Universiteit Utrecht

End-to-end length of a stiff polymer

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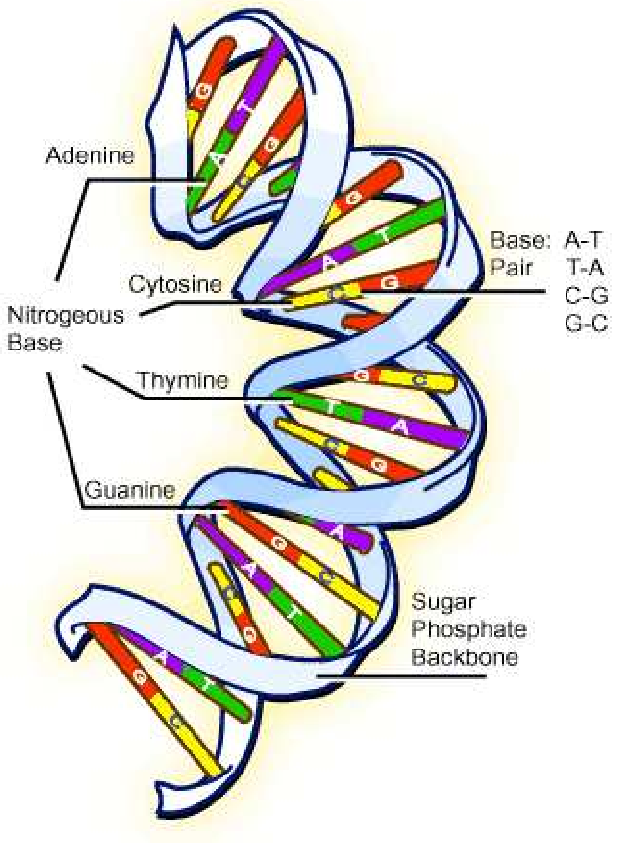

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1 Introduction

Polymers are long chains of repeating parts, called monomers.

We encounter polymers every day. We eat polymers like proteins and we have them in our body for instance in the form of DNA. Those polymers are found in nature and are therefore called biopolymers. Another group of polymers is called synthetic polymers, often referred to as plastics. These polymers are made with controlled chemical reactions.

This research is done on the behavior of polymers. Polymers can behave like self avoiding walks, twisting and turning in random directions, but never visiting the same spatial location more than once. This sounds trivial, since no two monomers can be at the same place in time, because they have dimensions. That is true, but under different circumstances a polymer can behave like a random walk, which in simulations means that two monomers are allowed on the same position in space.

But what happens when a polymer is stiff, so it cannot bend so easy and find its own tail? It is self avoiding, but it might show random walk behavior if the polymer is stiff enough and not infinitely long, since the probability of two monomers visiting the same position is very small.

This research is about what exactly happens for long and short polymers with varying stiffness.

2 Theory

2.1 Scaling of random and self avoiding walks

The most important relation for this research, is the scaling of the mean squared end-to-end length $\langle r_e^2(N)\rangle$ of different types of polymers. We will consider stiff self avoiding walks, which we will compare to equally stiff random walks to find out what the behavior of stiff polymers looks like most. The dependence of the mean squared end-to-end length from the length of the polymer (N) looks like:

- random walk: $$\langle r_e^2(N)\rangle \sim N; \tag{1}$$
- self avoiding walk: $$\langle r_e^2(N)\rangle \sim N^{2\nu}, \tag{2}$$

in which $\nu \approx 0.588$ [1].

Another important concept is the persistence length l_p. The persistence length is a quantity that tells something about the correlation in the orientation of the polymer. It is usually defined as the distance along the polymer after which this correlation has decayed to $1/e$. This definition is hard to use in the case of lattice polymers, due to discretization effects. We therefore use another approach to define the persistence length.

The mean squared end-to-end length of an ordinary random walk, making N steps of size b, is equal to

$$\langle r_e^2(N)\rangle = N \times b^2. \tag{3}$$

If the random walker does not make steps in uniformly random directions, but has a bias in favor of steps continuing in the same direction, its squared length $\langle \tilde{r}_e^2(N)\rangle$ will increase. To quantify this, we identify which ordinary random walker making $\tilde{N}$ steps of size $\tilde{b}$ has the same expected end-to-end length:

$$\langle \tilde{r}_e^2(N)\rangle = \tilde{N} \times \tilde{b}^2. \tag{4}$$

and the same contour length:

$$Nb = \tilde{N}\tilde{b}. \tag{5}$$

we will call the ratio of b and $\tilde{b}$ the persistence length (expressed in units of b):

$$l_p = \tilde{b}/b = \langle \tilde{r}_e^2(N)\rangle / \langle r_e^2(N)\rangle. \tag{6}$$

2.2 Thermalization

Before starting any real measurements, thermalization is required. This is necessary to make sure that the first configuration of measurement already satisfies the above equations. This means there should not be any correlation between the initial configuration and the configuration of the first measurement. Therefore, the thermalization time should exceed the correlation time. For good measurements it is important that the thermalization is long enough.

