Physics 4251/6250 – Fall 2019
Problem Set 2 Solutions
55 points in total

Problem 1 (20 pts): DNA unzipping

(a, 5) Derive the given form of the partition function.

$$Z = \sum_{s=0}^{N} e^{-\beta s\epsilon} = \sum_{s=0}^{N} (e^{-\beta\epsilon})^s = \frac{1 - \exp[-(N+1)\beta\epsilon]}{1 - \exp(-\beta\epsilon)} \tag{1}$$

where we use the formula for a geometric series $\sum_{n=0}^{N} x^n = (1 - x^{N+1})/(1 - x)$.

(b, 5) Derive an expression for $\langle s \rangle$.

$$\langle s \rangle = \frac{1}{Z}\sum_{s=0}^{N} s e^{-\beta s\epsilon} = \frac{1}{Z}\frac{-\partial}{\partial(\beta\epsilon)}\sum_{s=0}^{N}(e^{-\beta s\epsilon}) = \frac{1}{Z}\frac{-\partial}{\partial(\beta\epsilon)} Z = -\frac{1}{\epsilon}\frac{\partial}{\partial\beta}\ln Z. \tag{2}$$

(c, 5) Determine $\langle s \rangle$.

$$\ln Z = \ln[1 - \exp(-(N+1)\beta\epsilon)] - \ln[1 - \exp(-\beta\epsilon)] \tag{3}$$

$$\langle s \rangle = -\frac{\partial}{\partial(\beta\epsilon)}\ln Z = \frac{-(N+1)\exp[-(N+1)\beta\epsilon]}{1 - \exp[-(N+1)\beta\epsilon]} + \frac{\exp(-\beta\epsilon)}{1 - \exp(-\beta\epsilon)} \tag{4}$$

(d, 5) What are the high-T and low-T limits of $\langle s \rangle$?

As $T \to 0$, $e^{-\beta\epsilon} \to 0$, thus making $\langle s \rangle = 0/1 + 0/1 = 0$.

For $T \to \infty$, I tried simplifying the expressions using $e^{-\beta\epsilon} \approx 1 - \beta\epsilon$, which gives $\langle s \rangle = N$. It turns out this is wrong! If you use L'Hôpital's rule to take the limit properly, you get $N/2$. I convinced myself of this by revisiting the original definition of $\langle s \rangle$ and noting that $e^{-\beta s\epsilon} = 1$ now.

$$\langle s \rangle \frac{1}{Z}\sum_{s=0}^{N} s e^{-\beta s\epsilon} = \frac{1}{Z}\sum_{s=0}^{N} s = \frac{1}{Z}\frac{N(N+1)}{2} = \frac{1}{N+1}\frac{N(N+1)}{2} = \frac{N}{2} \tag{5}$$

where we also used the fact that $Z = \sum_{s=0}^{N} 1 = N + 1$. This makes intuitive sense, as at high temperature, all states are equally likely, making the average $N/2$.

Problem 2 (35 pts): Applying Jarzynski's Equality using simulated data

(c, 5) Make a figure of the starting and ending states of deca-alanine.

See Fig. 1.

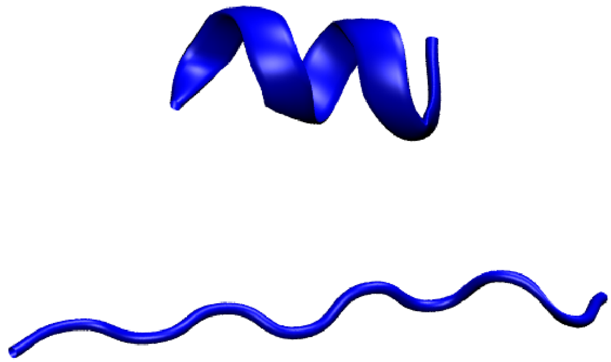

Figure 1:

