Fys2160 Oblig 2

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1 Exercise 1)

1.1 a)

The partition function is given as

$$Z = \sum_s e^{-E(s)/kT} = \sum_s e^{-E(s)\beta} \tag{1}$$

We have the energies $\epsilon_1 = \epsilon$ and $\epsilon_2 = \epsilon_3 = \epsilon_4 = 2\epsilon$, giving us the partition function:

$$Z = e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} \tag{2}$$

1.2 b)

From the partition function we are able to find the average energy from the following equation:

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} \tag{3}$$

So the average energy for our system is:

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln\left(e^{-\beta\epsilon} + 3e^{-2\epsilon\beta}\right) \tag{4}$$

$$= -\frac{-\epsilon e^{-\beta\epsilon} - 6\epsilon e^{-2\beta\epsilon}}{e^{-\beta\epsilon} + 3e^{-2\epsilon\beta}} = \epsilon \frac{e^{\beta\epsilon} + 6}{e^{\beta\epsilon} + 3} \tag{5}$$

As a function of temperature:

$$\langle E(T) \rangle = \epsilon \frac{e^{\frac{\epsilon}{kT}} + 6}{e^{\frac{\epsilon}{kT}} + 3} \tag{6}$$

Since we only have one molecule, this is also the total energy U.

1.3 c)

The heat capacity can be found from

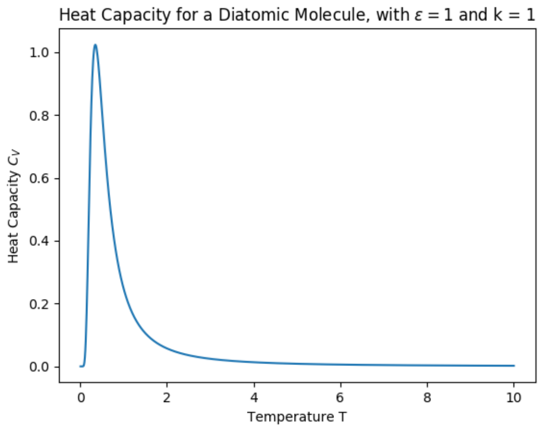
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial \langle E(T) \rangle}{\partial T}\right)_V \tag{7}$$

So using the energy found in eq. (1.2), but with the change of variable $1/kT = \beta$

$$C_V = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta}\epsilon \frac{e^{\beta\epsilon} + 6}{e^{\beta\epsilon} + 3} = -\frac{\epsilon}{kT^2} \frac{\epsilon e^{\beta\epsilon}\left(e^{\beta\epsilon} + 3\right) - \epsilon e^{\beta\epsilon}\left(e^{\beta\epsilon} + 6\right)}{\left(e^{\beta\epsilon} + 3\right)^2} \tag{8}$$

$$= \frac{\epsilon^2}{kT^2}\frac{3e^{\epsilon\beta}}{\left(e^{\beta\epsilon} + 3\right)^2} = \frac{\epsilon^2}{kT^2}\frac{3e^{\frac{\epsilon}{kT}}}{\left(e^{\frac{\epsilon}{kT}} + 3\right)^2} \tag{9}$$

For simplicity we are going to set $\epsilon = k = 1$ for the plot of the heat capacity. The code can be found at the end as **c.py**



Figur 1: The heat capacity of a simple diatomic molecule.

1.4 d)

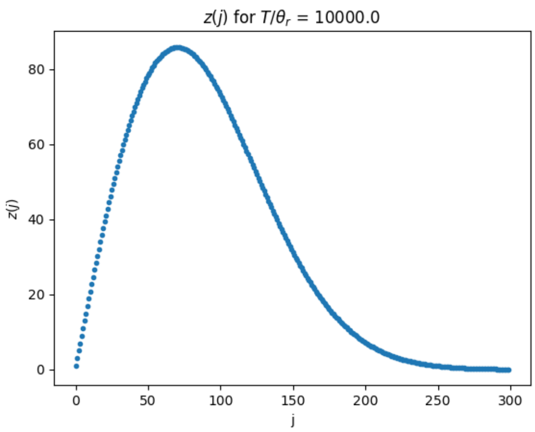
Because of degeneracy eq. (1.1) for the partition function becomes

$$Z_R(T) = \sum_j g(j) e^{-E(j)/kT} = \sum_j (2j+1) e^{-j(j+1)\theta_r/T} \tag{10}$$

