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:

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

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

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

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_{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 $\Delta/k_B T$.

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

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

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?

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

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

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}.

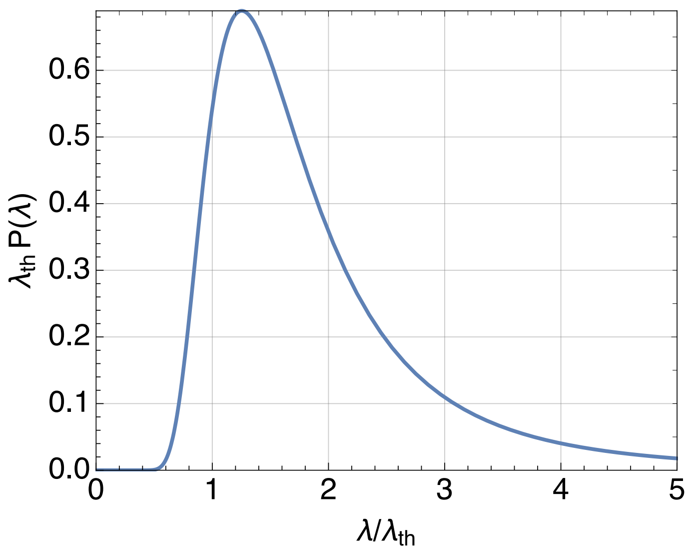

Figure 1: Probability density $P(\lambda) \equiv \mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ times a constant λ_{th}. Note that $\lambda_{\mathrm{th}} P(\lambda) = \lambda_{\mathrm{th}} \mathrm{d}\mathscr{P}/\mathrm{d}\lambda$ is the probability per $\mathrm{d}\lambda/\lambda_{\mathrm{th}}$. The integral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