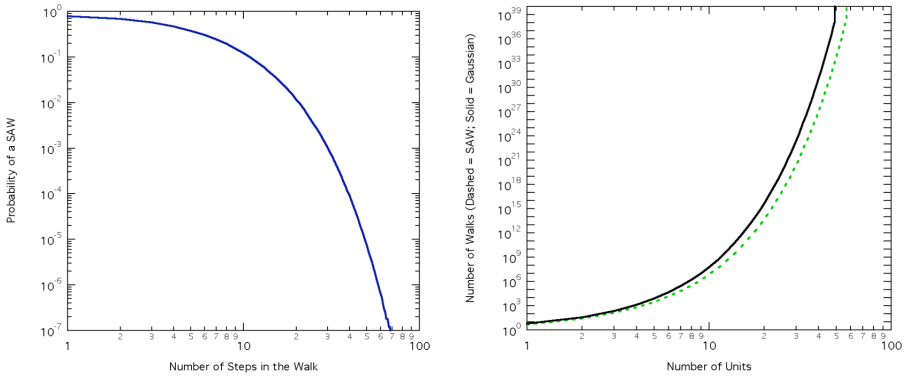
Quiz 2 Properties 070411



The total number of random walks on a cubic lattice for n-steps is $N_{Gaussian} = 6^n$. Of these walks a fraction will be SAW's. The number of SAW's is given by de Gennes as, $N_{SAW} = 4.68^n n^{1/6}$ so that the probability of a SAW is given by $(0.78)^n\, n^{1/6}$ and is plotted in the graph above (left). The right graph shows $N_{Gaussian}$ and N_{SAW}.

1) What is a SAW? Why would such a walk be so much less probable than a random walk?

2) In the function for the number of Gaussian walks where does "6" arise from? Explain why this value is "4.68" for a SAW (give a reason that it would be "5" and a reason that it would be less than "5").

3) The make-up computer programs involve the simulation of a random walk and of a SAW on a cubic lattice. Write a short algorithm to calculate a random walk (show the sequence of steps needed to calculate a random walk on a cubic lattice). How would the plots and functions given above impact your development of a second algorithm to calculate a SAW based on your random walk algorithm?

4) Explain what is meant by *excluded volume* for a ***non***-ideal gas and calculate the energy per gas molecule. Use the energy (entropy) of an ideal gas molecule, E = PV = nkT as a starting point and:

a) obtain an expression for the probability of exclusion p_{ex} similar to what was obtained for chain exclusion.

b) Compare this expression with the Boltzman function to obtain an expression for the energy of a non-ideal gas and add this term to the ideal energy given above.

c) For binary interactions we expect a lead term of n^2 since the expression reflect pairs of gas atoms interacting. Explain the two terms in your expression for the energy for a non-ideal gas.

d) Is *excluded volume* enthalpic or entropic?

5) How does the expression for a ***non***-ideal gas compare with the energy for an isolated SAW chain?

ANSWERS: *Quiz 2 Properties 070411*

1) A self-avoiding walk (SAW) is a series of continuous vector steps that do not cross themselves. In polymer physics the SAW is usually associated with long-range interactions between chain units separated by a large chain index difference. For short chains the probability of the path crossing itself is low. For longer chains it is difficult for the chain to not cross itself. The probability of a SAW from a series of random walks goes almost to 0 by about 70 chain steps.

2) "6" is the coordination number for a cubic lattice. For a SAW on the simplest local level there is no backstep so we expect the coordination number to be "5" or less. The exclusion from long-range chain overlap reduces this value to 4.68.

3) For a chain of n steps you need to randomly choose direction n times and add this direction to three vectors x, y, z so:

vectors of size n: x,y,z
x[0]=0, y[0]=0, z[0]=0
variable counter=1
Loop
    x[counter]=x[counter-1];y[counter]=y[counter-1];z[counter]=z[counter-1]
    pick a direction +x, - x, +y, -y, +z, -z this could be done by picking a random number between 1 and 6
    add the chosen step to x[counter], y[counter], or z[counter]
    increment counter
repeat n times

The plots show that the random walk approach will be difficult if we consider a SAW since most calculated walks will cross the chain and will not be useful if n is larger than about 10. It is possible to write a more efficient code compared to just inserting a test in the random walk algorithm to reject walks that cross the existing walk.

4) Excluded volume is the volume that cannot be occupied by an object due to the presence of another object. For example, for two spheres the spheres can touch at closest approach which excludes a volume of $4V_0$ where V_0 is the volume of a sphere. For a gas of density $\rho = n/V$, the probability of exclusion is $p_{ex} = (1 - 4\rho V_0)^{n\wedge 2/2} \sim \exp(-2n^2\rho V_0) \sim \exp(-E/kT)$ so that
$E = 2kTn^2\rho V_0$ which indicates that the excluded volume is entropic since the energy term is linearly dependent on temperature. The energy for a non-ideal gas is the ideal energy, $E = PV = nkT$ plus the expression above:
$E(n) = kT(n + 2n^2\rho V_0)$
where $2\rho V_0$ is the second virial coefficient associated with binary interactions. This expression contains only entropy since all terms are linearly dependent on temperature.

5) For a SAW chain we have:

$$E(R) = kT\left(\frac{3R^2}{2nl_K^2} + \frac{n^2V_c}{2R^3}\right)$$

This shows a second order term in n associated with excluded volume similar to the ideal gas.