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 $a_0 \simeq 0.5\,\text{Å}$

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

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 $r_0 \simeq 2a_0 \simeq 1\,\text{Å} = 0.1\,\text{nm}$. 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?

[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

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

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

$$\simeq 0.016 \, eV \qquad T = 180°K$$

- 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

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

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

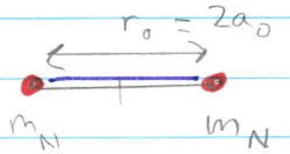
Now $k_B N_A = 8.32 \frac{J}{°K}$ $T = 180°K$

So mN_A = molar mass $\simeq 28g = 2 \times 14g$

$$V_{rms} = \left(\frac{3 \cdot 8.32 \frac{J}{K} \; 180°K}{28g} \right)^{1/2}$$

$\simeq 400 m/s$

b) The moment of inertia is



- So

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

- Then using the equipartition theorem

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

- 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

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

$$\simeq 0.5 meV$$

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

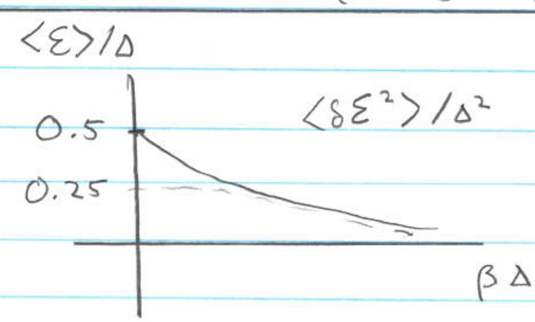
$$\langle \delta \varepsilon^2 \rangle = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2$$

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

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

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

So



$\langle \delta \varepsilon^2 \rangle / \Delta^2$ is dashed line. When $\beta \Delta \simeq 0$, 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 $v_* = (2k_B T/m)^{1/2}$.

(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 $u = v/\sqrt{k_B T/m}$, i.e. u is the speed in units of $\sqrt{k_B T/m}$, 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

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

Speed Distribution

So

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

- Maximizing $P(v)$ we have

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

$$P' = Ce^{v^2/2\sigma^2}\left(\frac{v^3}{\sigma^2} + 2v\right)$$

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

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

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

- Substituting

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

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

- So

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

$$\simeq 0.53$$

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

(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

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

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

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

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

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

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 $u = \beta \varepsilon$

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

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

Similarly

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

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

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

So

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

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

So

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

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

$$\mathrm{d}\mathscr{P}_{\vec{p}} = \left(\frac{1}{2\pi m k_B T}\right)^{3/2} e^{-p^2/2mk_BT}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \tag{8}$$

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

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

(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

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

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 $\lambda + \mathrm{d}\lambda$ is

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

The figure below shows the probability density $P(\lambda)$ (i.e. the formula above without the $\mathrm{d}\lambda$). From the figure, estimate the ratio between the most probable de Broglie wavelength and λ_{th}.

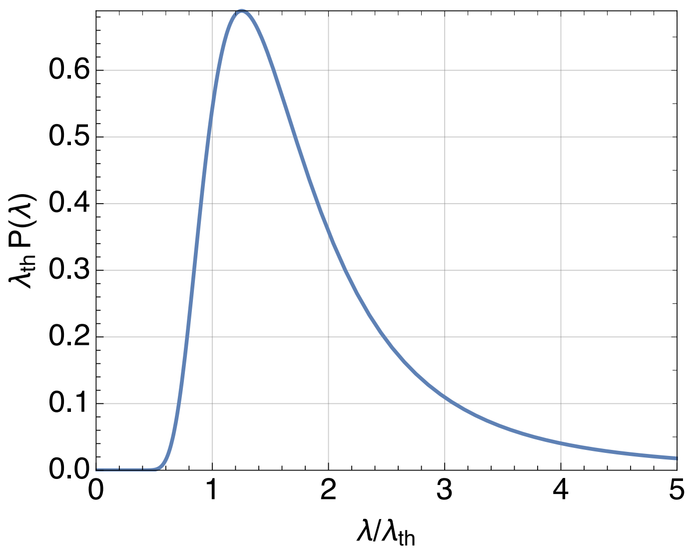


Figure 1: Probability density $P(\lambda) \equiv \mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ times a constant λ_{th}. Note that $\lambda_{\mathrm{th}}P(\lambda) = \lambda_{\mathrm{th}}\mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ is the probability per $\mathrm{d}\lambda/\lambda_{\mathrm{th}}$. The integral under the curve shown above is unity.

Change of Variables

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

  Then the leading factor is

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

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

- 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

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

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

So

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

So

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

Now

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

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)

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