

Problem Set 3 - Canonical ensemble

(Dated: PHYS403, Spring 2024)

I. Atmosphere

Consider examining a single gas particle taken from the earth's atmosphere. Assume the atmosphere is in thermal equilibrium at temperature T ¹. Denote the mass of the particle by m , acceleration due to gravity by g , and the height of the particle above the earth's surface by z (with the surface of the earth corresponding to $z = 0$).

1. What is the Hamiltonian for the particle?
2. What is the PDF, $p(z)$, for the particle's height, z ?
3. Using the result of the previous part, estimate the ratio of the density of air (which is mostly made up of N_2 molecules) at the top of Mt Everest compared to sea level. You may approximate the temperature to be equal to $270K$ at all elevations (see also the footnote).
Useful numbers:

- Mass of an N_2 molecule = $4.6528301 \times 10^{-26} kg$
- Boltzmann's constant: $k_B = 1.380649 \times 10^{-23} J/K$
- acceleration due to gravity = $9.81 m/s^2$.

Please express your answers to 2 significant figures.

¹ The real situation is much more complicated because there are always non-equilibrium air currents, wind, weather systems etc..., and the temperature tends to decrease with elevation since the atmosphere is constantly absorbing heat from the sun and radiating some of it back into space, but let's ignore all that and approximate this as a system in thermal equilibrium with constant temperature.

II. Impurity in a semiconductor

Consider an impurity in a semiconductor that has a single orbital. Each impurity has four possible states: 1) no electron, 2) electron with spin pointing up (along some fixed axis), 3) electron with spin pointing down, 4) two electrons (with opposite spins to satisfy the Pauli exclusion principle). Pauli exclusion prevents placing two electrons in a single orbital with the same spin, so there is no way to put three electrons on the impurity in this model.

Define the energy of state (1) (no electron) as 0, the energy of states (2,3) (single electron) as $-\varepsilon_b$ ($\varepsilon_b > 0$ is sometimes called the "binding energy"), and the energy of state (4) as $-2\varepsilon_b + U$ where U is the potential energy cost (due to repulsive Coulomb interactions between two electrons) of putting two electrons on the same orbital. You may assume that $U > 2\varepsilon_b$.

1. Compute the partition function for a single impurity.
2. Compute and sketch a plot of:
 - (a) The average number of electrons on one impurity
 - (b) The average energy of a single impurity
 - (c) The heat capacity of one impurity (the explicit expression for C is cumbersome, so you don't need to write it out, just plot it.)

as a function of temperature, T . For the plots, use $\varepsilon_B = 1$, and $U = 12$, and plot for $k_B T$ in the range $[0, 20]$.

III. Quantum Harmonic oscillator in thermal equilibrium, and diatomic gases

Consider a $1d$ quantum Harmonic oscillator with mass m and frequency ω : $H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$, where \hat{p}, \hat{x} are respectively the position and momentum operators. The energy levels of this system are labeled by a non-negative integer, $n = 0, 1, 2, 3, \dots$, and are given by the formula:

$$\varepsilon_n = \hbar\omega(n + 1/2)$$

.

1. Calculate the partition function for a harmonic oscillator in thermal equilibrium with a reservoir/bath at temperature T .
2. Compute the mean energy by differentiating the partition function.
Hint: the geometric series formula will be useful
3. Compute the heat capacity $C = d\langle E \rangle / dT$, and plot it as a function of T .
4. When does this result agree with the classical harmonic oscillator prediction?
5. Fig. 1 shows a measured spectrum of vibration and rotational modes in air (mostly N_2 and O_2). At approximately (estimate the order of magnitude) what temperature do you expect the vibrations and rotations of N_2 to behave classically? Sketch the heat capacity of N_2 as a function of temperature from room temperature, $\approx 300K$ up to around $4000K$ ² including all the translational, rotational modes, and a single vibrational mode corresponding to stretching or compressing the N_2 bond.
Note: for this problem, I am just looking for a semi-quantitative sketch that is accurate only in the order-of-magnitude (e.g. accurate to about ≈ 1 significant figure).

² At temperatures significantly above $4000K$ N_2 molecules tend to dissociate into unbound pairs of N atoms since $k_B T$ becomes larger than the binding energy of the N_2 molecule.)

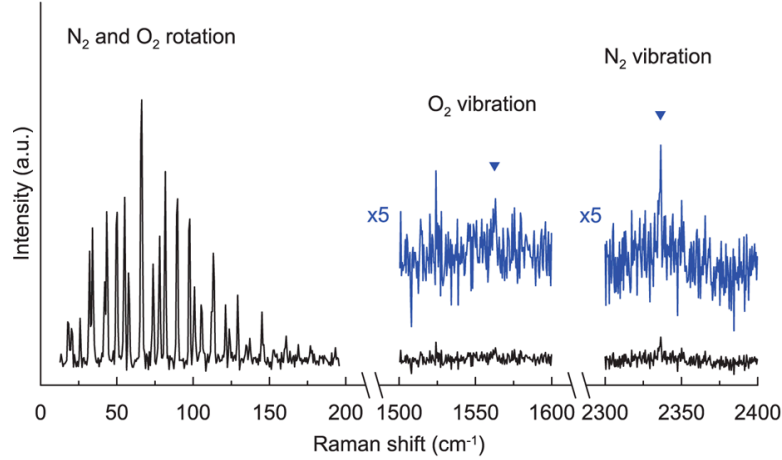


FIG. 1. Raman spectrum of N_2 and O_2 molecules in air. The x axis is: λ^{-1} , the inverse wavelength ($\lambda = 2\pi c/\omega$, where $c = 3 \times 10^8 m/s$ is the speed of light ^a). The peaks occur when the (angular) frequency, ω , of the light matches the frequency of a rotational or vibrational mode in the molecules in air. The "vibration" peak highlighted corresponds to a normal mode where the bond between the two atoms stretches/compresses.

^a Actually, Raman spectroscopy involves a more complicated process in which an incoming photon with a large, optical frequency excites a vibration with a much lower frequency, and the outgoing photon has slightly lower frequency than the incoming one. What is actually plotted corresponds to the difference in frequencies between the incoming and outgoing photon.