Problem 1. 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 $\omega_0 = \sqrt{k_{\rm sp}/m}$.

Recall that the energy levels of a quantum harmonic oscillator are

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

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

$$\epsilon_n = n\hbar\omega_0 \tag{2}$$

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

$$P_n = \frac{1}{Z} e^{-\epsilon_n/kT} = \frac{1}{Z} e^{-n\hbar\omega_0/kT} \tag{3}$$

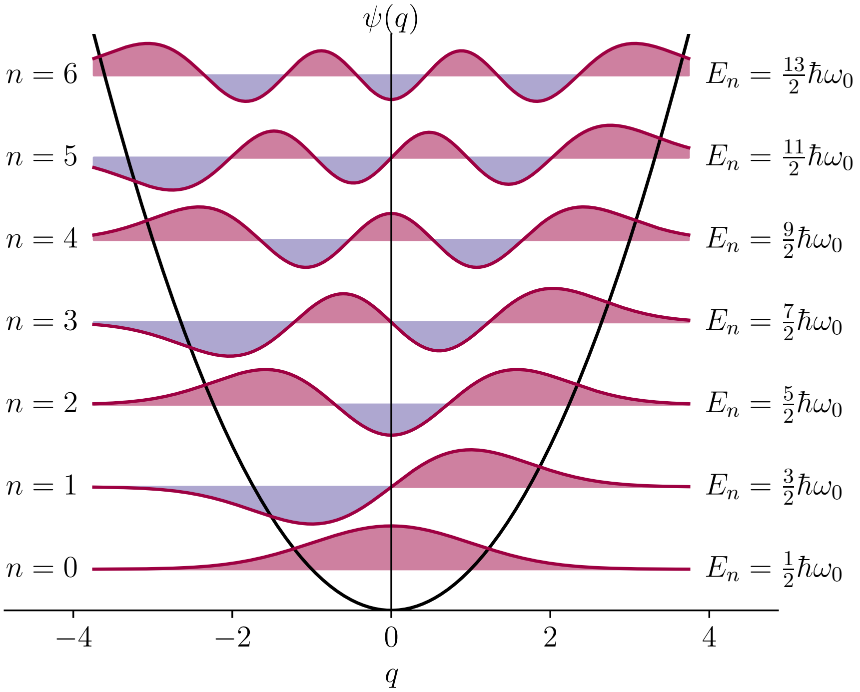


Figure 1: Energy levels $\epsilon_n \equiv E_n = (n + \frac{1}{2})\hbar\omega_0$ and wave functions for the first six levels of the quantum harmonic oscillator.

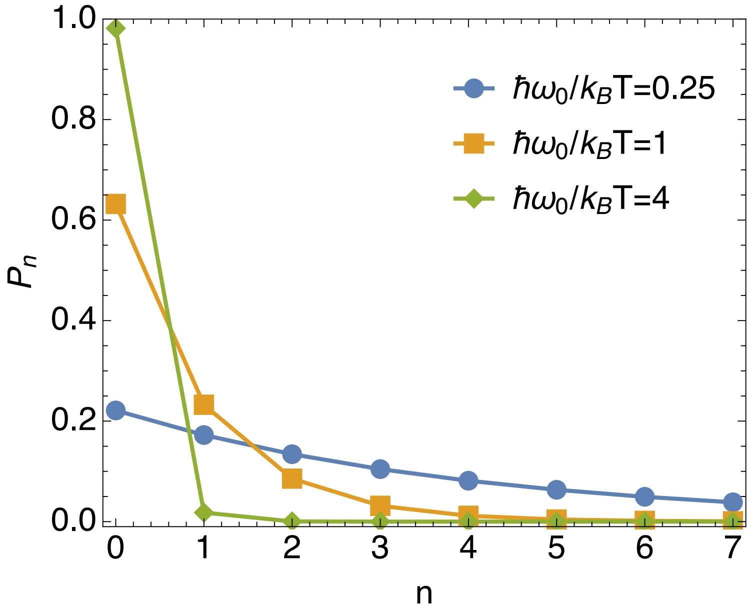


Figure 2: Probability for the oscillator to have n quanta of vibrational energy $\hbar\omega_0$ for different values $\hbar\omega_0/kT$.

