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]

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

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

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

Problem 2. Partial Derivatives

Consider a particle whose height z is a function of x, y

$$z = z_1(x,y) = x^2 + 2y^2 \tag{3}$$

Now assume $x = r\cos\theta$ and $y = r\sin\theta$. Expressed in terms of x and r the height reads (work this out!)

$$z = z_2(x,r) = 2r^2 - x^2 \tag{4}$$

The functions $z_1(x,y)$ and $z_2(x,r)$ return the same *value*

$$z = z_1(x,y) = z_2(x,r) \tag{5}$$

but the have different *functional forms*. A mathematician would correctly say that they are different functions, i.e. different maps from $\mathbb{R}^2 \to \mathbb{R}$. The first map z_1 adds the square of the first argument to twice the square of the second argument, while the second map z_2 takes twice the square of the second argument and subtracts the square of the first. For a mathematician the functional form is paramount, and the name of the arguments makes no difference, $z_2(a,b) = 2b^2 - a^2$. Having two different symbols, z_1 and z_2, for the same physical quantity would lead to an explosion of symbols and is not practical. So, physicists keep track of the function we are working with by indicating the arguments of the function:

$$z(x,y) \equiv z_1(x,y) \qquad z(x,r) \equiv z_2(x,r) \tag{6}$$

This sneakily uses the same symbol z for two *different* functions and it is not clear at all what $z(a,b)$ means, but clear enough that $z(x_2, r_2) = 2r_2^2 - x_2^2$.

When one takes derivatives one needs to be clearer

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{\partial z_1}{\partial x} = 2x \qquad \left(\frac{\partial z}{\partial x}\right)_r = \frac{\partial z_2}{\partial x} = -2x \tag{7}$$

Compute the following[3]

$$\left(\frac{\partial z}{\partial x}\right)_y, \left(\frac{\partial z}{\partial x}\right)_r, \left(\frac{\partial z}{\partial x}\right)_\theta, \left(\frac{\partial z}{\partial y}\right)_x, \left(\frac{\partial z}{\partial y}\right)_r, \left(\frac{\partial z}{\partial y}\right)_\theta, \frac{\partial z}{\partial x \partial \theta}$$

Problem 3. A classical solid

A solid consists of an array of atoms in a crystal structure shown below. In a simple model (used by Einstein at the advent of quantum mechanics) each atom is assumed to oscillate independently of every other atom [4].

In one dimension a "solid" of N atoms consists of N independent harmonic oscillators. The Hamiltonian[5] of each oscillator is

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2 \tag{8}$$

[3] Answers: $2x$, $-2x$, $2x(1 + 2\tan^2\theta)$, $4y$, $2y$, $2y(2 + \cot^2\theta)$, $8x\sec^2(\theta)\tan(\theta)$

[4] In reality the motions of the atoms are coupled to each other, and the oscillation pattern of the solid, may be found by breaking it up into normal modes.

[5] The Hamiltonian is as a function (or map) returning the energy of the particle for a given position and momentum.

where m is the mass of the atom. Here we have written the Hamiltonian in the "mature" way writing noting that

$$\frac{p^2}{2m} = \frac{1}{2}mv^2 \quad \text{and} \quad \frac{1}{2}m\omega_0^2 x^2 = \frac{1}{2}k_0 x^2 \tag{9}$$

where $\omega_0 = \sqrt{k_0/m}$ is the natural oscillation frequency of the oscillator. In two dimensions each atom can oscillate in the x direction and the y direction. Thus, the solid of N atoms consists of $2N$ independent oscillators. The Hamiltonian (or energy as a function of x, y, p_x, p_y) of each atom is a sum of two harmonic oscillators:

$$\begin{aligned} H(x,p) =& H_x + H_y \quad (10) \\ =& \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right) \quad (11) \end{aligned}$$

Finally in three dimensions (shown below) the solid of N atoms consists of $3N$ independent oscillators as shown below, and each atom can oscillate in the x, y, or z directions. The Hamiltonian of each atom shown in Fig. 1 consists of three harmonic oscillators:

$$\begin{aligned} H =& H_x + H_y + H_z \quad (12) \\ =& \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right) + \left(\frac{p_z^2}{2m} + \frac{1}{2}m\omega_0^2 z^2\right) \quad (13) \end{aligned}$$

The total Hamiltonian is a sum of the Hamiltonians of each atom.

(a) By appealing to the equi-partition theorem for a classical harmonic oscillator, determine the energy of the solid in a classical approximation. Determine the specific heat $C_V^{\rm 1ml}$ for one mole of substance in this case. You should find $C_V^{\rm 1mol} \simeq 25\,\mathrm{J/mol}$, known as the Dulong and Petit rule. The specific heat of a variety of solids is shown on the next page. What does the simple model get right and wrong?

