# Problem Set 2

1. *Thermodynamics of Hurricanes*

A Carnot engine is a device that uses heat to raise energy of material; subsequently, some of the additional energy is extracted *adiabatically*, i.e., with no heat flowing, to do work. Let's say this happens at a hot temperature $T_{\mathrm{H}}$. It is not possible to perfectly convert the heat absorbed into work (this is Kelvin's statement of the Second Law of Thermodynamics). As such, the excess heat in the system must be dumped into a heat sink, which is simply a thermal bath at temperature $T_{\mathrm{C}}$.

The efficiency of a Carnot engine is measures the fraction of work obtained from the input heat

$$\eta = \frac{\mathcal{W}}{Q_{\mathrm{H}}} \leq \frac{Q_{\mathrm{H}} - Q_{\mathrm{C}}}{Q_{\mathrm{H}}}. \tag{1}$$

Because the Carnot engine is idealized, it actually obtains this maximal efficiency and we can write

$$\eta_{\text{carnot}} = \frac{Q_{\mathrm{H}} - Q_{\mathrm{C}}}{Q_{\mathrm{H}}} = \frac{T_{\mathrm{H}} - T_{\mathrm{C}}}{T_{\mathrm{H}}}. \tag{2}$$

As you certainly learned in general chemistry, atmospheric pressure affects the boiling point of water. Normally, this is explained using the Clausius-Clapeyron equation, which says that the chemical potentials of the gas phase and the liquid phase are equal at coexistence, i.e.,

$$\mu_{\text{gas}}(T_*) = \mu_{\text{liq}}(T_*). \tag{3}$$

Here, we will derive this result using a more mechanical perspective, based on the notion of a Carnot engine, which is adapted from Mehran Kardar. Suppose we wanted to build an engine that uses one mole of water to drive a piston. Initially, the pressure is $P$ and the temperature is $T$. A quantity of heat $Q_L$ is used to produce steam from the water, leading to an increase in volume, $V$. All Carnot cycles involve an *adiabatic step*, in this case, the pressure is decreased to $P - \Delta P$. Finally, we use the heat sink to condense the steam back into water so that the system is at pressure $P - \Delta P$ and temperature $T - \Delta T$.

(a) Assuming that the work is done isothermally at temperature $T$, write an expression for the work in terms of the variables defined above (including but not limited to $P$, $V, T$).

(b) Assuming the Carnot efficiency is realized, derive an expression for the ratio of the change in pressure to the change in temperature at coexistence between liquid and gas. Your answer should only depend on the heat, volume, and temperature. *Hint: in class we used the Gibbs-Duhem equation; this is its moment to shine.*

(c) The expression you have derived tells you about how the coexistence pressure changes with temperature, which is also a formulation of the Clausius-Clapeyron equation. The inverse relation tells you that lowering the pressure will increase the coexistence temperature—it's cool! Interestingly, you can think of the planet like this. Assume that the ocean surface is 25 C and the upper atmosphere is -80 C. As the surface water evaporates, it condenses and does work on the planet. Assuming that 90 million

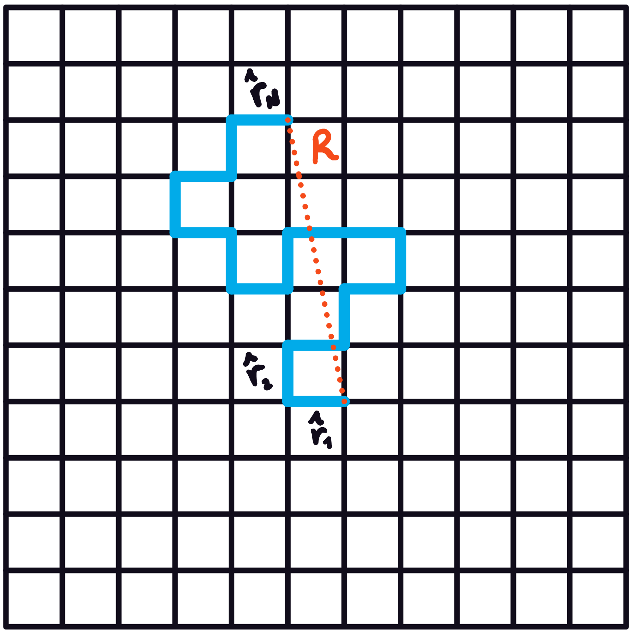

Figure 1: The random polymer model is specified by a set of $n$ random displacements $\hat{r}_i$ for $i = 1, \ldots, n$.

tons of water per hour are required to maintain a hurricane, estimate the maximum possible power output (work per unit time) of a hurricane. Assume that the latent heat of vaporization of water is $2.3 \times 10^6$ J/kg. What are the implications of ocean warming for hurricanes?

