

# ROTATION OF DIATOMIC MOLECULES

FYS2160

SEBASTIAN G. WINTHER-LARSEN  
GITHUB.COM/GREGWINTHER

## CONTENTS

1. Introduction	1
2. A simplified model system	1
3. Full model system of a rotating dimolecule	2

## 1. INTRODUCTION

This study shows how to connect a microscopic and macroscopic representation of a canonical system, as system with given  $N$ ,  $V$  and  $T$  (number of particles/-molecules, volume of the system and temperature respectively). A general method can be applied to all canonical systems. First, finding the partition function. Second, one derives a function for Hermholtz free energy. Lastly, the remaining interesting aspects of the system can be found, like the entropy and heat capacity.

## 2. A SIMPLIFIED MODEL SYSTEM

In this simple system we look at a diatomic molecule, which at low temperatures can be in four different states,  $i = 1, 2, 3, 4$ , with energies  $\varepsilon_i = \varepsilon$ ,  $\varepsilon_2 = \varepsilon_3 = \varepsilon_4 = 2\varepsilon$ . In other words, this system has two possible energies,  $\varepsilon$  and  $2\varepsilon$ . The highest energy has a degeneracy of 3.

The partition function is found by the following formula

$$(1) \quad Z = \sum_i e^{-\beta E_i}, \quad \beta = \frac{1}{kT},$$

colloquially, the sum of a special transform called the Boltzmann factor of every state. For this system the partition function is

$$(2) \quad Z = e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon}$$

One could employ Hermholtz' free energy

$$(3) \quad F = E - TS = -kT \ln Z.$$

First, computing

$$\begin{aligned} \ln Z &= \ln(e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon}) = \ln(e^{-\beta\varepsilon}) + \ln(1 + 3e^{-\beta\varepsilon}) \\ &\approx \ln(e^{-\beta\varepsilon}) + \ln(3e^{-\beta\varepsilon}) = -\beta\varepsilon + \ln(3) - \beta\varepsilon = -2\beta\varepsilon + \ln(3). \end{aligned}$$

The approximation on the second line might not strictly speaking be necessary because the expression for the partition function is simple enough as it is. Instead of going this way I will compute the average energy instead.

The average energy of this system can be found by differentiating  $Z$  with respect to  $\beta$ , and multiplying by  $-1/Z$ .

$$(4) \quad \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\varepsilon e^{-\varepsilon\beta} + 6\varepsilon e^{-2\varepsilon\beta}}{e^{-\varepsilon\beta} + 3e^{-2\varepsilon\beta}} = \frac{\varepsilon(e^{\exp(\varepsilon\beta)} + 6)}{e^{\varepsilon\beta} + 3}.$$

Because  $\beta = 1/kT$  we have the energy as a function of temperature.

The heat capacity, when no work is done on the system and volume is constant, is given by

$$(5) \quad C_V = \left( \frac{\partial E}{\partial T} \right)_V$$

In this case, the heat capacity is

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{3\varepsilon e^{\varepsilon/Tk}}{T^2 k (e^{\varepsilon/Tk} + 3)^2}$$

A plot of the heat capacity can be found in figure 1. We see that the heat capacity quickly approaches zero for larger temperatures. This result is further underlined by the results shown in table 1.

TABLE 1. Heat capacity for the simple diatomic molecule system.

T[K]	C[J/K]
1	$8.8114 \times 10^5$
25	$2.1152 \times 10^7$
50	$5.1519 \times 10^8$
100	$1.2707 \times 10^8$
273	$1.6902 \times 10^9$

This system is not a very realistic system. There are very few molecules involved, and the volume of the system is assumed to be unchanged as the temperature rises. One would assume that a system of gaseous nature would expand as the temperature increases. Furthermore, the temperature domain of the system is just around a few degrees Kelvin at which most, if not all, substances are liquid. There are very few systems able to sustain temperatures this low<sup>1</sup>.

### 3. FULL MODEL SYSTEM OF A ROTATING DIMOLECULE

For a diatomic molecule, the rotational energies are quantized into energy levels described by  $j$

$$(6) \quad \varepsilon_j = j(j+1)\theta_r k, \quad j = 0, 1, 2, \dots$$

where

$$(7) \quad \theta_r k = \frac{\hbar^2}{2I}$$

where  $I$  is the moment of inertia for the molecule. The values of  $\theta_r$  for some molecules are listed in table 2. The energy states are degenerate, and the degeneracy of each energy given by  $j$  is  $d(j) = 2j + 1$ .

TABLE 2.  $\theta_r$  for different molecules

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

<sup>1</sup>One example may be liquid helium, which has a temperature of around 4 Kelvin

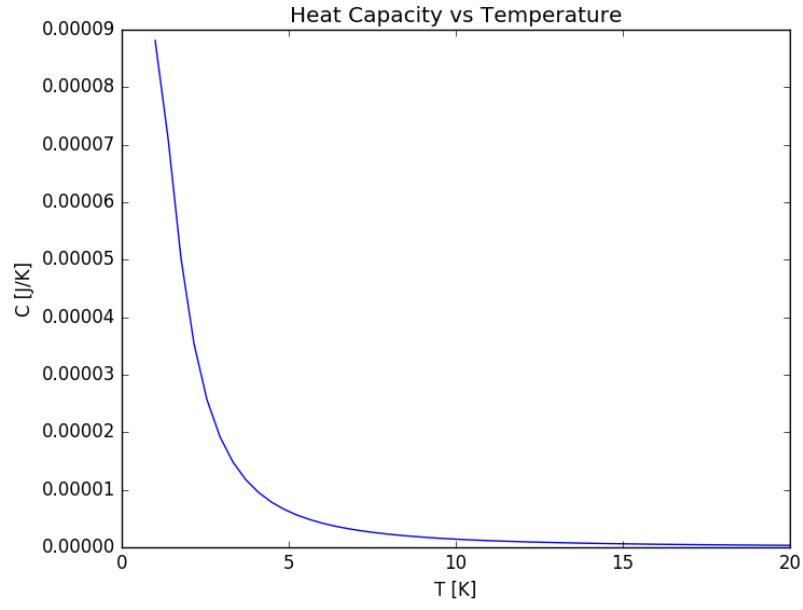


FIGURE 1. Plot of heat capacity vs temperature for the simple diatomic molecule system.

The partition function for this system is

$$(8) \quad Z_{rot} = \sum_j (2j+1)e^{-\beta\epsilon_j} = \sum_j (2j+1)e^{-\beta j(j+1)\theta_r k} = \sum_j (2j+1)e^{-j(j+1)\theta_r/T}$$