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.

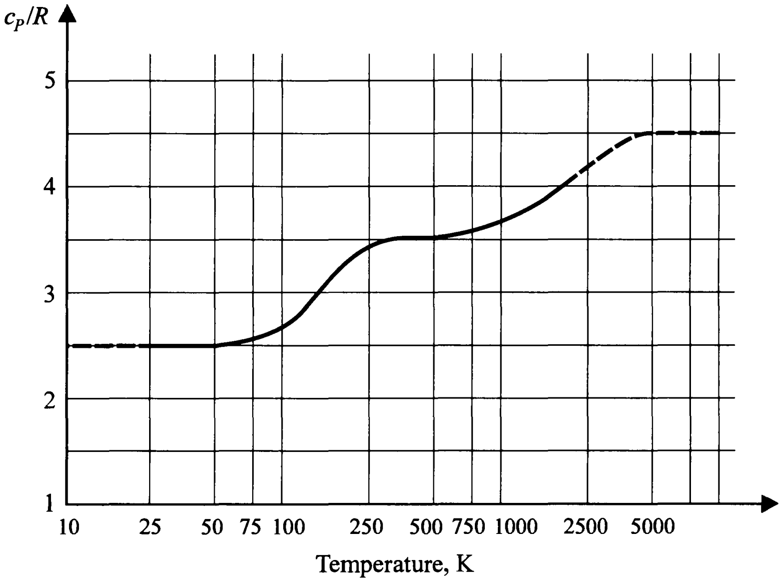
You should find

$$P_n = e^{-n\hbar\omega_0/kT}(1 - e^{-\hbar\omega_0/kT}) \tag{4}$$

(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 $\lambda_0 = 2270\,\mathrm{nm}$. 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 $\hbar = 1.05 \times 10^{-34}\,\mathrm{J\,s}$ and $k_B = 1.38 \times 10^{-23}\mathrm{J/^\circ K^{-1}}$, but rather try to put it in physical terms. For instance use $\hbar c = 197\,\mathrm{eV\,nm}$, and $k_BT \simeq 1/44\,\mathrm{eV}$ at freezing $273\,^\circ\mathrm{K}$. 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 $C_p^{\rm 1ml} = \frac{7}{2}\,R$ 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.



---

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

Problem 2. Paramagnets from the canonial ensemble

A primer/reminder on magnets and magnetic materials

Basic magnetism we need in this course: If I have a coil of wire carrying a current, it has a magnetic dipole moment of[2]:

$$\vec{\mu} \equiv \mu_0 I \vec{A} \,, \tag{5}$$

where $|\vec{A}|$ is the area of the loop. The direction of the area vector is normal to the face of the loop, according to the right hand rule. You can think of a current carrying loop as small magnet (or compass needle) with north pole and south pole. $\vec{\mu}$ is aligned with the north pole of the magnet and its magnitude gives the strength of the magnet.

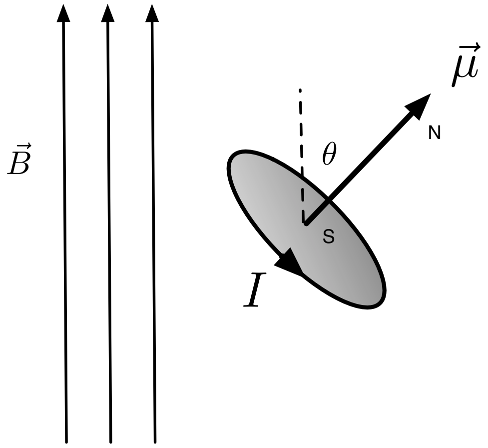


Figure 3: An explanation of magnetic moments.

