Problem 1.   Nitrogen gas

Two moles of nitrogen (N_2) are in a 6-L container at a pressure of $5\,$bar.

    Try not to look up numbers. Rather try to remember a few numbers and ratios, and put them in context, like I did in lecture. If you don't know a number look in the lecture which puts the numbers in context. Here are some things to consider: the Nitrogen atom has seven protons and seven neutrons, and the N_2 molecule contains two nitrogen atoms. In part (b) it is useful to know that the binding energy of an electron in the hydrogen atom is $13.6\,$eV, which is known as the Rydberg constant. The Bohr model relates the binding enegy to the Bohr radius $a_0 \simeq 0.5\,$Å

$$\frac{\hbar^2}{2m_e a_0^2} = 13.6\,\text{eV} \tag{1}$$

You will also need the ratio of the proton to electron mass, m_p/m_e, which was given in lecture.

(a) Find the average kinetic energy of one molecule of the gas in electron volts and the root-mean-square velocity in m/s. I find that the energy and rms velocity are, $0.04\,$eV and $400\,$m/s. Is the kinetic energy $\frac{1}{2}mv^2$?

(b) The bond length of N_2 (i.e. the distance between the N atoms) is $r_0 \simeq 2a_0 \simeq 1\,\text{Å} = 0.1\,$nm. Determine the moment of inertia, and use the equipartition theorem to determine the root-mean-squared angular momentum of the molecule in units of $\hbar$ in terms of the mass of a nitrogen atom m_N, the bound length r_0, the temperature, and fundamental constants, i.e. find[1]

$$\frac{L_{\text{rms}}}{\hbar} \equiv \frac{\sqrt{\left\langle \vec{L}^2 \right\rangle}}{\hbar} . \tag{2}$$

Evaluate the result numerically. The rotations of the molecule can be considered as classical when the angular momentum is large compared to $\hbar$, otherwise the angular motion is quantized. If the corrections to the classical description are of order $\sim \hbar/L$, how good is the classical description of the motion here? What is parametric dependence of L_{rms} on temperature[2]? Will the classical approximation get worse or better as the temperature increases?

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[1] *Hint:*   Recall that the rotational kinetic energy

$$\frac{1}{2}I\vec{\omega}^2 = \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 = \frac{L_x^2}{2I} + \frac{L_y^2}{2I} = \frac{\vec{L}^2}{2I}$$

has two degrees of freedom, while the translational kinetic energy has three. Technically this is because rotational kinetic energy (or Hamiltonian) has two quadratic forms, $\frac{1}{2}I\omega_x^2$ and $\frac{1}{2}I\omega_y^2$. You should find about $L_{\text{rms}} \simeq 8\,\hbar$.

[2] i.e. does it grow exponentially with temperature or as a power, and if a power, then what power?

Speed of Nitrogen Gas: N_2 diatomic nitrogen

$$PV = N k_B T$$

- So

$$k_B T = \frac{PV}{N} = \frac{(5 \times 10^5 \, N/m^2)(6 \times (0.1m)^3)}{2 \times 6 \times 10^{23}}$$

$$= 2.5 \times 10^{-21} \, J \qquad\qquad k_B = \frac{1/44}{273} \frac{eV}{^\circ K}$$

$$\simeq 0.016 \, eV \qquad\qquad T = 180 \, ^\circ K$$

- So the molecule has five degrees of freedom

$$E = \frac{5}{2} k_B T \simeq 0.040 \, eV$$

- The translational motion is 3-degrees of freedom

$$\left\langle \frac{1}{2} m v^2 \right\rangle = 3 \times \frac{1}{2} k_B T$$

So

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$

$$V_{rms} = \left(\frac{3 k_B N_A T}{m N_A} \right)^{1/2}$$

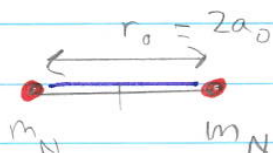Now $\quad k_B N_A = 8.32 \dfrac{J}{{}^\circ K}$ $\qquad T = 180^\circ K$