2. *Insights into polymer structure*
   You may have read about the recent advances in protein structure prediction. One of challenges in understanding protein structure relates to configurational entropy: the number of states accessible by a long polymer is large. Let's consider the following simple model of a polymer to help us suss out the contributions of entropy to polymer structure. In this model, the polymer is a random walk: each segment of the polymer is represented by a vector $\hat{r}_i$ of magnitude $\ell$ for $i = 1, \ldots, n$ where $n$ is the total number of monomers of the polymer. Let's make the approximation that each segment is an independent random displacement on a regular cubic lattice. Explicitly, in $d = 2$, the $i$th displacement of the vector $\hat{r}_i$ is $\uparrow$, $\downarrow$, $\rightarrow$, or $\leftarrow$ all with probability $1/4$. For simplicity, let's also assume, for simplicity, that the segments can overlap. See Fig. 1.

   (a) Compute the total number of states of a polymer of length $n$ in dimension $d$.

   (b) Write this expression in the form $\Omega = a^n$.

   (c) You can find the "end-to-end" vector by summing up the displacements along the polymer. That is,

   $$\boldsymbol{R} = \ell \sum_{i=1}^{n} \hat{r}_i \tag{4}$$

   Calculate the average value $\langle \boldsymbol{R} \rangle$.

(d) Calculate the mean-squared end-to-end distance of the polymer $\sqrt{\langle \boldsymbol{R} \cdot \boldsymbol{R} \rangle}$. How does your answer depend on the dimension $d$?

(e) A classical model of polymers in favorable solvent conditions predicts that the mean-squared end-to-end distance scales like $n^{3/5}$. Why might a good solvent—a solvent that binds favorably to the polymer and prevents it from binding with itself—change the scaling relative to your prediction?

3. *Simulating Random Polymers*

Computer simulations, a topic we will discuss in much greater depth later in the course, are an essential tool in theoretical chemistry. As we saw last week, we were able to extract some important *universal* information about the distribution of random spins and how it *scales* in the limit $n \to \infty$. Using the provided `python` template, or writing your own simulation from scratch, let's simulate the random polymer in Problem 2 in dimensions $d = 2$ and $d = 3$ to gain numerical insight.

(a) Write a function to collect samples of the polymers of length $n$. One way to do this would involve creating an $n$ by 3 `numpy` array to store the coordinates for each monomer. Set the starting point at the origin then use a random number generator to pick which direction the polymer moves. With each update, store the new data point in the array. Collect a few samples for $n = 100$ and plot them. 3D plots can be a little tricky, here's a clean way to generate them.

```
1 import matplotlib.pyplot as plt
2 from mpl_toolkits.mplot3d import Axes3D
3
4 %matplotlib notebook
5 fig = plt.figure()
6 ax = fig.gca(projection='3d')
7 ax.plot(x, y, z)
8 plt.show()
```

Line 4 is a nice command specifically when using a Jupyter notebook in order to get interactive figures. This will let you rotate the figure to see it from different angles. When running from the command line the figure should be interactive automatically. The input you need to give are 1-dimensional arrays containing each x, y, and z coordinate of all the data points.

Do the polymers look globular? Or are they more elongated?

(b) Estimate the average total displacement $\langle R \rangle$ for the polymer in $d = 2$ with $n = 500$ using a similar method to question 1b from homework 1. How many of your simulations actually realize the mean value?

(c) Based on your answer to (b), explain why the root mean squared end-to-end distance is a better measure of the extent of the polymer.

(d) Estimate $\sqrt{\langle \boldsymbol{R} \cdot \boldsymbol{R} \rangle}$ for polymers of lengths $n = 100, 500, 1000$ in $d = 3$. Is your answer consistent with the scaling you predicted in the previous problem?