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 $r_0 \simeq 2a_0 \simeq 1\,\text{Å} = 0.1\,\text{nm}$. Use the equipartition theorem to determine the root mean square angular momentum of the molecule in units of $\hbar$ numerically, i.e. find[1]

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

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 $L_{\rm rms}$ on temperature[2]? Will the classical approximation get worse or better as the temperature increases?

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 Δ/k_BT.

[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 $L_{\rm rms} \simeq 8\,\hbar$.

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

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

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

Problem 4. Distribution of energies

The speed distribution is

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

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

(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 $\beta = 1/k_BT$.

(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

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

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}.

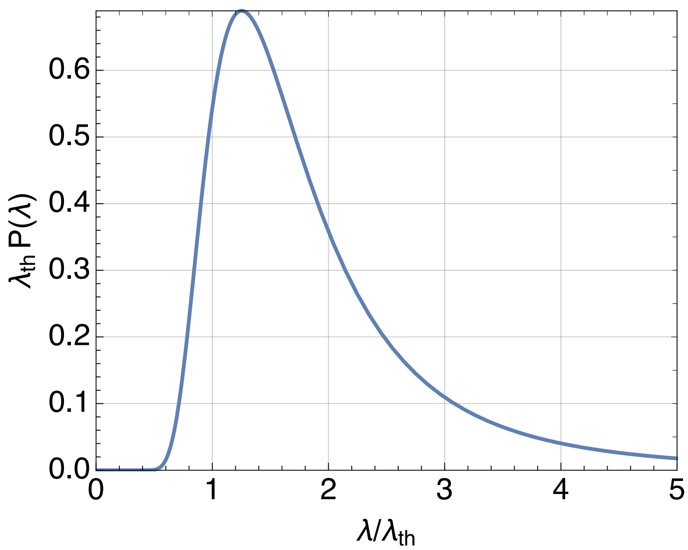

Figure 1: Probability density $P(\lambda) \equiv \mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ times a constant $\lambda_{\rm th}$. Note that $\lambda_{\rm th}P(\lambda) = \lambda_{\rm th}\mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ is the probability per $\mathrm{d}\lambda/\lambda_{\rm th}$. The integral under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