

ROTATION OF DIATOMIC MOLECULES

FYS2160

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1. INTRODUCTION

This study is an exercise in how to compute all interesting properties of a simple system consisting of diatomic molecules. A general method can be applied to all such systems. First, finding the partition function. Second, one computes the average energy of the system. Lastly, the remaining interesting aspects of the system can be found, like the entropy and heat capacity. Herein, a simple model system is studied first, and then similar methods are applied to a more general system. Both analytical and numerical methods are used on the latter. All program code for this project can be found at the github address stated above.

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 Helmholtz' 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 $-1/Z$.

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

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

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

TABLE 2. θ_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

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.

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 or solid. There are very few systems able to sustain temperatures this low¹. This is a good example of the third law of thermodynamics.

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 θ_r for some molecules are listed in table 2. The energy states are degenerate, and the degeneracy of each energy given by j is $d(j) = 2j + 1$.

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

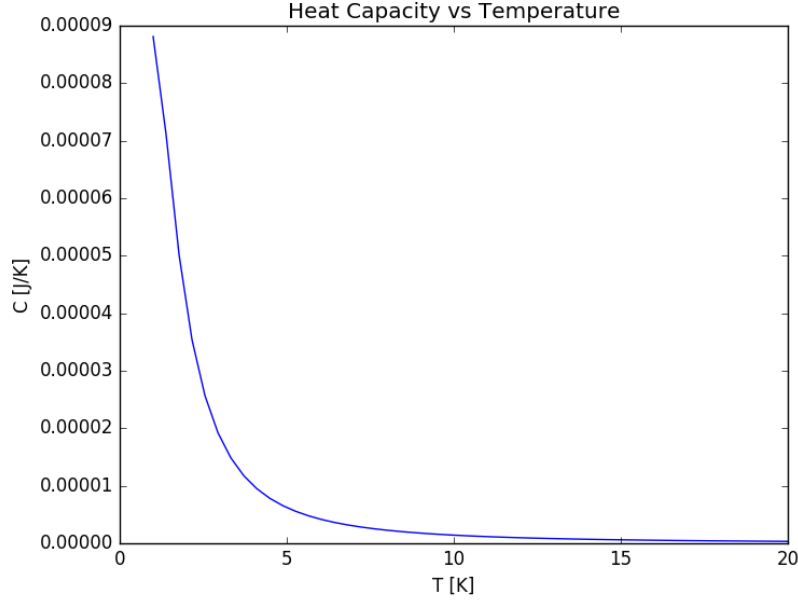


FIGURE 1. Plot of heat capacity vs temperature for the simple diatomic molecule system.

3.1. Analytical approach. The partition function for this system is

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

Figure 2 shows the terms in the sum of this function for various values of T/θ_r . The tendency is clear: as the temperature T gets higher relative to θ_r , the term $z(j)$ is more significant, especially as j increases as well. If T is small, relative to θ_r , $z(j)$ quickly drops to zero for higher states j .

The problem with the partition function in equation 8 is that it is difficult to evaluate a sum like this in closed form exactly. But for a sufficiently large T/θ_r , one can approximate the sum with an integral.

$$(9) \quad Z_{rot} \approx \int_0^\infty (2j+1)e^{-j(j+1)\theta_r/T} dj$$

This integral is relatively easy to solve by the substitution $x = j(j+1)\theta_r/T$ and $dx = (2j+1)\theta_r dj/T$ which gives

$$(10) \quad \frac{T}{\theta_r} \int_0^\infty e^{-x} dx = \frac{T}{\theta_r}$$

Well, what do you know? A (perhaps not so) surprisingly simple and nice expression fell out.

