Lab 2

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Code available on Github.

Exercise 1

The free energy F and entropy S are

$$\begin{aligned} F &= -k_B T \ln Z \\ S &= \frac{1}{T}\left(\langle E\rangle - F\right) \end{aligned} \tag{1}$$

The free energy is also written as

$$F = \langle E\rangle - TS \tag{2}$$

In the high-temperature limit, the entropy S of a system with N states becomes:

$$\begin{aligned} \lim_{T\to\infty} S &= \lim_{T\to\infty} \frac{\langle E\rangle - F}{T} \\ &= \lim_{T\to\infty} \frac{\sum_{n=0}^{N-1} p_n E_n + T \ln \mathcal{Z}}{T} \\ &= \lim_{T\to\infty} \frac{\sum_{n=0}^{N-1} p_n E_n}{T} + \lim_{T\to\infty} \ln \mathcal{Z} \\ &= 0 + \ln N = \ln N \end{aligned} \tag{3}$$

For $N = 2$, $\lim_{T\to\infty} S = \ln 2$. In the low-temperature limit, the entropy S of a system with N states becomes:

$$\begin{aligned}
\lim_{T\to 0} S &= \lim_{T\to 0} \frac{\langle E\rangle - F}{T} \\
&= \lim_{T\to 0} \frac{\sum_{n=0}^{N-1} p_n E_n + T \ln \mathcal{Z}}{T} \\
&= \lim_{T\to 0} \frac{\sum_{n=0}^{N-1} p_n E_n}{T} + \lim_{T\to 0} \ln(\sum_{n=0}^{N-1} e^{-\beta E_n}) \\
&= \lim_{T\to 0} \frac{E_0}{T} + \lim_{T\to 0} -\beta E_0 + \ln(1 + \sum_{n=0}^{N-1} e^{-\beta(E_n - E_0)}) \\
&= \lim_{T\to 0} \frac{E_0}{T} + -\frac{E_0}{T} + \ln(1 + \sum_{n=0}^{N-1} e^{-\beta(E_n - E_0)}) \\
&= \lim_{T\to 0} \ln\left(1 + \sum_{n=0}^{N-1} e^{-\beta(E_n - E_0)}\right) = \ln 1 = 0
\end{aligned} \tag{4}$$

For $N = 2$, $\lim_{T\to 0} S = 0$.

Exercise 2

At high temperatures, systems have an equal $\frac{1}{N}$ probability of being in any of the N states. The entropy is $\ln N$, and as there are N accessible states, the statement holds. At low temperatures, systems must be in the E_0 state. The entropy is $\ln 1 = 0$, and as there are 1 accessible states, the statement holds.

Exercise 4

Figure 1 is a plot of S vs. T for $N = 3$ and $E_0 = -3.7, E_1 = -3.5, E_2 = 0.5$. As $T \to \infty$, $S \to \ln 3 \approx 1.09$ and as $T \to 0$, $S \to 0$. This makes sense in terms of the results for Exercise 1. The entropy also has a steep increase whenever $E_n - E_0$ has a steep increase; here $E_1 - E_0 = 0.2$ and $E_2 - E_0 = 4.2$, and S increases significantly around $T = 0.2$ and $T = 4$.

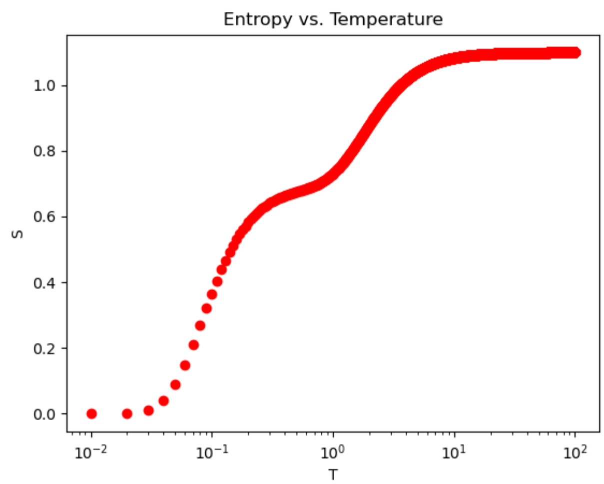

Figure 1: Plot of entropy vs. temperature ($E_0 = -3.7, E_1 = -3.5, E_2 = 0.5$).