When this coil is placed into a magnetic field $\vec{B}$, the magnetic moment (or compass needle) wants to align with the magnetic field. This is due to the net torque on the current carrying wire, ultimately produced by the magnetic forces on the wire, i.e. $F = I\ell B$. The potential energy of the current carrying loop is[3]

$$U_{\text{dip}} = -\vec{\mu} \cdot \vec{B} = -\mu B \cos\theta \,, \tag{6}$$

---

[2] μ_0 is the vacuum permeability (or magnetic constant), $\mu_0 = 4\pi \times 10^{-7}$H/m, and is not related to the magnetic dipole moment.

[3] We use U_{dip} for the potential energy of one magnetic dipole moment, e.g. from one atom. U is reserved for the internal energy of the entire paramagnet, i.e. N atoms (see below).

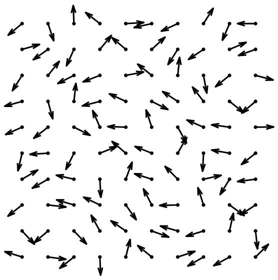
where the angle θ is between the magnetic dipole moment and the magnetic field (see below).

(a) Qualitatively, why is there a minus is in this equation? Using Fig. 3 as a guide, draw a coil of wire with the lowest potential energy and highest potential energy.

Paramagnets (lots of little magnets): In a paramagnetic substance, you should have a picture where each atom in the substance, can be treated as a tiny coil of wire with magnetic moment $\vec{\mu}$. The substance as a whole will not be magnetized, because the magnetic moments all point in all random directions, and cancel each other out, see Fig. 4(a). In math, the total magnetization $\vec{M}$, which is a sum of the magnetic moments, is approximately zero[4]

$$\vec{M} = \sum_i \vec{\mu}_i \simeq 0\,. \tag{7}$$

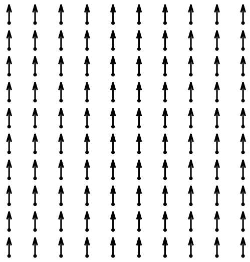
This sum is over all the atoms with μ_i being the magnetic moment of the i-th atom. When a strong magnetic field is applied, as Fig. 4(b), there is a preference for the atoms to align with the magnetic field, and the magnetization of the substance will be non-zero, i.e. there is a net north pole and south pole from the sum of atoms. This magnetization of the substance can easily be measured, heuristically by bring a compass needle close to the substance. In general the system the system will be between (a) and (b), i.e. partially aligned.



Weak Magnetic Field and High Temperature
$\vec{M} \simeq 0$

(a) high temperature

The system is in between these limits, and the arrows are partly oriented.



Strong Magnetic Field and Low Temperature
$\vec{M} \simeq$ strong

(b) low temperature

Figure 4: An explanation paramagnets.

---

[4] A paramagnetic substance is different from your kitchen magnet. In the kitchen magnet the magnetic moments remain aligned even without the magnetic field.

At high temperatures the atoms are more likely to point in random directions and the magnetization is small (Fig. 4(a)). Similarly, when the magnetic field is weak, the magnetization is small, since there is nothing to align the moments. Our goal in this course is to calculate how the magnetization depends on the temperature and applied magnetic field, i.e. to find

$$M(T, B)\,, \tag{8}$$

which measures the degree of partial alignment in the system. At small magnetic fields we can make a Taylor series expansion, noting that at zero magnetic field we must have no magnetization, and thus

$$M \simeq \frac{\partial M}{\partial B} B \equiv \chi(T) B\,. \tag{9}$$

Here we defined the "susceptibility"

$$\chi(T) \equiv \frac{\partial M}{\partial B}\,, \tag{10}$$

which records how much magnetization you get per magnetic field.

Since the magnetization also vanishes at high temperature, one would expect that at high temperature

$$\chi(T) \propto \frac{1}{T}\,, \tag{11}$$

This is known as the Curie Law and is seen in most paramagnetic materials.