So $\quad \underline{m N_A = \text{molar mass} \simeq 28_g = 2 \times 14_g}$

$$V_{rms} = \left(\dfrac{3 \cdot 8.32 \dfrac{J}{K} \; 180^\circ K}{28_g} \right)^{1/2}$$

$$\simeq 400 \, m/s$$

b) The moment of inertia is

$$r_0 = 2a_0$$

$$m_N \qquad m_N$$

- So

$$I = m_N a_0^2 + m_N a_0^2 = 2 m_N a_0^2$$

- Then using the equipartition theorem

$$\langle \mathcal{E}_{rot} \rangle = \langle \tfrac{1}{2} I (\omega_x^2 + \omega_y^2) \rangle = \left\langle \frac{L_x^2}{2I} + \frac{L_y^2}{2I} \right\rangle = 2 \left(\tfrac{1}{2} k_B T \right)$$

- So $\langle \vec{L}^2 \rangle$ is

$$\langle L^2 \rangle = 2 I k_B T$$

And

$$\frac{\langle L^2 \rangle}{\hbar^2} = 2 \left(\frac{2 m_N a_0^2}{\hbar^2} \right) k_B T$$

- So now we estimate

$$\frac{\hbar^2}{2 m_N a_0^2} = \frac{1}{14 \cdot 2000} \left(\frac{\hbar^2}{2 m_e a^2} \right) = \frac{13.6 eV}{.14 \cdot 2000} = 0.0005 eV$$

$$\simeq 0.5 \, meV$$

While

$$k_B T = \frac{1/40 \, eV}{300°K} \cdot 180°K = 15 \, meV$$

So

$$\frac{\langle L^2 \rangle}{\hbar^2} = 2 \cdot \frac{(15 \, meV)}{0.5 \, meV} \simeq 60$$

So

$$\frac{L_{rms}}{\hbar} \simeq \sqrt{60} \simeq 7.8$$

Problem 2.   Two State System

Consider an atom with only two states: a ground state with energy 0, and an excited state with energy Δ. Determine the mean energy $\langle \epsilon \rangle$. Sketch the mean energy versus $\Delta/k_B T$.

Two State

$$\langle \varepsilon \rangle = 0 \cdot P_0 + \Delta P_1$$

$$P_n = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{e^{-\beta E_n}}{1 + e^{-\beta \Delta}}$$

⭐
$$\boxed{\langle \varepsilon \rangle = \frac{\Delta e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}}$$

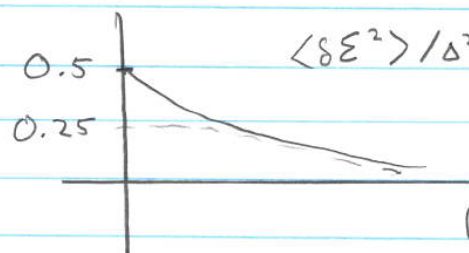$$\langle \varepsilon^2 \rangle = 0^2 P_0 + \Delta^2 \frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})}$$

So

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

$$= \Delta^2 \frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})} - \frac{e^{-2\beta \Delta}}{(1 + e^{-\beta \Delta})^2}$$

$$= \Delta^2 \left[e^{-\beta \Delta} (1 + e^{-\beta \Delta}) - e^{-2\beta \Delta} \right] / (1 + e^{-\beta \Delta})^2$$

⭐
$$\boxed{\delta \varepsilon^2 = \Delta^2 \left(\frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})^2} \right)}$$

So

$\langle \varepsilon \rangle / \Delta$

0.5

0.25

$\beta \Delta$

$\langle \delta \varepsilon^2 \rangle / \Delta^2$ is dashed line. When $\beta \Delta \approx 0$, then the atoms are equally likely to be in either state $\langle \varepsilon \rangle = 0 \cdot \frac{1}{2} + \Delta \frac{1}{2}$

Problem 3.   Working with the speed distribution

Consider the Maxwell speed distribution

(a) Evaluate the most probable speed v_*, i.e the speed where $P(v)$ is maximized. You should find $v_* = (2k_BT/m)^{1/2}$.

