n\hbar\omega_0/kT}(1 - e^{-\hbar\omega_0/kT}) \tag{28}$$

(c) 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 $\lambda_0 = 2270\,\text{nm}$. This wavelength is typical of molecular vibrations – is the photon, ifrared, 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 $\hbar = 1.05 \times 10^{-34}\,\text{J s}$ and $k_B = 1.38 \times 10^{-23}\text{J}/^\circ\text{K}^{-1}$, but rather try to put it in physical terms. For instance use $\hbar c = 197\,\text{eV nm}$, and $k_B T \simeq 1/44\,\text{eV}$ at freezing $273\,^\circ\text{K}$. A summary of constants you will need for the course are given on the website.

Discussion: I find $T \simeq 6000^o$K. Indeed this is about right. At room temperatures ($T = 300\,^\circ$K) diatomic molecules translate and rotate but do not vibrate significantly. And so[1], $\langle \epsilon \rangle = \frac{5}{2}kT$ and $C_p^{1ml} = \frac{7}{2}R$ as seen in the figure below for the specific heat of H_2. At higher temperatures (at around 1000^oK) 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 increase starting at around 1000^oK reflects the fact vibrational degrees of freedom becoming "active", i.e. this means that the average n is becoming significantly larger than zero.

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

Probability of a Quantum Harmonic Oscillator

a) We have

$$P_n = \frac{1}{Z} e^{-\beta \varepsilon_n} = \frac{e^{-n\hbar\omega_o\beta}}{Z} \qquad \text{then} \qquad \sum_n P_n = 1$$

So multiply b Z

and we have

$$\sum_n Z P_n = Z \qquad \text{and thus} \qquad \boxed{\sum_n e^{-n\hbar\omega_o\beta} = Z}$$

b) We use $u \equiv e^{-\beta\hbar\omega_o}$ so

$$Z = \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega_o})^n = \sum_{n=0}^{\infty} u^n = 1 + u + u^2 + \dots$$

$$= \frac{1}{1-u} \Rightarrow \boxed{Z = \frac{1}{1-e^{-\beta\hbar\omega_o}}} \qquad \text{and} \qquad \boxed{P_n = e^{-\beta\hbar\omega_o^n}(1-e^{-\beta\hbar\omega_o})}$$

The graphs show the probability of the oscillator vibrating with n quanta of energy $\hbar\omega_o$. At high T, $\hbar\omega_o/kT \ll 1$ then there is a significant probability, that the oscillator will have more than one quanta of energy.

$\hbar\omega_o/kT = 0.25$ $\qquad \langle n \rangle$ just above 0

$\hbar\omega_o/kT \simeq 1$ $\qquad \langle n \rangle$ just below 1, 60% have $n=0$, and the remaining 40% have $n=1$ or above

$\hbar\omega_o/kT = 4$ $\qquad \langle n \rangle$ is probablly about 2

The molecule is excited from the ground to the first excited state by the photon:

