Quiz 6 Polymer Physics
February 21, 2020

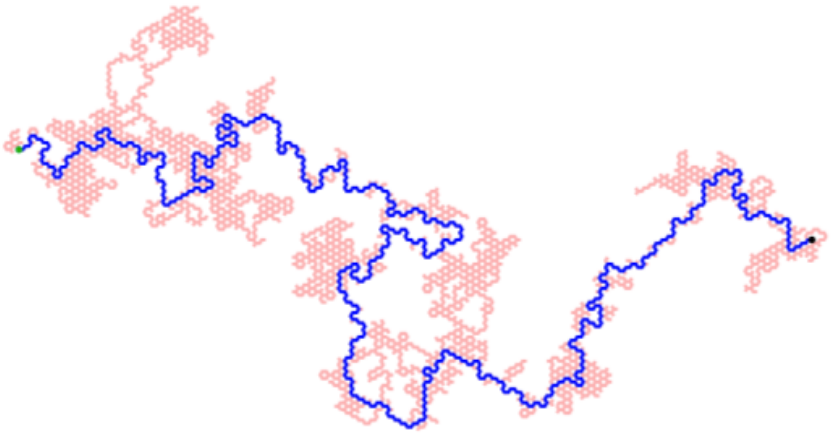
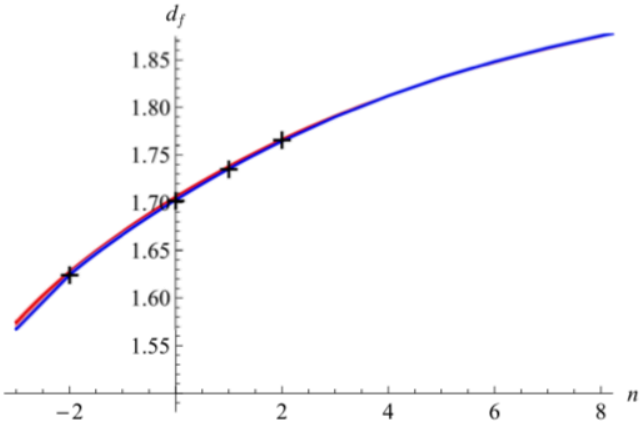


FIG. 1. Example of a loop-erased random walk on the hexagonal lattice with 3000 steps, starting at the black point to the right and arriving at the green point to the left.



d_f	n	SC	KP17	simulation
LERW	−2	1.6243(10)	1.623(6)	1.62400(5) [45]
SAW	0	1.7027(10)	1.7025(7)	1.701847(2) [24]
Ising	1	1.7353(10)	1.7352(6)	1.7349(65) [46]
XY	2	1.7644(10)	1.7642(3)	1.7655(20) [46, 47]

FIG. 2. Fractal dimensions of lines in dimension $d = 3$. Two expansions are shown: Direct (in red) and expansion for $1/d_f$ (blue). The table compares our values to results from the literature.

M. Kompaniets, K. J. Wiese *Fractal dimension of critical curves in the O(n)-symmetric φ4 model and crossover exponent at 6-loop order: Loop-erased random walks, self-avoiding walks, Ising, XY , and Heisenberg models* Phys. Rev. E **101** 012104 (2020) discusses simulations of self-avoiding walks in 2 and 3 dimensional space. They compare five simulation methods as mentioned in the title. The paper discusses critical phenomena where a critical temperature is reached, T_c, above or below which some type of ordering occurs such as phase separation or magnetization. A length scale, the correlation length, describes the length over which ordering is observed. In the disorder state correlation is over short distances and beyond the critical point correlation becomes infinite in a first order transition. The approach to the critical temperature follows a fractal scaling law analogous to the random walk. For this reason, critical phenomena and fractal walks are linked. Kompaniets and Wiese have developed a parameter "*n*" that describes the relationship between different algorithms and theories describing this critical phenomena and random walks. The table in Figure 2 above lists "*n*" for the loop-erased random walk (LERW), self-avoiding walk, and two models based on statistical thermodynamics. The two columns at the end are the fractal dimension that results for self-avoiding walks for these four computation methods.

a) In class the Flory-Krigbaum model was discussed. This is an analytic calculation not a computer simulation. What fractal dimension does the FK ***approximation*** yield? What is the approximation? What fractal dimension results from a ***numerical integration*** of the FK model?

How do these analytic values compare with the simulated values shown in the table of Figure 2? (The FK analytic value has been verified by experiment.)

b) The loop-erased random walk (LERW) method, Figure 1, involves 1) make a random walk, similar to the first computer program; 2) erase loops. Write an algorithm (sketch of a computer program) that would accomplish this loop-erasure task on the random walk chains you simulated to produce self-avoiding walks.

c) The LERW algorithm results in a fractal dimension of 1.62 which is smaller than the analytic solution of FK from part "a". Identify bias in your LERW algorithm that leads to a more linear structure compared to a true self-avoiding walk?

d) The SAW model carries out a random walk simulation but for each step the free energy of the system is calculated and a step is rejected if it leads to an increase in the free energy due to close approach of the chain to itself (with some randomness, that is bad steps are sometimes accepted depending on temperature). This approach yields a result, 1.70, very close to the analytic FK integration. Do you see any possibility of bias in the SAW algorithm?

e) The Ising approach is based on considering a binary potential of interaction between chain units and solvent sites in a Cartesian grid. 1) First a chain is created in an arbitrary form, for instance a straight line. 2) Then the chain is is allowed to "equilibrate" by random motion of individual mer units considering minimization of the free energy of the entire system for each motion of a mer unit with some randomization (sometimes bad things occur but rarely depending on the temperature relative to T_c). The Ising model results in a fractal dimension, 1.74, larger than the analytic solution of FK from numerical integration. What bias in the Ising model would lead to a more compact structure (closer to a random walk, $d_f = 2$) compared to the FK analytic solution?

