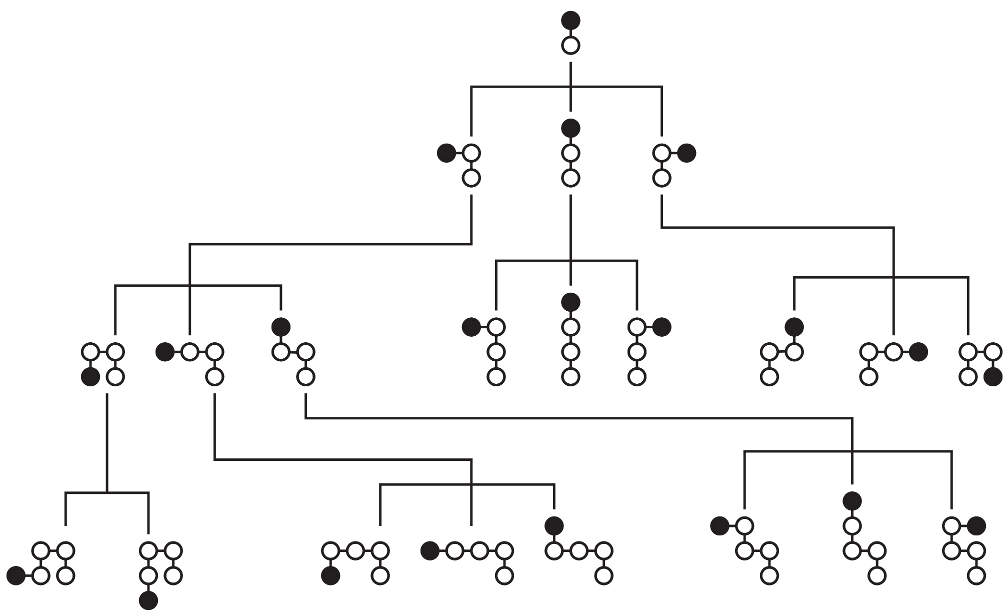
Physics 727: Assignment 3

(to be submitted by Thursday, March 7, 2024)

We consider the statistical mechanics of self-avoiding walks (SAWs) on the square lattice (i.e., on $\mathbb{Z}^2$, the infinite, two-dimensional Cartesian grid). To obtain the various SAW configurations, we undertake an enumeration, which is the strategy of exhaustively generating all valid arrangements up to some cutoff length. Each SAW proceeds vertex-to-vertex along lattice links in the north, south, west, or east directions; it is grown stepwise from the current head (drawn as solid black in the diagram below) by considering all possible non-backtracking moves that are consistent with the excluded volume constraint.

The configurations can be organized into a branching tree diagram with SAWs of equal length at the same depth. Each node at level N has children corresponding to all the allowed walks of length $N + 1$. We can take advantage of the 90-degree rotation symmetry by assuming that the first step is north, thus reducing the computational work by a factor of four.



The following problems are best carried out with machine assistance. I have provided sample codes in `julia` and `c++` on the course website that implement the breadth-first-search algorithm. If you are uncomfortable with programming, you may elect to complete just the $N = 4$ case by hand.

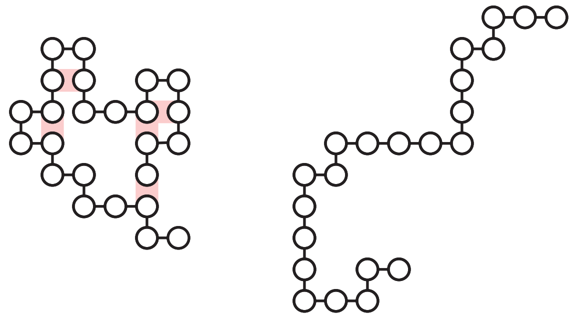
1. The following table shows the number of valid SAW configurations ($|\mathcal{C}_N|$) for a given walk length (N), along with the unbiased average of the square of the end-to-end distance ($\langle r_N^2 \rangle$).

N	$\lvert\mathcal{C}_N\rvert$	$\langle r_N^2 \rangle$
1	4	1
2	12	2.666 67
3	36	4.555 56
⋮	⋮	⋮
15	6416596	47.2177
16	17245332	51.9925
17	46466676	56.7164

   Use the code provided on the class website to determine the missing table entries for $N = 4, 5, \ldots, 14$.

2. Absent a specific interaction model, the SAWs are athermal and unbiased: each configuration carries the same weight as all the others. For concreteness, let us suppose that the system is in contact with a heat

bath at temperature $k_B T$ and that there is an interaction W between occupied vertices that are adjacent on the square lattice but not along the SAW path (i.e., not connected by a link of the chain backbone). Then, the weight associated with each configuration is $e^{n\beta W} = (e^{\beta W})^n = x^n$, where n is the non-backbone, nearest-neighbour (nbnn) count and $x = e^{\beta W} = e^{W/k_B T}$ is the exponential of the ratio of interaction strength to temperature. A collapsed walk (favoured by an attractive $W > 0$) with $n = 5$ and a swollen walk (favoured by a repulsive $W < 0$) with $n = 0$ are shown below.



Make a plot of

$$\langle r_N^2 \rangle = \frac{\sum_{C \in \mathcal{C}_N} r(C)^2 x^{n(C)}}{\sum_{C \in \mathcal{C}_N} x^{n(C)}}$$

as a function of x (for values $0 \le x \le 2$, say) with the results for each of $N = 4, 5, \ldots, 14$ superimposed. Here, $\mathcal{C}_N$ is the set of all valid SAW configurations of length N. Explain the shapes of the curves on your graph in physical terms.