(b) Is the magnetization as defined here an intensive or extensive quantity? Explain.

The First Law for Magnets:

If the magnetic field is increased and I do work, then the potential energy of each atom is increased (from Eq. (6))

$$\mathrm{d}U_{\mathrm{dip}} = -\vec{\mu} \cdot \mathrm{d}\vec{B}\,, \tag{12}$$

Assuming that no heat flows into or out of the magnet (adiabatically), we can sum over all of the atoms, and the total change in the energy U of the magnet is

$$dU_{adiab} = -\vec{M}(T, B) \cdot \mathrm{d}\vec{B}\,. \tag{13}$$

In general, heat will flow in and out of the magnet and we have then

$$\mathrm{d}U = \mathrm{d}Q_{\mathrm{in}} - \vec{M}(T, B) \cdot \mathrm{d}\vec{B}\,, \tag{14}$$

which is

$$\mathrm{d}U = \mathrm{d}Q_{\mathrm{in}} - p\mathrm{d}V\,. \tag{15}$$

To summarize the work done on the system by increasing the magnetic field by $\mathrm{d}B$ is

$$\mathrm{d}W_{\mathrm{in}} = -\vec{M} \cdot d\vec{B}\,. \tag{16}$$

Problem:

In a model of a paramagnet, there are N independent atoms. Each atom can be in one of two spin states: "up" or "down" (see below). We use $N_\uparrow$ to notate the number of up spins and $N_\downarrow$ for down spins (see Fig. 5).

The magnetic moment of each atom is proportional to its spin and has magnitude μ. Thus the magnetic moment the i-th atom is $\vec{\mu}_i = \pm\mu$, with the sign indicating wether the magnetic moment points up or down. The magnetization of the magnet, which is a sum of the magnetic moments of the atoms, is thus proportional to the difference in up versus down spins, $M \equiv \mu(N_\uparrow - N_\downarrow)$.

A magnetic field, B, points in the z direction, and the spins tend to align with this field. The energy of an up spin is (from Eq. (6)) $\epsilon_\uparrow = -\mu B$, where μ is the atom's magnetic moment. On the other hand, the energy of a down spin is $\epsilon_\downarrow = +\mu B$. The reason why up spins have lower energy than down spins, is that up spins are aligned with the magnetic field, while the down spins are aligned opposite to the field.

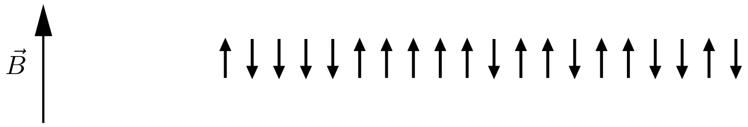


Figure 3.6. A two-state paramagnet, consisting of N microscopic magnetic dipoles, each of which is either "up" or "down" at any moment. The dipoles respond only to the influence of the external magnetic field B; they do not interact with their neighbors (except to exchange energy). Copyright ©2000, Addison-Wesley.

Figure 3.7. The energy levels of a single dipole in an ideal two-state paramagnet are $-\mu B$ (for the "up" state) and $+\mu B$ (for the "down" state). Copyright ©2000, Addison-Wesley.

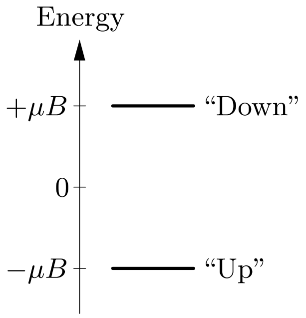


Figure 5: (a) A visualization of the paramagnet (Schroeder). (b) The energy levels of a paramagnet (Schroeder).

(c) The hyperbolic cosine, sine, and tangent are defined by

$$\cosh(x) \equiv (e^x + e^{-x})/2 \tag{17}$$

$$\sinh(x) \equiv (e^x - e^{-x})/2 \tag{18}$$

$$\tanh(x) \equiv \frac{\sinh(x)}{\cosh(x)} = \frac{1 - e^{-2x}}{1 + e^{-2x}} \tag{19}$$

and arise frequently in stat mech and quantum mechanics. Sketch these functions and show that the Taylor series expansion of $\tanh(x)$ is $\tanh(x) \simeq x - x^3/3$.