Note:
An example of an Ising model for phase separation in 2d is available at:
https://physics.weber.edu/schroeder/software/demos/IsingModel.html
This program starts with a random array of boxes. One box is flipped in color and the free energy for the system is calculated. If the free energy is reduced the flip is accepted, if not a dice is rolled and if it comes up 1-5 you reject the flip. If 6 it is accepted depending on the temperature.
If you look at this program, try to find the critical temperature, the point between phase separation and single-phase behavior. Notice that the program creates percolation pathways through the 2d Cartesian system near the critical temperature. The loops of these pathways do not contribute to percolation (connection across the 2d grid). So, only the SAW path is important to percolation (connection) which is used to define the point of phase separation. This is the link between SAWs and critical phenomena. (The θ-temperature for polymers is an example of a critical point of this type as is the critical point on a PV phase diagram.)

ANSWERS: **Quiz 6 Polymer Physics**
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a) What fractal dimension does the FK ***approximation*** yield? What fractal dimension results from a ***numerical integration*** of the FK model? How do these analytic values compare with the simulated values shown in the table of Figure 2? (The FK analytic value has been verified by experiment.)

$d_f = 5/3 = 1.67$ for the approximation that R is much larger than R for the θ condition.

$d_f = 1.72$ for the numerical integration of the FK equation.

LERW is more linear
SAW is close, a bit smaller so a bit biased to linear
Ising is larger than the integration, biased towards the θ-condition.
XY is biased towards the θ-condition.

b) Write an algorithm (sketch of a computer program) that would accomplish this loop-erasure task on the random walk chains you simulated to produce self-avoiding walks.

1) Inspect each chain unit position starting with (000) and compare it with all of the higher chain positions, i+1 to the end of the chain.

2) If a crossing point is found delete the points between your starting index and the matching index.

3) Continue searching for a crossing at that point until the end of the chain.

4) Move on to the next chain position and redo steps 1-4.

5) Continue moving on to the next chain unit until you reach the end of the chain.

c) The LERW algorithm results in a fractal dimension of 1.62 which is smaller than the analytic solution of FK from part "a". Identify bias in your algorithm that leads to a more linear structure compared to a true self-avoiding walk?

The loop units that are deleted are more compact than the chain segments that do not cross. This is evident in the 2-d walk shown in figure 1. By deleting these loops we are selecting more linear compared to the tight loop area. This would seem to lead to a non-random self-avoiding walk.

d) The SAW model carries out a random walk simulation but for each step the free energy of the system is calculated and a step is rejected if it leads to an increase in the free energy due to close approach of the chain to itself (with some randomness, that is bad steps are sometimes accepted). This approach yields a result, 1.70, very close to the FK integration result. Do you see any possibility of bias in the SAW algorithm?

Bias in the SAW model depends on the interaction potential that is considered. If it is too large or over too large of a distance it can lead to a lower dimension than analytic. If it is too small and too many chains are allowed to cross it can lead to more of a Gaussian chain and a higher dimension. The interaction could be tuned to match any desired mass-fractal dimension so it is arbitrary, that is it isn't really the correct approach.

e) The Ising approach is based on considering a binary potential of interaction between chain units and solvent sites in a Cartesian grid. 1) First a chain is created in an arbitrary form, for instance a straight line. 2) Then the chain it is allowed to "equilibrate" by random motion of individual mer units considering minimization of the free energy of the entire system for each motion of a mer unit with some randomization (sometimes bad things occur but rarely depending on the temperature relative to T_c). The Ising model results in a fractal dimension, 1.74, larger than the analytic solution of FK from numerical integration. What bias in the Ising model would lead to a more compact structure (closer to a random walk, $d_f = 2$) compared to the FK analytic solution?

One problem with equilibrating models is determining when it is equilibrated. Typically, the steps in the energy minimization are on the nanosecond scale. A polymer can take many hours or days to reach equilibrium in a melt. A quantifiable parameter like the radius of gyration can be plotted as a function of time and a plateau can be found but this does not mean that the internal structure has reached an equilibrium. There is no absolutely valid test for the final point of the simulation. With this in mind, the result of the Ising simulation may depend on the starting state and the time the simulation was run to reach "equilibrium". Perhaps the initial state was a collapsed chain or a Gaussian chain. Some starting states are easier to make and converge to a solution faster. Any starting state induces a bias in the simulation that cannot be completely removed.