On the other hand, we have the opposite situation where $T \ll \theta_r$. It is sufficient to only look at the first few terms within the sum of the partition function (equation 8) in this case (e.g. $j = 0, 1, 2, 3$)

$$(11) \quad Z_{rot} \approx 1 + e^{-\theta_r/T} + 3e^{-2\theta_r/T} + 5e^{-6\theta_r/T} + 7e^{-12\theta_r/T}$$

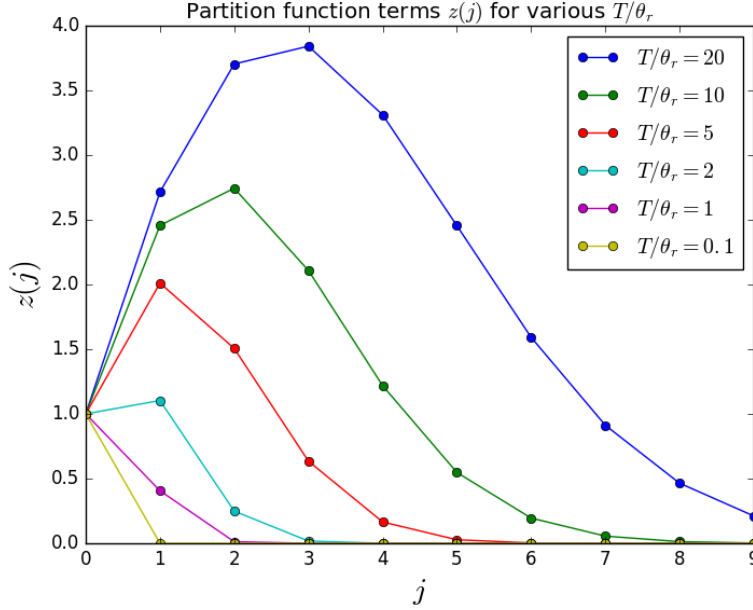


FIGURE 2. The terms in the partition function in equation 8 for various values of $\frac{T}{\theta_r}$

which for the borderline case $T = \theta_r$ will form a convergent series²

$$Z_{rot} \approx 1 + \frac{3}{e^2} + \frac{5}{e^6} + \frac{7}{e^{12}} + \dots \approx 1 + 0.406006 + 0.012394 + 0.0000430 + \dots \approx 1.41844$$

while for the case $T \gg \theta_r$, all terms except the first one will disappear and we get

$$Z_{rot} = 1$$

The average energy of the system can be calculated in the same way as for the simplified system in the previous section, with the following equation

$$(12) \quad \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}, \quad \beta = \frac{1}{kT}$$

In our situation we must have that $T = 1/k\beta$. Then we get the following for the high temperature system, where $Z = T/\theta_r$

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\theta_r}{T} \frac{\partial}{\partial \beta} \frac{T}{\theta_r} = -\frac{1}{T} \frac{\partial}{\partial \beta} \frac{1}{k\beta} = \frac{1}{T} \frac{k}{\beta^2} = \frac{k^2 T^2}{kT} = kT$$

While for the low temperature system, the average energy must be zero, because the partition function is a constant.

The heat capacity, assuming that the volume of the system is constant, is given by

$$(13) \quad C_V(T) = \left(\frac{\partial E}{\partial T} \right)_V$$

which for the high temperature system gives us a heat capacity of Boltzmann's constant k . At a low temperature, the heat capacity is zero, in accordance with the simple system in the previous section. Furthermore, this is in accordance with *the*

²This is easy to check with the ratio test, where one would formulate the test limit $L = \lim_{n \rightarrow \infty} |a_{n+1}/a_n|$. If $L < 1$ the series converges absolutely.

third law of thermodynamics. At zero temperature, a system should settle into its unique lowest-energy state. where

$$(14) \quad C_v \rightarrow 0 \text{ as } T \rightarrow 0$$

3.2. Numerical approach. In order to get a fuller understanding of the diatomic system, similar calculations like the ones above will be done, but now numerically.

