FYS2160 - Oblig 2

a. Partition function, Z, for the system

$i = 1, 2, 3, 4$

Energies: $\varepsilon_i$ : $\varepsilon_1 = \varepsilon$, $\varepsilon_2 = \varepsilon_3 = 3_4 = 2\varepsilon$

$$Z = \sum_i^4 e^{-\frac{\varepsilon_i}{kT}} = e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + e^{-\frac{\varepsilon_3}{kT}} + e^{-\frac{\varepsilon_4}{kT}}$$

$$= e^{-\frac{\varepsilon}{kT}} + e^{-\frac{2\varepsilon}{kT}} + e^{-\frac{2\varepsilon}{kT}} + e^{-\frac{2\varepsilon}{kT}}$$

$$= e^{-\frac{\varepsilon}{kT}} + 3e^{-\frac{2\varepsilon}{kT}} \qquad \boxed{-2\frac{\varepsilon}{kT} = -\frac{\varepsilon}{kT} - \frac{\varepsilon}{kT}}$$

$$= e^{-\frac{\varepsilon}{kT}} + 3e^{-\frac{\varepsilon}{kT}} e^{-\frac{\varepsilon}{kT}}$$

$$= e^{-\frac{\varepsilon}{kT}}\left(1 + 3e^{-\frac{\varepsilon}{kT}}\right)$$

b.

$$\bar{E} = \sum_i \varepsilon_i \frac{1}{Z} e^{-\frac{\varepsilon_i}{kT}} = \frac{1}{Z}\left(\varepsilon_1 e^{-\frac{\varepsilon_1}{kT}} + \varepsilon_2 e^{-\frac{\varepsilon_2}{kT}} + \varepsilon_3 e^{-\frac{3_3}{kT}} + \varepsilon_4 e^{-\frac{3_4}{kT}}\right)$$

$$= \frac{1}{Z}\left(\varepsilon e^{-\frac{\varepsilon}{kT}} + 6\varepsilon e^{-\frac{2\varepsilon}{kT}}\right) = \frac{1}{Z}\left(\varepsilon e^{-\frac{\varepsilon}{kT}} + 6\,\varepsilon e^{-\frac{\varepsilon}{kT}}\,\varepsilon e^{-\frac{\varepsilon}{kT}}\right)$$

$$= \frac{\varepsilon \cancel{e^{-\frac{\varepsilon}{kT}}}\left(1 + 6e^{-\frac{\varepsilon}{kT}}\right)}{\cancel{e^{-\frac{\varepsilon}{kT}}}\left(1 + 3e^{-\frac{\varepsilon}{kT}}\right)} = \varepsilon \frac{1 + 6e^{-\frac{\varepsilon}{kT}}}{1 + 3e^{-\frac{\varepsilon}{kT}}}$$

c. Heat capacity as a function of temperature.

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} \rightarrow \frac{\partial}{\partial T}\, \varepsilon\left(\frac{1+6e^{-\frac{\varepsilon}{kT}}}{1+3e^{-\frac{\varepsilon}{kT}}}\right)$$

$$u = 1+6e^{-\frac{\varepsilon}{kT}} \qquad du = \frac{6\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}}$$

$$v = 1+3e^{-\frac{\varepsilon}{kT}} \qquad dv = \frac{3\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}}$$

$$\boxed{\frac{du\cdot v - u\cdot dv}{v^2}}$$

$$\rightarrow \varepsilon\left(\frac{\left(\frac{6\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}}\right)\left(1+3e^{-\frac{\varepsilon}{kT}}\right) - \left(1+6e^{-\frac{\varepsilon}{kT}}\right)\left(\frac{3\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}}\right)}{\left(1+3e^{-\frac{\varepsilon}{kT}}\right)^2}\right)$$

$$\varepsilon\left(\frac{\frac{6\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}} + \frac{6\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}}3e^{-\frac{\varepsilon}{kT}} - \left(\frac{3\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}} + \frac{3\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}}6e^{-\frac{\varepsilon}{kT}}\right)}{\left(1+3e^{-\frac{\varepsilon}{kT}}\right)^2}\right)$$

$$\varepsilon\left(\frac{\frac{6\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}} + \cancel{\frac{18\varepsilon}{kT^2}e^{-\frac{2\varepsilon}{kT}}} - \frac{3\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}} - \cancel{\frac{18}{kT^2}e^{-\frac{2\varepsilon}{kT}}}}{\left(1+3e^{-\frac{\varepsilon}{kT}}\right)^2}\right)$$

$$= \frac{\frac{3\varepsilon}{kT^2}e^{-\frac{\varepsilon}{kT}}}{\left(1+3e^{-\frac{\varepsilon}{kT}}\right)^2} = \frac{\frac{3\varepsilon e^{-\frac{\varepsilon}{kT}}}{kT^2}}{\left(1+3e^{-\frac{\varepsilon}{kT}}\right)^2} = \frac{3\varepsilon e^{-\frac{\varepsilon}{kT}}}{kT^2\left(1+3e^{-\frac{\varepsilon}{kT}}\right)^2}$$

d. $$Z_R = \sum_{j=0}^{\infty} (2j+1)\, e^{-\beta E(j)} \quad , \quad \beta = \frac{1}{kT}$$

$$= \sum_{j=0}^{\infty} \underbrace{(2j+1)}_{g(j)}\, e^{-\beta j(j+1)\varepsilon}$$

e. See script below. Figure 1 shows the plot.