Exercise 5

Figure 2 is a plot of S vs. T for $N = 7$ and $E_0 = 0.3, E_1 = 0.4, E_2 = 0.5, E_3 = 5.0, E_4 = 6.0, E_5 = 300.0, E_6 = 400.0$. As $T \to \infty$, $S \to \ln 7 \approx 1.95$ and as $T \to 0$, $S \to 0$. This makes sense in terms of the results for Exercise 1. The entropy also has a steep increase whenever $E_n - E_0$ has a steep increase; here $E_1 - E_0 = 0.1$, $E_3 - E_0 = 4.7$, and $E_5 - E_0 = 297.7$, and S increases significantly around $T = 0.2$, $T = 5$, and $T = 300$.

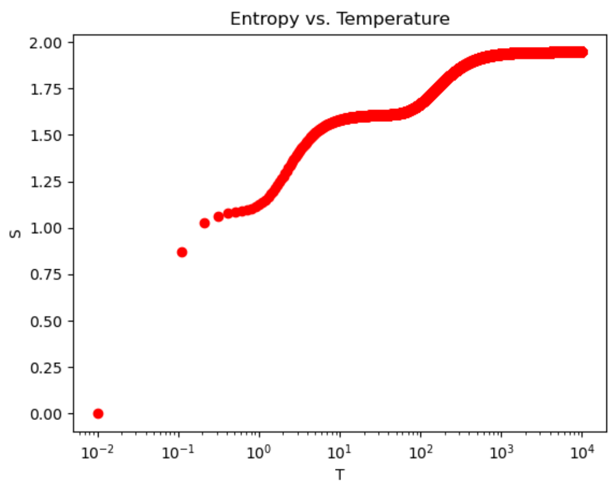

Figure 2: Plot of entropy vs. temperature ($E_0 = 0.3, E_1 = 0.4, E_2 = 0.5, E_3 = 5.0, E_4 = 6.0, E_5 = 300.0, E_6 = 400.0$)

Exercise 6

The entropy can also be calculated by integrating the specific heat.

$$S(T) = \int_0^T \frac{C(T')}{T'}\, \mathrm{d}T' \tag{5}$$

Figure 3 is a plot of S vs. T for $N = 3$ and $E_0 = -3.7, E_1 = -3.5, E_2 = 0.5$. This makes sense in terms of the results for Exercise 1. The entropy also has a steep increase whenever $E_n - E_0$ has a steep increase; here $E_1 - E_0 = 0.2$ and $E_2 - E_0 = 4.2$, and S increases significantly around $T = 0.2$ and $T = 4$. The entropies calculated using (1) and (5) agree, although the second method is very slightly off at high temperatures; this is likely because the size of the subintervals are too large for the trapezoidal method to be accurate.

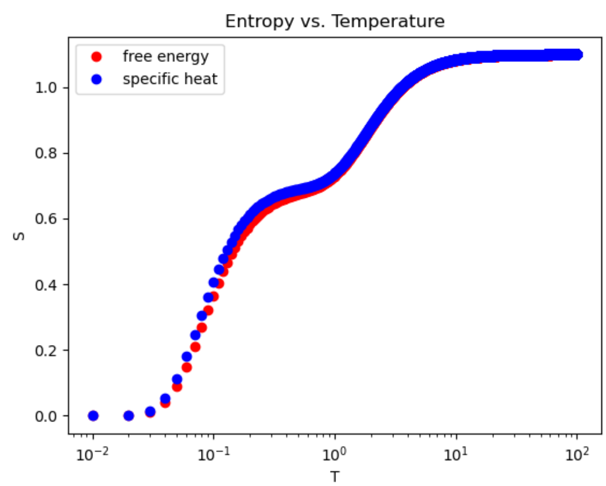

Figure 3: Plot of entropy vs. temperature ($E_0 = -3.7, E_1 = -3.5, E_2 = 0.5$)