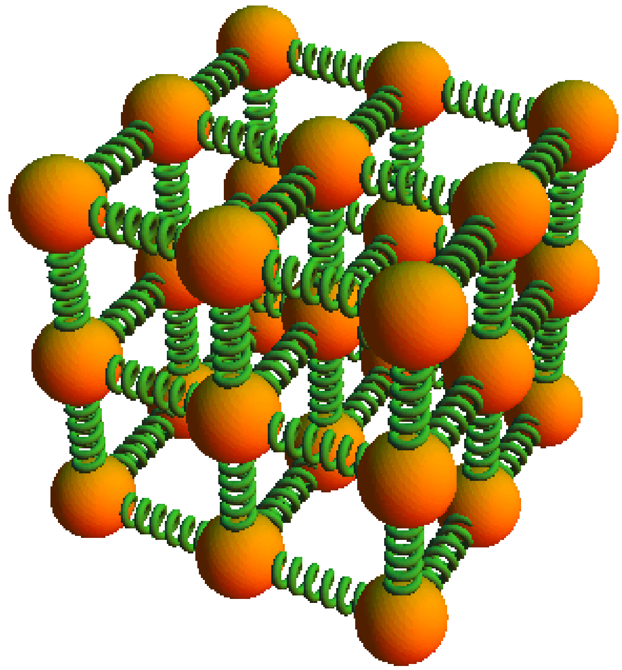
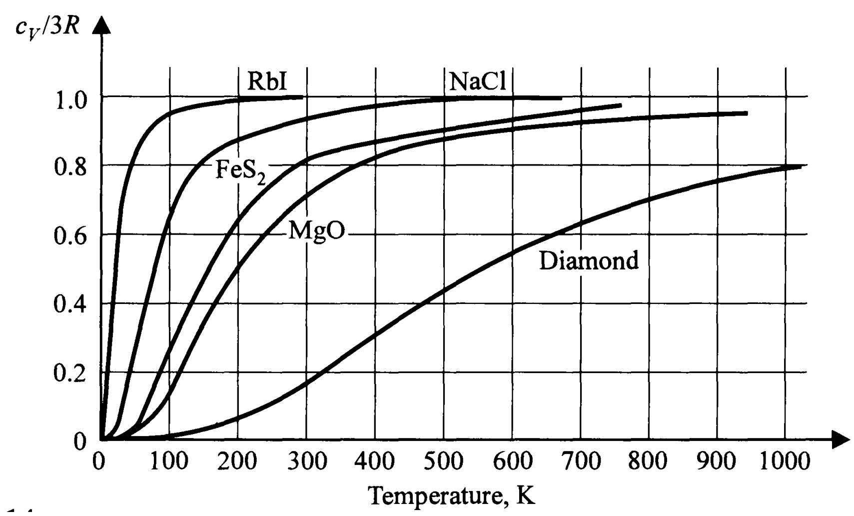


Figure 1:



$c_V/3R$
1.0
0.8
0.6
0.4
0.2
0
RbI
NaCl
FeS$_2$
MgO
Diamond
0
100
200
300
400
500
600
700
800
900
1000
Temperature, K

Problem 4. The generating function trick

Consider integrals of the form

$$I_n = \int_0^\infty e^{-x} x^n \, \mathrm{d}x \tag{14}$$

We will evaluate this by exploiting a simple trick, which occurs throughout statistical mechanics. I will call this the generating function trick. Generalize the integral by inserting a parameter β

$$I_n(\beta) = \int_0^\infty e^{-\beta x} x^n \, \mathrm{d}x \tag{15}$$

(a) Without doing any integrals, show that

$$I_1(\beta) = -\frac{\partial I_0(\beta)}{\partial \beta} \tag{16}$$

Show more generally that

$$I_n(\beta) = \left(-\frac{\partial}{\partial \beta}\right)^n I_0(\beta) \tag{17}$$

We say that $I_0(\beta)$ "generates" the other integrals by differentiation.

(b) Compute $I_0(\beta)$ and show that

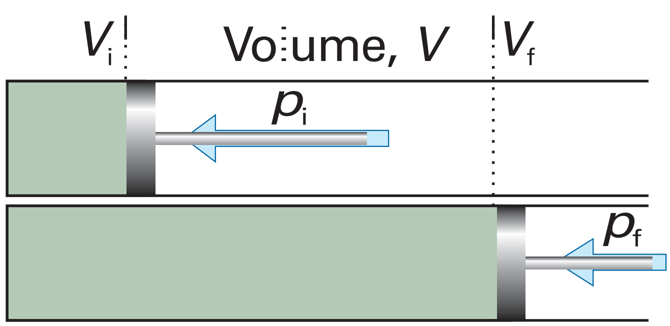
$$I_n(\beta) = \frac{1}{\beta}\left(\frac{n!}{\beta^n}\right) \tag{18}$$

Setting $\beta = 1$, we have established that

$$\boxed{I_n = \int_0^\infty e^{-x} x^n \, \mathrm{d}x} \tag{19}$$

Problem 5. Adiabatic Expansion

In an adiabatic expansion of an ideal gas with constant specific heat C_V, the gas in a cylinder exchanges no heat with its environment. This often a very good idealization when the motion is relatively rapid. Consider the adiabatic expansion from initial volume V_i to final volume V_f.



The temperature changes from T_i to T_f and the pressure changes from p_i to p_f. Use the first law, and properties of specific heats to show that

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad \text{and} \quad p_i V_i^{\gamma} = p_f V_f^{\gamma} \tag{20}$$

Here $\gamma = C_p/C_v$. If you get stuck you may look in the lecture notes.

Problem 6. Energy Derivatives (Optional)

Optional problems should *not* be turned in. The volume expansion coefficient is β_p describes how much a substance expands upon heating at constant pressure.

$$\beta_p \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{21}$$

Strictly β_p is the percent change in volume dV/V per dT. Use the First Law to show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_v}{V\beta_p} - p \tag{22}$$

Is the result consistent for an ideal gas? Explain why or why not.