The following python function evaluates the partition function for various T/θ_r .

```
def partitionFunction(T_over_theta):

    # Tolerance for when to stop adding
    eps = 1e-12

    # Partition function
    # Starting at state j = 0
    Z = 1

    # Current term of partition function
    # State j = 0 already stored
    Z_ = 1

    # State counter
    j = 1

    # T_over_theta inverse
    theta_prime = 1.0/T_over_theta

    while (Z_ > eps):
        Z_ = (2*j + 1)*np.exp(-j*(j+1)*theta_prime)
        Z += Z_
        j += 1

    return Z
```

The function will continue to compute new terms of the sum $Z_$ until these terms are lower than a tolerance $\epsilon = 1.0 \times 10^{-12}$. A plot of the value of the partition function for values of T/θ_r from 1.0×10^{-3} to 1.0×10^3 is shown in figure 3. It is evident, that for temperatures $T \ll \theta_r$ not much is happening in the system as the partition function asymptotically approaches a low value.

It would be interesting to see how the numerical computation compares with the analytical approximation. Such a comparison is shown in figure 4. We can see that there is some difference between the two functions, especially at low levels. This makes sense because one of the assumptions that was made in order to find an analytical approximation was that $T \gg \theta_r$. we see that the two solutions converge as the temperature T increases relative to θ_r . The values plotted in figure 4 are absolute values, the relative error will be insignificant at high temperatures. For high T , the analytical approximation misses by $1/3$.

The energy and the heat capacity can also be computed numerically. In this system we have an average energy of

$$(15) \quad \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \approx -\frac{1}{Z} \frac{\Delta Z}{\Delta \beta}$$

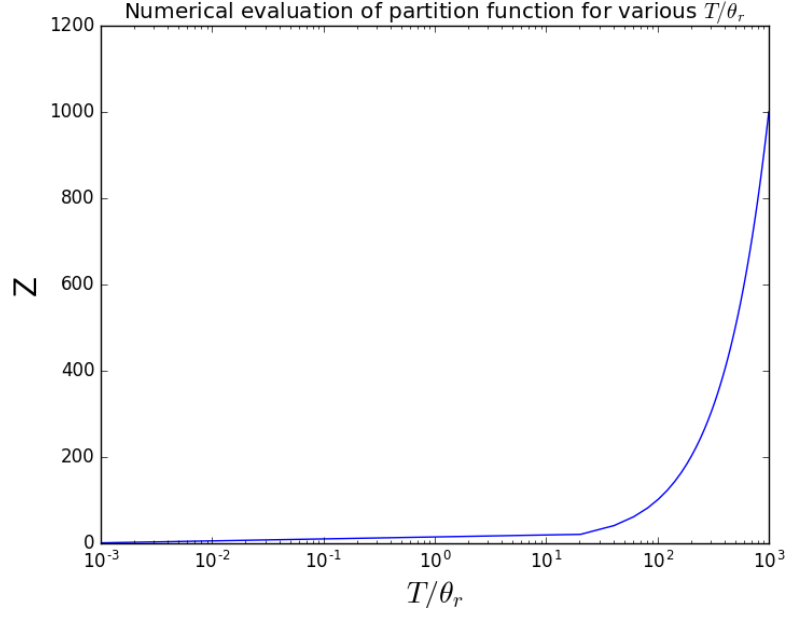


FIGURE 3. Numerical computation of the partition function plotted against various values of T/θ_r . The figure has a logarithmic scale on the x-axis.