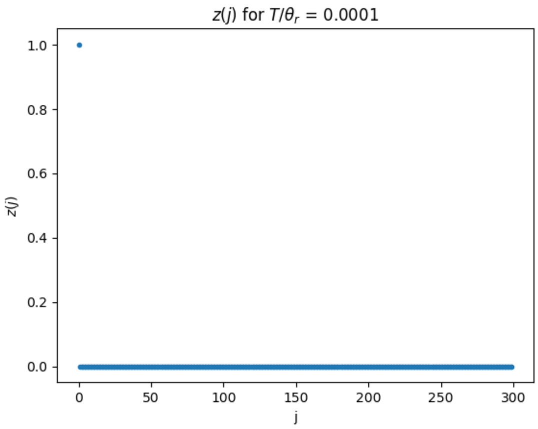
Where $\theta_r = \frac{\hbar^2}{2Ik}$

1.5 e)

The code can be found at the end as **e.py**:



Figur 2: The terms of the partition function for $T/\theta_r >> 1$.



Figur 3: The terms of the partition function for $T/\theta_r << 1$.

We can see that for large values for T/θ_r terms for large values of j contribute, but for small values of T/θ_r the only term that contributes is $z(0) = 1$ and the rest goes to zero.

1.6 f)

We can see in fig. 1.5 that when $T >> \theta_r$ that we can make a good approximation of the terms $z(j)$ as a continuous distribution, and therefore let the eq. (1.4) go towards a integration:

$$Z_r \approx \int_0^{\infty} (2j+1)e^{-j(j+1)\theta_r/T} dj \tag{11}$$

To solve this integral we use the change of variable

$$x = j(j+1) = j^2 + j, \qquad \frac{dx}{dj} = 2j+1 \Rightarrow dj = \frac{dx}{2j+1} \tag{12}$$

To the integral becomes

$$Z_r \approx \int_0^{\infty} e^{-x\theta_r/T} dx = -\frac{T}{\theta_r} e^{-x\theta_r/T} \Big|_0^{\infty} = \frac{T}{\theta_r} \tag{13}$$

So in the limit $T >> \theta_r$ $Z_r(T) = T/\theta_r$.

1.7 g)

For the limit $T << \theta_r$, we can see from fig. 1.5 that only the first term contribute. To we only need to write out the first few terms of eq. (1.4):

$$Z_r \approx 1 + 3e^{-2\theta_r/T} \tag{14}$$

The rest of the term goes very rapidly to zero, and is unnecessary to use.

1.8 h)

1.8.1 High T

For the high temperature approximation we can use eq. (1.2) to get

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial}{\partial \beta} Z = -\beta k \theta_r \frac{\partial}{\partial \beta} \frac{1}{\beta k \theta_r} \tag{15}$$

$$= \beta k\theta_r \frac{1}{\beta^2 k\theta_r} = \frac{1}{\beta} = kT \tag{16}$$

So for high temperature $\langle E \rangle = kT$

1.8.2 Low T

We again use eq. (1.2):

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln 1 + 3e^{-2\theta_r k\beta} = \theta_r k \frac{6e^{-2\theta_r k\beta}}{1 + 3e^{-2\theta_r k\beta}} = \frac{6\theta_r k}{e^{2\theta_r/T} + 3} \tag{17}$$

So for low temperatures $\langle E \rangle = \frac{6\theta_r k}{e^{2\theta_r/T}+3}$

1.9 i)

To find the heat capacity we use eq. (1.3):

1.9.1 High T

For high temperatures we use eq. (1.8.1) and find the heat capacity

$$C_v = \frac{\partial}{\partial T} kT = k \tag{18}$$

So for high temperatures the hear capacity is simply $C_v = k$

1.9.2 Low T

For low temperatures we use eq. (1.8.2). First we do a change of variable $\beta = 1/kT$

$$C_v = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \frac{6\theta_r k}{e^{2\theta_r k\beta} + 3} = \frac{-1}{kT^2} \frac{6\theta_r k e^{2\theta_r k\beta} \cdot 2\theta_r k}{\left(e^{2\theta_r k\beta} + 3\right)^2} = \frac{12\theta_r^2 k e^{2\theta_r/T} \cdot}{T^2 \left(e^{2\theta_r/T} + 3\right)^2} \tag{19}$$

So for low temperatures the heat capacity is $C_v = \frac{12\theta_r^2 k e^{2\theta_r/T} \cdot}{T^2\left(e^{2\theta_r/T}+3\right)^2}$

1.10 j)

The code can be found at the end as **j.py**.