3. Imagine that the SAW is analogous to a long, flexible, linear molecule. In the canonical ensemble, the molecule is stable and the number of atoms is fixed; the partition function for a molecule of length N is

$$Z_N = \sum_{C \in \mathcal{C}_N} e^{-\beta(-W)n(C)} = \sum_{C \in \mathcal{C}_N} \left(e^{\beta W}\right)^{n(C)} = \sum_{C \in \mathcal{C}_N} x^{n(C)} = \sum_{j=0}^{\infty} g_j^{(N)} x^j.$$

The value $n = n(C)$ is the number of nbnn interactions for the particular configuration C. After the final equality in the expression above, the summation index has been changed to range over powers of x;

$$g_j^{(N)} = \sum_{C \in \mathcal{C}_N} \delta_{j,n(C)}$$

is a degeneracy factor that gives the number of SAWs of length N that have j nbnn interactions.

(a) Compute $g_j^{(N)}$ for $N = 4, 5, \ldots, 14$. Present a table of the nonzero $g_j^{(N)}$ values for $N = 4$.

(b) Draw two configurations that contribute to $g_0^{(14)}$ and $g_8^{(14)}$.

(c) Make a plot of U/W versus x, again for $N = 4, 5, \ldots, 14$, taking advantage of the fact that

$$Z_N = \sum_{j=0}^{\infty} g_j^{(N)} x^j = \sum_{j=0}^{\infty} g_j^{(N)} e^{\beta W j} \implies U = \langle \epsilon \rangle = -W \frac{\partial \ln Z_N}{\partial \ln x} = -W \frac{\sum_{j=1}^{\infty} j\, g_j^{(N)} x^j}{\sum_{j=0}^{\infty} g_j^{(N)} x^j}.$$

Explain all the important features of the plot.

4. Now let's tease out the difference between the canonical and grand canonical ensembles. In the canonical ensemble, the number of atoms in the molecule is constant. In the grand canonical ensemble, however, the molecule can gain or shed atoms at its ends, and its total length fluctuates. We suppose that the SAW system is immersed in a free-atom reservoir. The grand partition function is

$$Z = \sum_{C \in \mathcal{C}} e^{-\beta(-W)n(C)+\alpha N(C)} = \sum_{C \in \mathcal{C}} \left(e^{\beta W}\right)^{n(C)} \left(e^{\alpha}\right)^{N(C)} = \sum x^n y^N.$$

Here, $\mathcal{C} = \mathcal{C}_1 \cap \mathcal{C}_2 \cap \mathcal{C}_3 \cdots$ is the union of the configuration sets in all the length sectors. There are now two free parameters, $x = e^{\beta W}$ and $y = e^{\alpha}$. The average SAW length is

$$\begin{aligned}
\langle N \rangle = \frac{1}{Z}\frac{\partial Z}{\partial \alpha} = \frac{\partial \ln Z}{\partial \ln y} = \frac{\sum N x^n y^N}{\sum x^n y^N} &= \frac{\sum_{\mathcal{C}_1} x^n + 2y^2 \sum_{\mathcal{C}_2} x^n + 3y^3 \sum_{\mathcal{C}_2} x^n + \cdots}{\sum_{\mathcal{C}_1} x^n + y^2 \sum_{\mathcal{C}_2} x^n + y^3 \sum_{\mathcal{C}_2} x^n + \cdots} \\
&= \frac{yZ_1 + 2y^2 Z_2 + 3y^3 Z_3 + \cdots}{yZ_1 + y^2 Z_2 + y^3 Z_3 + \cdots} \\
&= y\frac{\partial}{\partial y} \ln \sum_{N=1}^{\infty} y^N Z_N.
\end{aligned}$$

At very high temperatures or very low interaction strength, $\beta W \approx 0$ and $x \approx 1$, and the canonical partition function for a given N is simply the number of valid SAWs for that chain length:

$$Z_N = \sum_{C \in \mathcal{C}_N} x^{n(C)} \approx \sum_{C \in \mathcal{C}_N} 1 = |\mathcal{C}_N|.$$

For sufficiently short walks ($N = 1, 2, 3$), the excluded volume constraint plays no role. The sizes of those configuration sets follow the pattern $|C_1| = 4$, $|C_1| = 4 \cdot 3$, $|C_3| = 4 \cdot 3 \cdot 3$, which accounts for the 4 choices of initial move and the 3 ways to move without backtracking at subsequent steps. A reasonable guess is that for large N the behaviour will be of the form $|C_N| \sim \zeta^N$ for some value of ζ with a value less than 3 (because of the reduction in the freedom of movement when the excluded volume constraint is operative). Fit your data to extract a reasonable value of the ζ parameter. Here, for example, is a `gnuplot` session that carries out the fit. But please use whichever tools you're comfortable with.

```
$ head -n 3 output.dat
 1          4       1
 2         12       2.66667
 3         36       4.55556
$ tail -n 3 output.dat
15      6416596    47.2177
16     17245332    51.9925
17     46466676    56.7164
$ gnuplot
> count(N) = c * zeta**N
> c=4
> zeta=2.75
> fit[9:] count(x) "output.dat" using 1:2 via c, zeta
> set logscale
> set key bottom right
> set xlabel "N"
> set ylabel "configuration count"
> plot "output.dat" using 1:2 title "enumerated", count(x) title "best fit"
> print c,"+/-",c_err
> print zeta,"+/-",zeta_err
```

Now make the replacement $Z_N = |\mathcal{C}_N| = c\zeta^N$. Find an analytic expression for $\langle N \rangle$, and show that the fugacity takes values $0 \le y < 1/\zeta$.