(d) Use the canonical ensemble to show that the magnetization can be written

$$M = N\mu \tanh(\mu B/kT)\,, \tag{20}$$

and that the energy is

$$U = -N\mu B \tanh(\mu B/kT)\,. \tag{21}$$

Using the Taylor expansion of the previous part show that at small magnetic fields the magnetization is proportional to the applied magnetic field

$$M \simeq \chi(T) B \quad \text{with a proportionality constant} \quad \chi(T) \equiv \frac{N\mu^2}{kT} \propto \frac{1}{T}\,, \tag{22}$$

and that

$$U \simeq -\chi(T) B^2 \tag{23}$$

The proportionality constant $\chi(T)$ is known as the magnetic susceptibility. The fact that magnetization is inversely proportional to the temperature is known as the Curie Law. A comparison of the Curie Law and the $\tanh(x)$ form to experimental data on the magnetization of paramagnets is shown below. Answer the following:

(i) Qualitatively why would one expect the magnetization to disappear at high temperatures?

(ii) When is the Curie Law and the Taylor series expansion valid, i.e. what conditions should be satisfied by the magnetic field and temperature for its validity? Do you see deviations from the Curie Law in comparison with experiment in the right place? Explain.

(e) Consider a paramagnet *maintained* at temperature T. The magnetic field is increased from $B = 0$ up to B_{max}. Using the high temperature approximations of (b) (where $M \simeq \chi(T)B$ and $U = -\chi B^2$), compute the heat flow into and or out of the system as B is increased to B_{max}.

Hint: Use the first law. You should find, $Q_{\text{in}} = -\chi(T)B_{\text{max}}^2/2$ so heat flows out of the magnet.

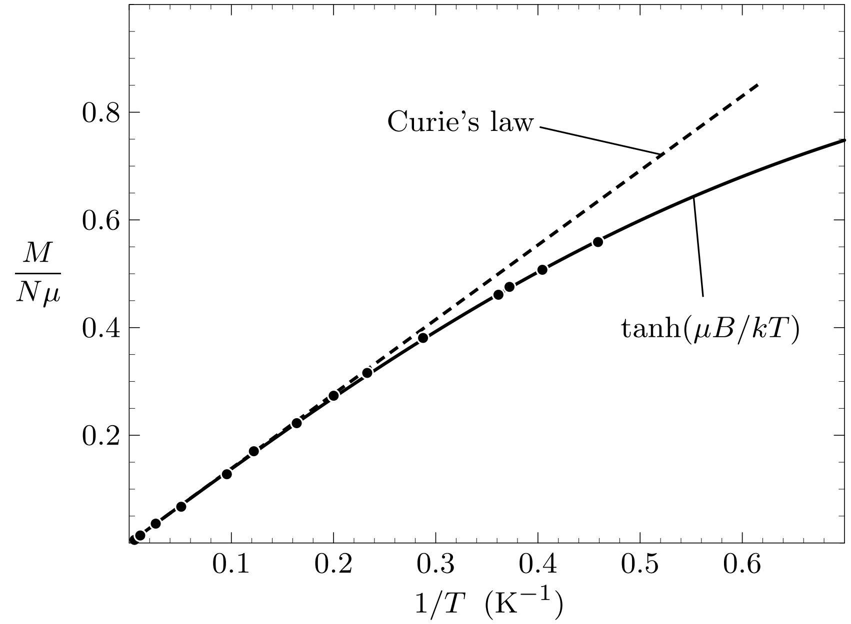


Figure 3.12. Experimental measurements of the magnetization of the organic free radical "DPPH" (in a 1:1 complex with benzene), taken at $B = 2.06$ T and temperatures ranging from 300 K down to 2.2 K. The solid curve is the prediction of equation 3.32 (with $\mu = \mu_\mathrm{B}$), while the dashed line is the prediction of Curie's law for the high-temperature limit. (Because the effective number of elementary dipoles in this experiment was uncertain by a few percent, the vertical scale of the theoretical graphs has been adjusted to obtain the best fit.) Adapted from P. Grobet, L. Van Gerven, and A. Van den Bosch, *Journal of Chemical Physics* **68**, 5225 (1978). Copyright ©2000, Addison-Wesley.