(b) Determine the probability to have speed in a specific range, $v_* < v < 2v_*$. Follow the following steps:

   (i) Write down the appropriate integral.

   (ii) Change variables to a dimensionless speed $u = v/\sqrt{k_BT/m}$, i.e. u is the speed in units of $\sqrt{k_BT/m}$, and express the probability as an integral over u.

   (iii) Write a short program (in any language) to evaluate the dimensionless integral, by (for example) dividing up the interval into 200 bins, and evaluate the integral with Riemann sums. You should find

$$\mathscr{P} \simeq 0.53 \tag{3}$$

<u>Speed Distribution</u>

So

a) $\quad P(v) \, dv = \left(\dfrac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} \, 4\pi v^2 \, dv$

- Maximizing $P(v)$ we have

$$P(v) = C \, e^{-v^2/2\sigma^2} v^2 \quad \text{with} \quad \sigma \equiv \left(\dfrac{kT}{m}\right)^{1/2}$$

$$P' = C e^{v^2/2\sigma^2} \left(\dfrac{v^3}{\sigma^2} + 2v\right)$$

- So P is maximized when $P'(v) = 0$ or

$$v^2 = 2\sigma^2 \implies \boxed{v_* = \sqrt{\dfrac{2kT}{m}}}$$

<u>b)</u> $\quad \mathscr{P} = \displaystyle\int_{v_*}^{2v_*} \left(\dfrac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} \, 4\pi v^2 \, dv$

- Substituting

$$u = \dfrac{v}{(kT/m)^{1/2}} \quad \text{this becomes}$$

$$\mathcal{P} = \int_{\sqrt{2}}^{2\sqrt{2}} \frac{1}{(2\pi)^{3/2}} \, 4\pi \, e^{-u^2/2} \, u^2 \, du$$

- So

$$\mathcal{P} = \sqrt{\frac{2}{\pi}} \int_{\sqrt{2}}^{2\sqrt{2}} e^{-u^2/2} \, u^2 \, du$$

$$\approx 0.53$$

See program

```python
from math import *

xmin = sqrt(2.)
xmax = sqrt(2.)*2.

n = 1000
dx = (xmax - xmin)/n

s = 0.
for i in range(0, n):
    x = i * dx + xmin
    s = s + dx * sqrt(2./pi) * exp(-x*x/2.) * x * x
    print(s)
```

Problem 4. Distribution of energies

The speed distribution is

$$\mathrm{d}\mathscr{P} = P(v)\,\mathrm{d}v \tag{4}$$

where $P(v) = (m/2\pi k_B T)^{3/2}\, e^{-mv^2/2k_B T} 4\pi v^2$.

(a) Show that the probability distribution of energies $\epsilon = \frac{1}{2}mv^2$ is

$$\mathrm{d}\mathscr{P} = P(\epsilon)\,d\epsilon \tag{5}$$

where

$$P(\epsilon) = \frac{2}{\sqrt{\pi}}\beta^{3/2} e^{-\beta\epsilon}\,\epsilon^{1/2} \tag{6}$$

Note: that the distribution of energies is independent of the mass, and recall $\beta = 1/k_B T$.

(b) Compute the variance in energy using $P(\epsilon)$. Express all integrals in terms $\Gamma(x)$ (as given in the previous homework) – it is helpful to change to a dimensionless energy $u = \beta\epsilon$. You should find (after evaluating these Γ functions as in the previous homework) that

$$\langle (\delta\epsilon)^2 \rangle = \frac{3}{2}(k_B T)^2 \tag{7}$$

Energies

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

$$v = \left(\frac{2E}{m}\right)^{1/2} \qquad dv = \frac{1}{2\left(\frac{2E}{m}\right)^{1/2}} \frac{2E}{m} = \frac{dE}{(2mE)^{1/2}}$$