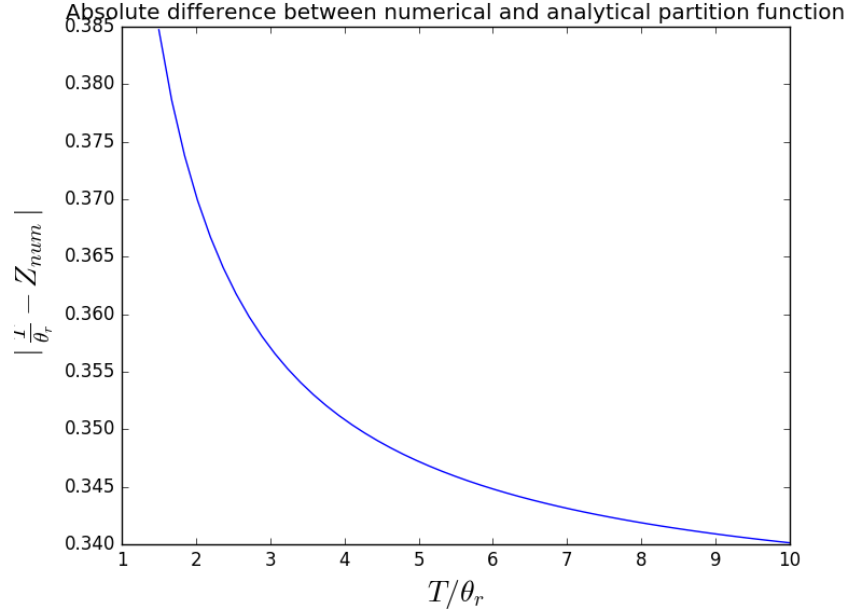


FIGURE 4. Absolute difference between the numerical computation and the analytical computation of the partition function. The analytical solution improves for higher temperatures, according to assumption.

elaborating on this

$$(16) \quad \Delta\beta = \Delta \frac{1}{kT} = \frac{1}{k} \left(\frac{1}{T_{i+h}} - \frac{1}{T_i} \right)$$

where h is a tiny step. Putting equation 16 into equation 16 we get something like

$$(17) \quad \frac{\bar{E}_i}{k} = - \frac{k}{Z_i} \frac{Z_{i+h} - Z_i}{\frac{1}{T_{i+h}} - \frac{1}{T_i}}$$

A functiong that attempts this computation would look something like this

```
def energyCompute():

    start = 1
    stop = 10
    n = 100

    # Assuming theta_r is constant.
    T = np.linspace(start, stop, n)

    E = np.zeros(n)
    Z = np.zeros(n)

    k = 0
    for thing in T:
        Z[k] = partitionFunction(thing)
        k += 1

    for i in range(n-1):
        E[i] = -(1/T[i])*(Z[i+1] - Z[i]) / ((1/T[i+1]) - (1/T[i]))
```

A plot of the results from the program listing above is shown in figure 5. The plot forms a straight line, which is in accordance with the analytical result in equation 3.1.

Employing the same finite difference scheme to compute the heat capacity would only result in a straight line, but would be done in a similar manner by computing

$$(18) \quad C_{V,i} = \frac{E_{i+h} - E_i}{T_{i+1} - T_i}$$

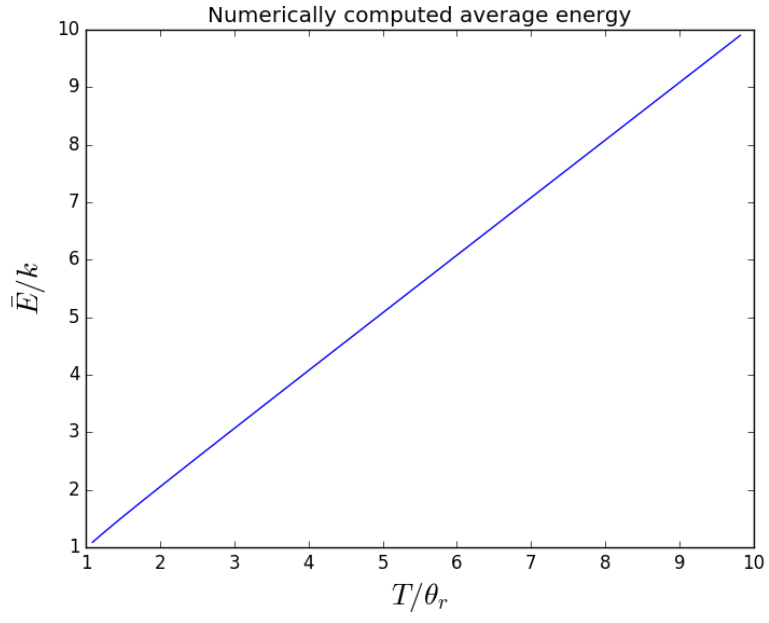


FIGURE 5. Numerically computed average energy of the system.