

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 how the Bohr radius a_0 is related to the binding energy of an electron in the hydrogen atom, 13.6 eV. This relation comes from the Bohr model where:

$$\frac{\hbar^2}{2m_e a_0^2} = 13.6 \text{ eV} \quad (1)$$

The constant 13.6 eV is known as the Rydberg constant. 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 $r_0 \simeq 2a_0 \simeq 1 \text{ \AA} = 0.1 \text{ nm}$. Use the equipartition theorem to determine the root mean square angular momentum of the molecule in units of \hbar , i.e. find¹

$$\frac{L_{\text{rms}}}{\hbar} \equiv \frac{\sqrt{\langle \vec{L}^2 \rangle}}{\hbar}. \quad (2)$$

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_{rms} on temperature²? 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 $\Delta/k_B T$.

¹Hint: Recall that the rotational kinetic energy

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

You should find about $L_{\text{rms}} \simeq 8\hbar$.

²i.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 $v_* = (2k_B T/m)^{1/2}$.
- (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

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

Problem 4. Distribution of energies

The speed distribution is

$$d\mathcal{P} = P(v) dv \tag{4}$$

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

$$d\mathcal{P} = P(\epsilon) d\epsilon \tag{5}$$

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

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

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

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

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

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

- (b) Show that

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

with $u = -x$.

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

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

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

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

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} .

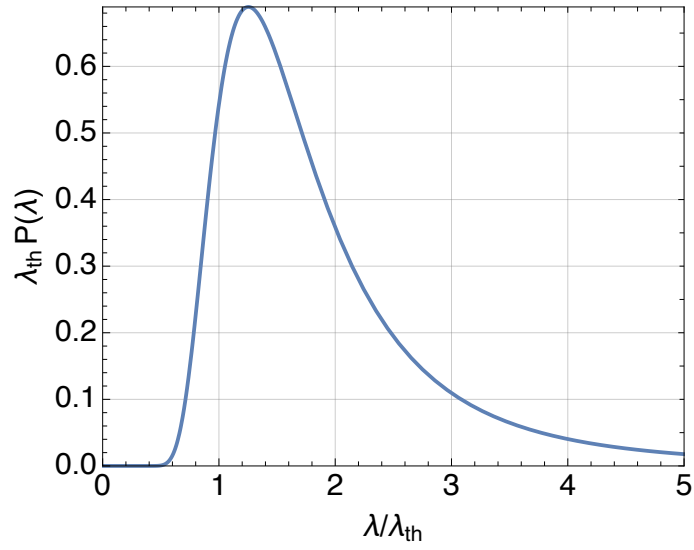


Figure 1: Probability density $P(\lambda) \equiv d\mathcal{P}/d\lambda$ times a constant λ_{th} . Note that $\lambda_{\text{th}}P(\lambda)$ is the probability per $d\lambda/\lambda_{\text{th}}$, or $\lambda_{\text{th}}d\mathcal{P}/d\lambda$. The integral under the curve shown above is unity.