Problem 3. Paramagnet from the micro-canonical ensemble

This problem is a continuation of the previous and follows the same setup and notation. In this part the energy difference between spin down energy and the spin up energy is written, $\Delta \equiv \epsilon_{\downarrow} - \epsilon_{\uparrow} = 2\mu B$. The number of excited atoms (spin down) per site is written $n \equiv N_{\downarrow}/N$.

(a) Determine the state of lowest possible energy (the ground state), and show that the energy of this state is $-\mu BN$. Define the *excitation* energy $\mathcal{E} = E - (-N\mu B)$, i.e. the energy *above* the ground state energy. Show that

$$\frac{\mathcal{E}}{N} = n\Delta \tag{24}$$

where $n = N_{\downarrow}/N$ is the number of excited atoms.

(b) By directly counting the states $\Omega(N_{\downarrow}, N_{\uparrow})$ show that the entropy as a function of energy is

$$S(\mathcal{E}) = Nk_B \left[-(1-n)\log(1-n) - n\log n\right] \tag{25}$$

(c) Using Eq. (25) show that the temperature of the system with a given $\mathcal{E}$ is related to the fraction of atoms that are excited (down arrows)

$$\frac{\Delta}{kT} = \ln\left(\frac{1-n}{n}\right) . \tag{26}$$

Show that

$$n = \frac{e^{-\Delta/kT}}{1 + e^{-\Delta/kT}} , \tag{27}$$

as can be found with the canonical approach.

(d) How is n related to the magnetization? Use this relation and the n of part (b) to find the magnetization. Does your result for the magnetization agree with the previous problem?

Problem 4. Distribution of Debroglie Wavelengths

(a) (Optional, but do it for yourself!) Show that

$$\int_{-\infty}^{\infty} dx f(x) = \int_{-\infty}^{\infty} du\, f(-u) \tag{28}$$

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[5]

$$\lambda_{\rm th} \equiv \frac{h}{\sqrt{2\pi m k T}}\,, \tag{29}$$

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 $\lambda \sim h/\sqrt{mkT}$.

(ii) Evaluate $\lambda_{\rm th}$ defined in Eq. (29) numerically for He gas at room temperature $T = 300^\circ$K, and show that

$$\lambda_{\rm th} = 0.50\,\text{Å} \left(\frac{4m_p}{m}\right)^{1/2} \left(\frac{300^\circ\text{K}}{T}\right)^{1/2} \tag{30}$$

where m_p is the proton mass. Use the scaling in Eq. (30) to evalute $\lambda_{\rm th}$ for Ne at $100\,^\circ$K

As always try to use interpretable constants that you can remember and avoid using things like $\hbar = 1.05 \times 10^{-34}\,$J s and $k_B = 1.38 \times 10^{-23}$J/°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 $\lambda + \mathrm{d}\lambda$ is

$$\mathrm{d}\mathscr{P} = \frac{1}{\lambda_{\rm th}} \left(\frac{\lambda_{\rm th}}{\lambda}\right)^4 e^{-\pi(\lambda_{\rm th}/\lambda)^2}\, 4\pi \mathrm{d}\lambda\,. \tag{31}$$