- So

$$P(\varepsilon)\,d\varepsilon = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\varepsilon/kT} \frac{2}{m}\varepsilon \frac{d\varepsilon}{\sqrt{2m}\,\varepsilon^{1/2}}$$

$$= 2\pi \frac{2^{3/2}}{2^{3/2}} \frac{m^{3/2}}{m^{3/2}} \frac{\varepsilon^{1/2}\,d\varepsilon}{(k_B T)^{3/2}} \frac{1}{\pi^{3/2}} e^{-\varepsilon/kT}$$

$$\boxed{P(\varepsilon)\,d\varepsilon = \frac{2}{\sqrt{\pi}}\,\beta^{3/2}\, e^{-\beta\varepsilon}\, \varepsilon^{1/2}\, d\varepsilon}$$

So

- $$\langle \varepsilon \rangle = \int_0^\infty \varepsilon\, P(\varepsilon)\, d\varepsilon$$

$$= \int_0^\infty \frac{2}{\sqrt{\pi}}\,\beta^{3/2}\, e^{-\beta\varepsilon}\, \varepsilon^{1/2}\, d\varepsilon \times \varepsilon$$

- Change vars $u = \beta \varepsilon$

$$\langle \varepsilon \rangle = \frac{1}{\beta} \int_0^\infty \frac{2}{\sqrt{\pi}} e^{-u} u^{3/2} \, du$$

$$\langle \varepsilon \rangle = \frac{1}{\beta} \frac{2}{\sqrt{\pi}} \Gamma(5/2) = \frac{1}{\beta} \frac{2}{\sqrt{\pi}} \frac{3}{2} \Gamma\left(\frac{3}{2}\right)$$

Similarly

$$= \frac{1}{\beta} \cdot 2 \cdot \frac{3}{2} \cdot \frac{1}{2} = \frac{3}{2} k_B T$$

$$\langle \varepsilon^2 \rangle = \frac{1}{\beta^2} \int_0^\infty \frac{2}{\sqrt{\pi}} e^{-u} u^{5/2} \, du$$

$$\langle \varepsilon^2 \rangle = \frac{1}{\beta^2} \frac{2}{\sqrt{\pi}} \Gamma(7/2)$$

So

$$\langle \varepsilon^2 \rangle = \frac{1}{\beta^2} \cdot \frac{2}{\sqrt{\pi}} \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} \Gamma(1/2)$$

$$= \frac{1}{\beta^2} \frac{2 \cdot 5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} = \frac{1}{\beta^2} \frac{15}{4}$$

So

$$\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 = \frac{1}{\beta^2} \left(\frac{15}{4} - \frac{9}{4} \right) = \frac{3}{2} (k_B T)^2$$

Problem 5. Change of variables

(a) (Optional, but read it and do it for yourself in one sec; maybe it helps for part (c)) Starting from the speed distribution, show that the distribution of momenta is

$$d\mathscr{P}_{\vec{p}} = \left(\frac{1}{2\pi m k_B T} \right)^{3/2} e^{-p^2/2mk_B T} dp_x dp_y dp_z \tag{8}$$

where $p^2 = p_x^2 + p_y^2 + p_z^2$ and that the distribution of momentum magnitudes is

$$d\mathscr{P}_p = \left(\frac{1}{2\pi m k_B T} \right)^{3/2} e^{-p^2/2mk_B T} 4\pi p^2 dp \tag{9}$$

(b) Show that

$$\int_{-\infty}^{\infty} dx f(x) = \int_{-\infty}^{\infty} du\, f(-u) \tag{10}$$

with $u = -x$.

