

ROTATION OF DIATOMIC MOLECULES

FYS2160

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CONTENTS

1. Introduction	1
2. A simplified model system	1

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, ε and 2ε . 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 β , 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

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

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

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

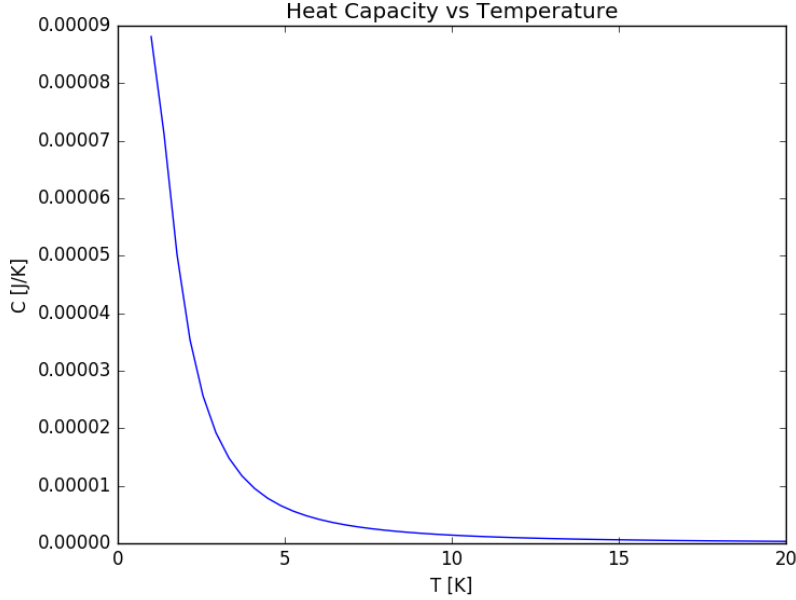


FIGURE 1. Plot of heat capacity vs temperature for the simple diatomic molecule system.