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

---

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

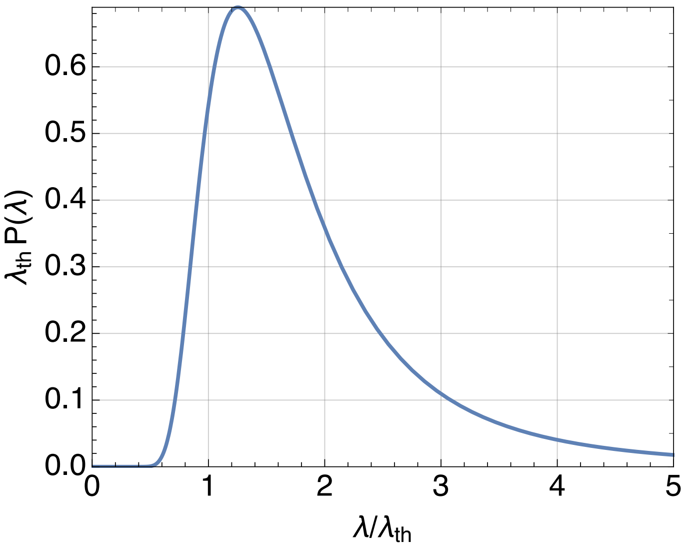
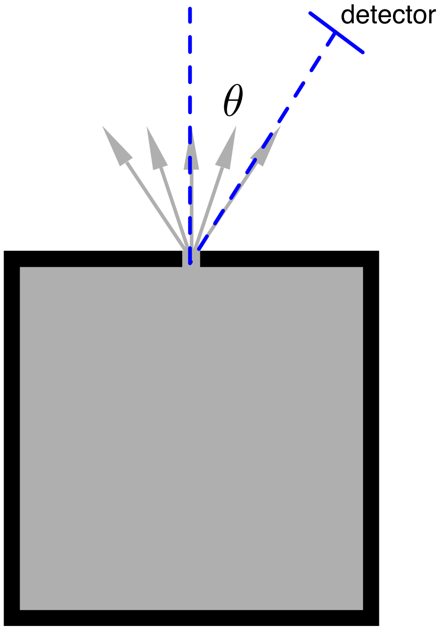


Figure 6: Probability density $P(\lambda) \equiv \mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ times a constant λ_{th}. Note that $\lambda_{\mathrm{th}}P(\lambda) = \lambda_{\mathrm{th}}\mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ is the probability per $\mathrm{d}\lambda/\lambda_{\mathrm{th}}$. The integral under the curve shown above is unity.

Problem 5. Probabilities for escaping particles



In class we showed the number of particles per area per second escaping through a hole in the container (see above) with speeds between $(v, v + dv)$, and angles between $(\theta, \theta + d\theta)$ and $(\phi, \phi + d\phi)$ is

$$d\Phi = nP(v)\, v \cos\theta \, dv \, \frac{d\Omega}{4\pi} \, . \tag{32}$$

Here $d\Omega = \sin\theta d\theta d\phi$ is the differential solid angle; $n = N/V$ is the number of particles per volume and the speed distribution is

$$P(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} 4\pi v^2 \, . \tag{33}$$

Note $P(v)$ is not explicitly needed in this problem. If we integrate over the possible velocities, the flux per solid angle is:

$$\frac{d\Phi}{d\Omega} \equiv \frac{1}{\sin\theta} \frac{d\Phi}{d\theta d\phi} \propto \cos\theta \, . \tag{34}$$

This distribution is illustrated on the next page.

(a) Show that the total number of particles escaping through a hole per (hole) area per time per solid angle is

$$\frac{d\Phi}{d\Omega} = \frac{1}{4\pi} n \langle v \rangle \cos\theta \, , \tag{35}$$

and that

$$\Phi = \frac{1}{4} n \langle v \rangle \, . \tag{36}$$

For reference $\langle v \rangle = (8kT/\pi m)^{1/2}$ but you do not need to show this.