$E = hc/\lambda$

vibrating molecule

$\Delta E = \hbar \omega_0$

Initial State

Final State
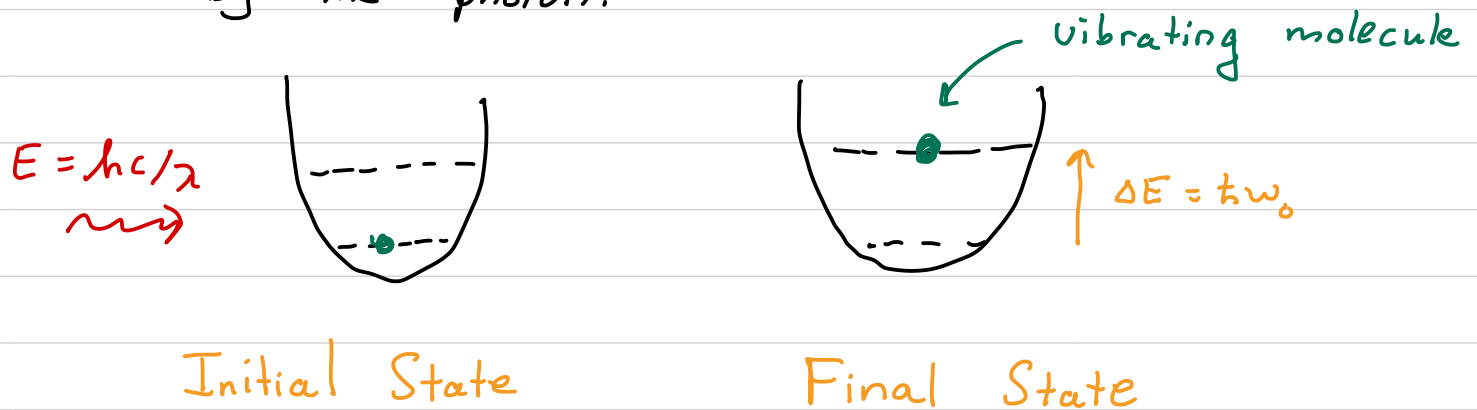
So

$\dfrac{hc}{\lambda} = \hbar \omega_0$

$\boxed{\hbar \omega_0 = \dfrac{1240 \, eV \cdot nm}{2270 \, nm} \simeq 0.55 \, eV}$

The temperature when $\langle n \rangle \sim 1$ is when $\dfrac{\hbar \omega}{kT} \sim 1$, and so

$kT \sim 0.55 \, eV$ or $\boxed{T \simeq \dfrac{0.55 \, eV}{\left(\dfrac{1/40 \, eV}{300^\circ k} \right)} \simeq 6600^\circ k}$

Problem 4.   Working with the speed distribution

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

(a) In three dimensions, evaluate the most probable speed v_*. You should find $v_* = (2kT/m)^{1/2}$.

(b) Determine the normalized speed distributions $\mathrm{d}\mathscr{P}_v = P(v)\mathrm{d}v$ 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 $\mathrm{d}\mathscr{P}_{v_x,v_y,v_z}$ in three dimensions and generalize it to two dimensions. Then go through the steps to get from the velocity distribution to the speed distribution $\mathrm{d}\mathscr{P}_v$ 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

$$\mathscr{P} \simeq 0.428 \tag{29}$$

Working @ the Speed Distribution

a)

$$P(v) = C e^{-\frac{1}{2}mv^2/kT} v^2$$

To find the max we differentiate

$$\frac{dP}{dv} = 0 = C e^{-\frac{1}{2}mv^2/kT} \cdot 2v + Cv^2 e^{-\frac{1}{2}mv^2/kT}\left(\frac{-mv}{kT}\right)$$

$$0 = C e^{-\frac{1}{2}mv^2/kT}\left[2v - \frac{mv^3}{kT}\right]$$

Setting the square bracket to zero we have

$$v = \left(\frac{2kT}{m}\right)^{1/2}$$

b) We need to generalize the discussion from class to 2d:

$$dP_{r,p} \propto e^{-p^2/2mkT} \, d^2r \, d^2p$$

We are not interested in $\vec{r} = (x, y)$ so we integrate over it, with $0 < x, y < L$. This just changes the norm constant. So

$$dP_{\vec{p}} = C \, e^{-p^2/2mkT} \, dp_x \, dp_y$$

Changing to velocity $\vec{v} = \vec{p}/m$ just changes C again

$$dP_{\vec{v}} = C \, e^{-\frac{1}{2}mv^2/kT} \, dv_x \, dv_y$$

We can find the normalization by integrating:

$$\int dP = \int C \, e^{-\frac{1}{2}m(v_x^2 + v_y^2)/kT} \, dv_x \, dv_y = 1$$

$$= C \int_{-\infty}^{\infty} dv_x \, e^{-\frac{1}{2}mv_x^2/kT} \int_{-\infty}^{\infty} dv_y \, e^{-\frac{1}{2}mv_y^2/kT} = 1$$

$$= C \left(\frac{2\pi kT}{m} \right)^{1/2} \left(\frac{2\pi kT}{m} \right)^{1/2} = 1$$

So the normalized velocity distribution is

$$\boxed{dP = \frac{m}{2\pi kT} \, e^{-\frac{1}{2}mv^2/kT} \, dv_x \, dv_y}$$

The speed distribution is

$$d\mathcal{P}_{v,\theta} = \frac{m}{2\pi kT} e^{-\frac{1}{2}mv^2/kT} \underbrace{v \, dv \, d\theta}$$

Change of vars, from v_x, v_y
to speed $v = \sqrt{v_x^2 + v_y^2}$ and
angle θ. Like in Jacobian
Homework.