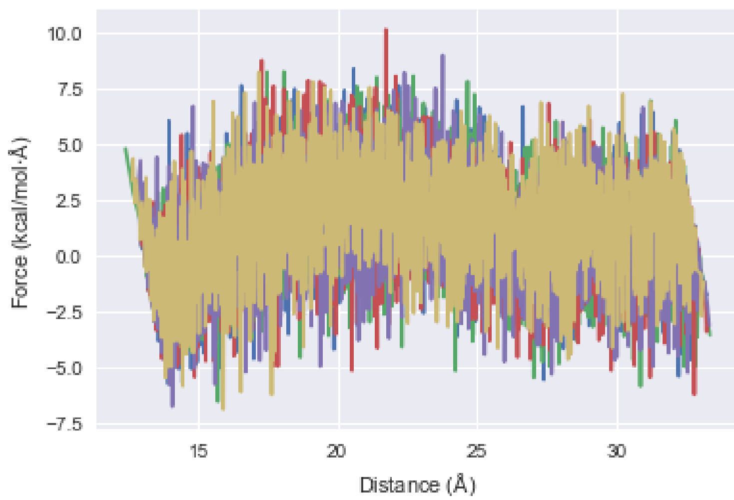

Figure 2:

(d, 5) Plot the force curves.

See Fig. 2.

(e, 5) Calculate the work, $W(x)$.

The work curves are plotted in Fig. 3.

(f, 5) Do any of the work curves violate the Second Law?

Two of mine appear to violate the Second Law for some values of x.

(g-h, 10) Plot the average work as well as the Jarzynski-averaged work along with the exact PMF.

See Fig. 4.

(i, 5) How do the curves all compare?

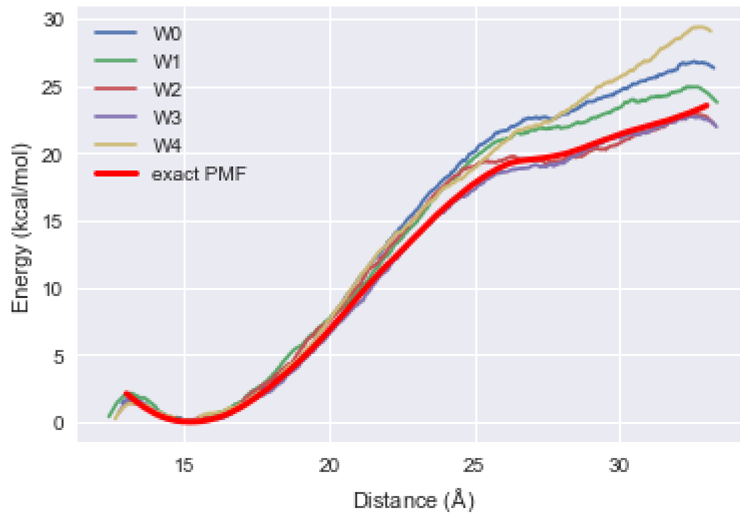

Figure 3:

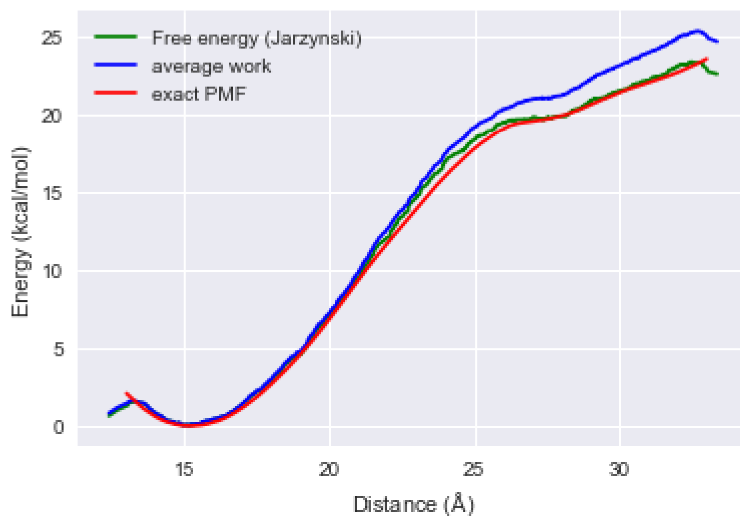

Figure 4:

The first-order approximation, $\langle W \rangle$, clearly diverges significantly more from the exact PMF than the estimate from Jarzynski's identity.