(b) Take a gas of Helium at room temperature and pressure of one bar. There is a pinhole in the container of radius 1 mm. Consider two detectors each of collecting area $1\,\mathrm{cm}^2$, both placed at angle of 30^o relative to the normal (see figure). The first is placed 10 cm away, while the second is placed 20 cm away. What is the total number of particles emitted per second and what is the number of particles collected per second by the two detectors? Use Fig. 7 to explain why $\mathrm{d}\Phi/d\Omega$ a more experimentally relevant quantity for these detectors, than $\mathrm{d}\Phi/\mathrm{d}\theta\mathrm{d}\phi \propto \sin\theta\cos\theta$, which carries the same information.

You should find $0.04\,\mathrm{mol}/s$, 1.1×10^{-4}mol/s, and 2.7×10^{-5}mol/s. Questions to consider: What is the solid angle $\Delta\Omega$ subtended by the two detectors? What fraction of the sphere do they cover and how is this related to $\Delta\Omega$?

(c) Show that the average value of $\cos\theta$ for these escaping particles is $2/3$. What does this number represent physically? How would Fig. 7 look like if this number was 0.99?

(d) (Optional) Your bicycle tire has a slow leak, so that it goes flat within about an $\tau\simeq 1$ hour after being fully inflated. Make an estimate for the radius of the hole when the tire is fully inflated. Take any reasonable estimate for the volume of an inflated tire, the temperature, and a typical mass for air.

Hint: show that the loss of atoms per time takes the form $dN/dt = -N/\tau$, where $\tau^{-1} \equiv A(kT/2\pi m)^{1/2}/V$ is a characteristic decay time, and $A = \pi R^2$.

For reasonable estimates of the volume and temperature I find a hole radius of about $R\sim 30$ microns. But of course if your results could differ from mine by factors of two or three.

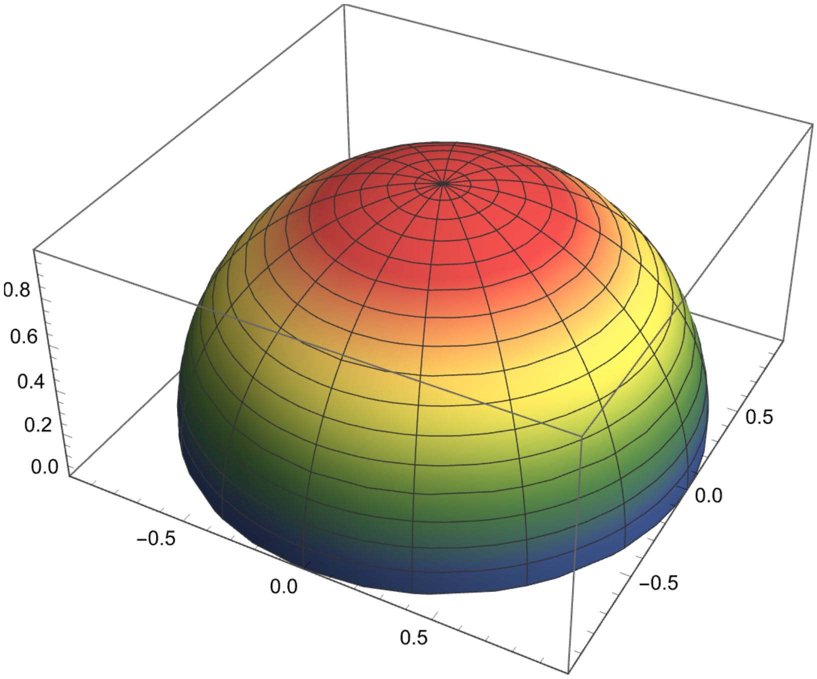


Figure 7: (a) Distribution of escaping particles over the solid angle, $\mathrm{d}\Phi/\mathrm{d}\Omega \propto \cos\theta$. . The red means more particles per per time per solid angle, i.e. per area on this spherical plot. If particles were emitted uniformly over the sphere $\mathrm{d}\Phi/\mathrm{d}\Omega$ would be constant, but $\mathrm{d}\Phi/\mathrm{d}\theta\mathrm{d}\phi$ would not be constant.