If we don't care about θ we
integrate over it $\theta \in [0, 2\pi]$

$$\boxed{d\mathcal{P}_v = \frac{m}{2\pi kT} e^{-\frac{1}{2}mv^2/kT} \cdot 2\pi v \, dv}$$

Now to find the most probable we procede as before

$$P'(v) = 0 \qquad P(v) = C e^{-\frac{1}{2}mv^2/kT} v$$

Differentiating:

$$P'(v) = C e^{-\frac{1}{2}mv^2/kT} + Cv \, e^{-\frac{1}{2}mv^2/kT} \left(-\frac{mv}{kT} \right)$$

$$= C e^{-\frac{1}{2}mv^2/kT} \left(1 - \frac{mv^2}{kT} \right) = 0$$

So

$$\boxed{v = \left(\frac{kT}{m} \right)^{\frac{1}{2}}}$$

c) The probability is

$$\mathscr{P}_{v < v_*} = \int_0^{v_*} \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT} \, 4\pi v^2 \, dv$$

Now introduce: $u = \dfrac{v}{(kT/m)^{1/2}}$ = velocity in some appropriate units

$\rightsquigarrow$ Just look at exponent mv^2/kT is dimensionless
this will help to find the right combos

So

$$v_* = \left(\frac{2kT}{m}\right)^{1/2} \qquad u_* = \frac{v_*}{(kT/m)^{1/2}} = \sqrt{2}$$

So also $u^2 du = \dfrac{v^2 \, dv}{(kT/m)^{3/2}}$ leading to

$$\mathscr{P}_{v < v_*} = \int_0^{\sqrt{2}} \frac{1}{(2\pi)^{3/2}} e^{-\frac{1}{2}u^2} \, 4\pi u^2 \, du$$

$$= \sqrt{\frac{2}{\pi}} \int_0^{\sqrt{2}} e^{-\frac{1}{2}u^2} \, u^2 \, du \approx 0.428$$

hwsol.py

```
from math import *

du = 0.001   # bin size

s = 0.   # sum
u= 0.     # current value of u
while u < sqrt(2.) :
    s = s + exp(-u*u/2) * u * u  * du
    u = u + du

# don't forget to multiply by the overall constant
print( "The integral is ", s * sqrt(2./pi))
```

Problem 5. Distribution of Debroglie Wavelengths

(a) Show that

$$\int_{-\infty}^{\infty} dx\, f(x) = \int_{-\infty}^{\infty} du\, f(-u) \tag{30}$$

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[2]

$$\lambda_{\text{th}} \equiv \frac{h}{\sqrt{2\pi mkT}}, \tag{31}$$

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[3] for the typical thermal wavelength of a gas of photons at temperature T? Note the energy of a photon is related to its momentum, $\epsilon \equiv c\,p$.

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

$$\lambda_{\text{th}} = 0.50\,\mathring{\text{A}} \left(\frac{4m_p}{m}\right)^{1/2} \left(\frac{300°\text{K}}{T}\right)^{1/2} \tag{32}$$

  where m_p is the proton mass. Use the scaling in Eq. (24) to evalute λ_{th} for Ne at $100\,°\text{K}$

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 $k_B = 1.38 \times 10^{-23}\text{J}/°\text{K}^{-1}$.

(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 λ and $\lambda + d\lambda$ is

$$\text{d}\mathscr{P} = \frac{1}{\lambda_{\text{th}}} \left(\frac{\lambda_{\text{th}}}{\lambda}\right)^4 e^{-\pi(\lambda_{\text{th}}/\lambda)^2} 4\pi \text{d}\lambda. \tag{33}$$

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 λ_{th}. Also make a rough graphical estimate for the ratio between mean wavelength and λ_{th}, and the ratio between the standard deviation $\sqrt{\langle \delta\lambda^2 \rangle}$ and λ_{th}. Hopefully the meaning and utility of "typical" is becoming clear.

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[2] Our textbook uses the word "quantum length", $\ell_Q \equiv \lambda_{\text{th}}$ for λ_{th}.

[3] By a "parametric estimate" we mean an estimate that shows how a typical λ 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 .
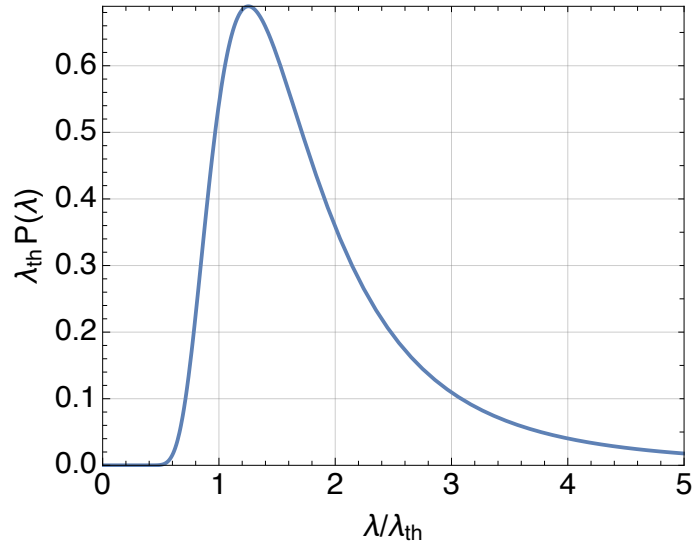
Figure 3: Probability density $P(\lambda) \equiv \mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ times a constant λ_{th}. Note that $\lambda_{\mathrm{th}}P(\lambda) = \lambda_{\mathrm{th}}\mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ is the probability per $\mathrm{d}\lambda/\lambda_{\mathrm{th}}$. The integral under the curve shown above is unity.