(c) Consider the de Broglie wavelength $\lambda \equiv h/p$. Recall that we defined a *typical* thermal de Broglie wavelength as

$$\lambda_{\text{th}} \equiv \frac{h}{\sqrt{2\pi m k_B T}} . \tag{11}$$

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

$$d\mathscr{P} = \frac{1}{\lambda_{\text{th}}} \left(\frac{\lambda_{\text{th}}}{\lambda} \right)^4 e^{-\pi(\lambda_{\text{th}}/\lambda)^2} 4\pi d\lambda . \tag{12}$$

The figure below shows the probability density $P(\lambda)$ (i.e. the formula above without the $d\lambda$). From the figure, estimate the ratio between the most probable de Broglie wavelength and λ_{th}.
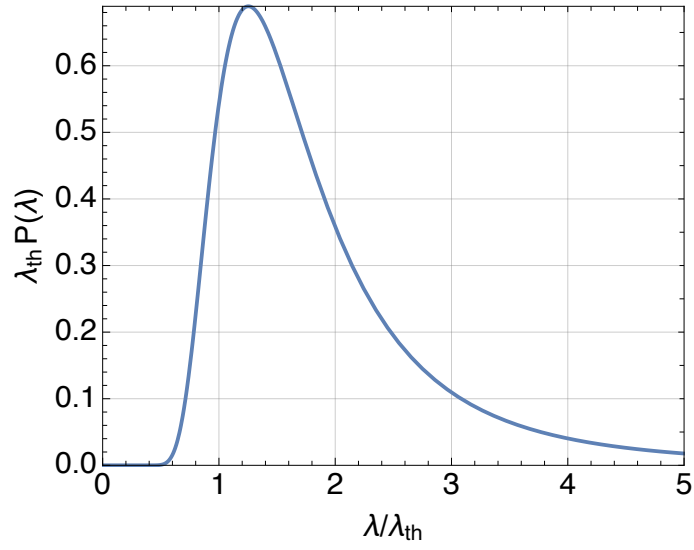
Figure 1: Probability density $P(\lambda) \equiv \mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ times a constant λ_{th}. Note that $\lambda_{\mathrm{th}}P(\lambda) = \lambda_{\mathrm{th}}\mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ is the probability per $\mathrm{d}\lambda/\lambda_{\mathrm{th}}$. The integral under the curve shown above is unity.

Change of Variables

- We have $\qquad dv_x \, dv_y \, dv_z = \dfrac{d^3p}{m^3}$

  Then the leading factor is

  $$d\mathcal{P} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT} d^3v = \frac{1}{(2\pi mkT)^{3/2}} e^{-p^2/2mkT} d^3p$$

  We used $\left(\dfrac{m}{2\pi kT}\right)^{3/2} \dfrac{1}{m^3} = \dfrac{1}{(2\pi mkT)^{3/2}}$

- Then I will use the "unoriented approach"

  $$I = \int_{-\infty}^{\infty} f(x)\,dx = \int_{[-\infty,\infty]} f(x)\,dx = \int_{[-\infty,\infty]} f(-u)\cdot 1 \, du$$

  $$u = -x \qquad dx = \left|\frac{dx}{du}\right| du$$

  $$x = -u$$

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

- The change of variables is from p to λ

  $$\lambda = \frac{h}{p} \implies p = h/\lambda$$

  $$d\lambda = \left|-\frac{h}{p^2}\right| dp = \frac{h}{p^2}\,dp \implies dp = \frac{p^2}{h}\,d\lambda = \frac{d\lambda}{\lambda^2}$$

So

$$d\mathcal{P} = \frac{h^3}{(2\pi mkT)^{3/2}} e^{-p^2/2mkT} \, 4\pi p^2 \frac{dp}{h^3}$$

So

$$d\mathcal{P} = \lambda_{th}^3 \, e^{-p^2/2mkT} \frac{4\pi}{\lambda^4} \, d\lambda$$

Now

$$\frac{p^2}{2mkT} = \left(\frac{h^2}{2\pi mkT}\right) \pi \frac{p^2}{h^2} = \pi \frac{\lambda_{th}^2}{\lambda^2}$$

So we have finally

$$\boxed{d\mathcal{P} = \left(\frac{\lambda_{th}}{\lambda}\right)^3 e^{-\pi \lambda_{th}^2/\lambda^2} \frac{d\lambda}{\lambda}}$$

This is maximized when (see graph)

$$\frac{\lambda_{max}}{\lambda_{th}} \sim 1.25 \qquad \text{or} \qquad \boxed{\lambda_{max} \simeq 1.25\,\lambda_{th}}$$