# Oblig02 — Fys2160 — 2016

**Exercise 0.3.** Rotation of diatomic molecules

**Learning outcomes.** In this project you will learn how to connect the microscopic and the macroscopic for a canonical system — a system with given $N,V,T$. You will learn to find the partition function for a simple and a complicated system, use the partition function to derive macroscopic properties, and discuss the macroscopic consequences of the model system. The idea is that you apply a general method and a general approach that can be applied to all canonical systems. You should reflect on this method and see how you reuse it across different examples throughout your studies.

**Part 1 — Simplified model system.** We will address the rotational motion of a single diatomic molecule, first in a simplified system, which corresponds to a low temperature approximation, and then for a full model. For low temperatures, a diatomic molecule may be in four different states, $i = 1,2,3,4$, with energies $\varepsilon_i$ that are $\varepsilon_1 = \varepsilon$, $\varepsilon_2 = \varepsilon_3 = \varepsilon_4 = 2\varepsilon$.

**Unstructured problem formulation.** Find the heat capacity as a function of temperature for this system.

**Structured problem formulation.** We will first find the partition function, then use this to find the energy and the heat capacity of the system.

**a)** Find the partition function, $Z$, for this system.

**b)** Write down an expression to find the energy from the partition function, $Z$. Use this expression to find the energy as a function of temperature.

**c)** Find the heat capacity as a function of temperature. Plot the results using reasonable scales. Comment on the implications of this result on the heat capacity of a gas?

**Part 2 — Full model system of a rotating dimolecule.** For a diatomic molecule, the rotational energies are quantized into energy levels described by $j$:

$$\varepsilon_j = j(j+1)\theta_r k \quad j = 0,1,2,\ldots \tag{0.19}$$

where

$$\theta_r k = \frac{\hbar^2}{2I} , \tag{0.20}$$

where $I$ is the moment of inertia for the molecule. The values of $\theta_r$ for some molecules are listed in the following table:

| | $H_2$ | HCl | HI | $N_2$ | $Cl_2$ | $I_2$ |
|---|---|---|---|---|---|---|
| $\theta_r$(K) | 85.4 | 15.2 | 9.0 | 2.86 | 0.346 | 0.054 |

The energy states are degenerate, and the degeneration of each energy given by $j$ is $g(j) = 2j+1$.

**Unstructured problem formulation.** Using a combination of analytical and computational methods, discuss the energy and heat capacity of the rototional aspects of an ideal gas and how this will affect our models of gases.

**Structured problem formulation.** Our strategy will be to first find the partition function. This function is complex to evaluate, and we will address its behavior in the low and high temperature limit using analytical an computational methods. Then we will use the partition function to find the energy and the heat capactiy of the system.

**d)** Write down an expression for the partition function $Z_R(T)$. (You are not asked to evalute the sum, simply to write it down.)

**e)** The partition function consists of terms, $z(j)$, in a sum, $Z = \sum_j z(j)$. Make a script to plot the terms, $z(j)$, in the partition function as a function of $j$ for various values of $T/\theta_r$. Choose reasonable examples of $T/\theta_r$ to illustrate the behavior. Include examples where $T/\theta_r \ll 1$ and where $T/\theta_r \gg 1$.

**f)** Find an expression for $Z_r$ in the limit of $T \gg \theta_r$ by converting the sum to an integral and show that the integral is $Z_r(T) = T/\theta_r$ in this limit.

**g)** Find $Z_r$ in the limit of $T \ll \theta_r$. (Only include a few terms of the sum).

**h)** Find the energy $E(T)$ of the system for high and low $T$.

**i)** Find the heat capacity $C_V(T)$ for high and low $T$.

We will now calculate the partition function, the energy and the heat capacity numerically to get the full behavior of the curve $E(T)$ and $C_V(T)$ as functions of $T$.

**j)** Write a program that calculates a reasonable approximation to the partition function $Z(T,V,N)$ for a particular value of $T/\theta_r$. (Subject for class discussion: How to ensure that you include a reasonable number of terms in the sum.)

**k)** Use the program to calculate $Z(T)$ for $T$ ranging from $T \ll \theta_r$ to $T \gg \theta_r$. Plot the result as a function of $T/\theta_r$.

**l)** Show that your estimate for the high temperature limit above was a bit too low and estimate by how much. Can you explain this by referring to the plots of the terms in the partition function?

**m)** How can you calculate the energy and heat capacity when you know $Z(N,V,T)$? Find expressions you may use to find $E(T)$ and $C_V(T)$ numerically from $Z(N,V,T_i)$ calculated at discrete values of $T_i$.

**n)** Include as many terms as you deem necessary and plot $E(T)$ and $C_V(T)$. Compare with your analytical results in the low and high temperature limit. Comment on the results.