Distribution of Debroglie waves:

a) First we will used unoriented (or Lebegue) integrals

$$I = \int dx\, f(x) = \int du\, \left|\frac{du}{dx}\right| f(-u) = \int f(-u)\, du$$

$[-\infty,\infty] = R \qquad [-\infty,\infty] = R' \qquad\qquad [-\infty,\infty]$

mapped region under
map $x \longrightarrow u = -\backslash$

Alternatively with oriented integrals:

$$I = \int_{-\infty}^{\infty} dx\, f(x) = \int_{+\infty}^{-\infty} du\, \left(\frac{dx}{du}\right) f(-u) = \int_{+\infty}^{-\infty} du\, (-)\, f(-u)$$

$$= \int_{-\infty}^{\infty} du\, f(-u)$$

b) In thermal systems the typical energy is $E \sim kT$
Then since $E \sim p^2/2m$, we have $p \sim \sqrt{mkT}$, where
I dropped the 2 in the spirit of making an estimate
So

$$\lambda \sim \frac{h}{p} \sim \frac{h}{(mkT)^{1/2}}$$

Photons have $\varepsilon \sim kT$ but their energy is $\varepsilon = cp$. So
the typical wavelength is

$$\lambda = \frac{hc}{cp} \sim \frac{hc}{kT}$$

The distribution of speeds is

$$dP_v = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT} \, 4\pi v^2 dv$$

We have
$$\boxed{\lambda = \frac{h}{P} = \frac{h}{mv} \quad \text{or} \quad v = \frac{h}{m\lambda}}$$

So using in an unoriented sense (i.e. the sense of Probability
-- is it in a bin or not, not is dv positive or negative)

$$dv = \left|\frac{dv}{d\lambda}\right| d\lambda = \frac{h}{m}\frac{d\lambda}{\lambda^2} \quad \text{or} \quad \frac{dv}{v} = \frac{d\lambda}{\lambda}$$

logarithmic derivatives!

We get:

$$\frac{v}{(kT/m)^{1/2}} = \frac{h}{(mkT)^{1/2}}\frac{1}{\lambda} = \sqrt{2\pi}\,\frac{\lambda_{th}}{\lambda}$$

And so

$$dP = \frac{4\pi}{(2\pi)^{3/2}} e^{-\pi(\lambda_{th}/\lambda)^2} \cdot \left(\frac{m}{kT}\right)^{3/2} v^3 \frac{dv}{v}$$

$$= \frac{4\pi}{(2\pi)^{3/2}} e^{-\pi(\lambda_{th}/\lambda)^2} \cdot \left(\sqrt{2\pi}\,\frac{\lambda_{th}}{\lambda}\right)^3 \frac{d\lambda}{\lambda}$$

Leading ultimately to the result:

$$d\mathcal{P} = 4\pi \, e^{-\pi(\lambda_{th}/\lambda)^2} \left(\frac{\lambda_{th}}{\lambda}\right)^4 \frac{d\lambda}{\lambda_{th}}$$

So from the graph. The most probable λ is at the maximum

$$\lambda_{mp} = 1.2 \, \lambda_{th}$$

Estimating the mean $\langle\lambda\rangle \sim 2\,\lambda_{th}$ and $\langle\delta\lambda^2\rangle \sim 1 \, \lambda_{th}^2$.
We can of course compute $\langle\lambda\rangle$ precisely

$$\langle\lambda\rangle = \int_0^\infty P(v) \, dv \quad \frac{h}{mv}$$

$$= \int_0^\infty \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT} \, 4\pi v^2 \, dv \quad \frac{h}{mv}$$

$$= 1.13 \, \lambda_{th} \quad \Longleftarrow \text{do it yourself! So our estimate}$$
$$\text{of } \langle\lambda\rangle \sim 2\lambda_{th} \text{ was a bit off.}$$