f. When the number of terms that contributes significantly to the partition function, we can write it as an integral

$$Z_R \simeq \int_0^{\infty} (2j+1)\, e^{-\beta j(j+1)\varepsilon}\, dj$$

In the high-temperature limit, where $Z_R \gg 1$, we can evaluate the integral to show $Z_R(T) = T/\theta_r$

We make the substitution

$$x = j(j+1) = j^2 + j \quad \rightarrow dx = 2j+1$$

$$\rightarrow Z_R = \int_0^{\infty} e^{-\beta x \varepsilon}\, dx \quad , \quad \beta = \frac{1}{kT} \quad , \quad \varepsilon = \theta_R k$$

$$\rightarrow Z_R = \int_0^{\infty} e^{-\frac{x\theta_R}{T}}\, dx = -\frac{T}{\theta_R} e^{-\frac{x\theta_R}{T}} \Big|_0^{\infty} = \frac{T}{\theta_R}$$

g. For low temperatures, only a few terms is enough. I'll include three:

$$Z_R = \sum_j (2j+1) e^{-j(j+1)\frac{\theta_r}{T}}$$

$$\rightarrow (2(0)+1)e^{-0} + (2(1)+1)e^{-1(1+1)\frac{\theta_r}{T}} + (2(2)+1)e^{-2(2+1)\frac{\theta_r}{T}}$$

$$= 1 + 3e^{-2\frac{\theta_r}{T}} + 5e^{-6\frac{\theta_r}{T}}$$

h. Energy E(T) of the system for high and low T

<u>High T:</u> ($T \gg \theta_r$)

$$U = -\frac{\partial \ln(Z)}{\partial \beta} = kT^2 \frac{\partial \ln Z}{\partial T} = kT$$

Which corresponds to $\frac{1}{2}kT$ per degree of freedom (diatomic molecules has two degrees of freedom)

<u>Low T:</u> ($T \ll \theta_r$)

$$\ln(Z) = \ln(1 + 3e^{-2\frac{\theta_r}{T}})$$

$$\overset{\text{Taylor}}{\approx} 3e^{-2\frac{\theta_r}{T}}$$

$$\frac{\partial \ln(Z)}{\partial T} = \frac{\partial}{\partial T} 3e^{-\frac{2\theta_r}{T}} = 3e^{-2\frac{\theta_r}{T}} \cdot \left(\frac{2\theta_r}{T^2}\right)$$

$$= 3\left(\frac{2\theta_r}{T^2}\right)e^{-\frac{2\theta_r}{T}} = \frac{6\theta_r}{T^2} e^{-\frac{2\theta_r}{T}}$$

$$U = kT^2 \frac{\partial \ln(Z)}{\partial T} = k\cancel{T^2} \frac{6\theta_r}{\cancel{T^2}} e^{-\frac{2\theta_r}{T}}$$

$$= k6\theta_r e^{-\frac{2\theta_r}{T}}$$

i. Heat capacity $C_v(T)$ for high and low T.

Heat capacity is found by taking the derivative of the energy

High $\left(\frac{T}{\theta_r} >> 1\right)$

$$E(T) = kT \rightarrow \frac{dE}{dT} = k$$

Low $\left(\frac{T}{\theta_r} << 1\right)$

$$E(T) = k6\theta_r e^{-\frac{2\theta_r}{T}}$$

$$\rightarrow \frac{dE}{dT} = k6\theta_r e^{-\frac{2\theta_r}{T}}\left(\frac{2\theta_r}{T^2}\right)$$

$$= 12k\left(\frac{\theta_r}{T}\right)^2 e^{-\frac{2\theta_r}{T}}$$

j. Code is listed below.

k. Figure 2 shows the plot.

l. From the plot, we can see that $Z$ is linear for large values, but lies slightly below the graph where $Z = T/\theta_r$. This happens because the integral produces an error, which underestimates the partition function sum.

m. We can find the energy by

$$E = kT^2 \frac{\partial \ln Z}{\partial T}$$

If we make the substitution $u = T/\theta_r$

We can write

$$E = k(u\theta_r)^2 \frac{\partial Z}{\partial T} = k u^2 \theta_r^2 \frac{\partial \ln Z}{\partial u} \cdot \frac{\partial u}{\partial T}$$

$$= k u^2 \theta_r \frac{\partial \ln Z}{\partial u}$$

If we know $Z(N, V; u)$ numerically, we can find the energy $E$.

We can find the heat capacity by

$$c_v = \frac{\partial E}{\partial T} = \frac{\partial E}{\partial u} \cdot \frac{\partial u}{\partial T} = \frac{1}{\theta_r} \frac{\partial E}{\partial u}$$

$$= k \frac{\partial u^2}{\partial u} \cdot \frac{\partial \ln z}{\partial u}$$

n. See plot below.