In literature [3] we find that, for the pivot algorithm, which we used in our simulations, and which is described in the next section, the minimal thermalization time scales with N divided by the acceptance probability. The acceptance probability in this case is defined by the acceptance due to self avoidance and stiffness. Since the acceptance probability wasn't measured in the simulation used, another way to reach a similar result is used. This uses the following relation:

$$r_t - r_{t\to\infty} = ae^{-t/\tau} \Rightarrow r_t = r_{t\to\infty} + ae^{-t/\tau}, \tag{7}$$

in which $r_t = \langle|\mathbf{r}_{i+2} - \mathbf{r}_i|_t\rangle$, a is a constant and τ is the correlation time. At $t = 0$, r_t is 2, so r_t at $t = 0$ is equal to $r_{t\to\infty} + a$ is 2. This leads to

$$r_t = 2 - a(1 - e^{-t/\tau}). \tag{8}$$

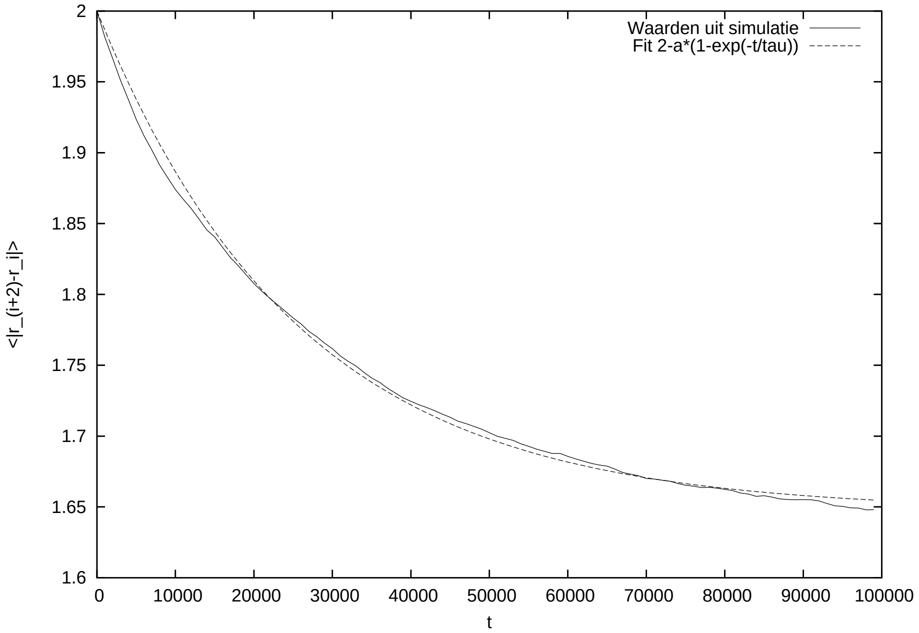

Figure 1: *Result from fitting equation 8 for* $N = 10^4$*. The fit converges for* $a = 0.35$ *and* $\tau = 2.6 \times 10^4$

Plotting $\mathbf{r}_t$ as a function of t and fitting equation (8) gives a correlation time τ. The result for $N = 10^4$ and $l_p = 2$ is plotted in figure 1. The result for the thermalization time is 2.6×10^4. To make sure that the thermalization is long enough, we take at least five or six times τ. So in the case of figure 1 thermalization should be about 1.5×10^5 steps.

3 Methods

To find out how polymers behave, computer simulations were performed of polymers on a cubic lattice, using the pivot algorithm [4]. The pivot algorithm does the following. Take an initial configuration, randomly select a monomer and rotate one side of the polymer around that monomer, over 90 or 180 degrees in a random direction. This gives a new polymer configuration.

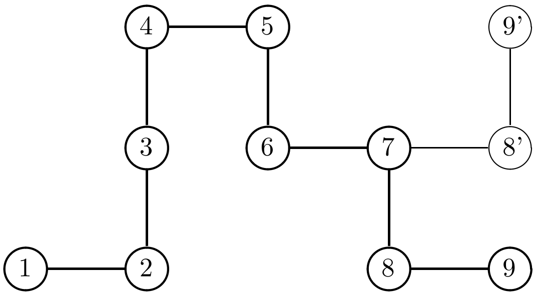

Figure 2: *An example of the pivot algorithm. Here, monomer 7 is the pivot, around which one of the tails is rotated. The numbers 8' and 9' stand for the positions of monomers 8 and 9 after the rotation.*

Self avoidance is built in by checking, for every step, if the places where the monomers will be after rotation are occupied by the ones that remain on their original position. If this is the case, the configuration is rejected and a new random monomer and a new direction of rotation is chosen.

To simulate the stiffness of a polymer, a certain dislike to bend is built in. When the polymer configuration immediately around the pivot changes from straight to a ninety degree angle, the configuration is only accepted with a probability $p < 1$. The parameter p has a relation with the persistence length. If the polymer configuration changes in the other direction or changes from one angle to another, the only condition for acceptance of the configuration is self avoidance.

The relation between the parameter p and the persistence length can be found in the following way. From equations (3) and (6) we know that for long random walks

$$l_p = \langle r_e^2(N)\rangle / N. \tag{9}$$

For a random walk in which 180 degree angles are not allowed the mean squared end-to-end length $\langle r_e^2(N)\rangle$ can be calculated theoretically using

$$\langle r_e^2(N)\rangle = \sum_{i=0}^{N-1}\sum_{j=0}^{N-1} q^{|i-j|} = \frac{N(1+q)(1-q) - 2q(1-q^N)}{(1-q)^2}, \tag{10}$$

where $q = 1/(1+4p)$ is the probability that the polymer goes to a straight configuration immediatly around the pivot. For large N, this becomes

$$\langle r_e^2(N)\rangle = \frac{N(1+q)(1-q)}{(1-q)^2} = \frac{N(1+q)}{1-q}. \tag{11}$$

This, in combination with equation (9) leads to

$$l_p = \frac{1+q}{1-q}. \tag{12}$$

As initial configuration a straight polymer was chosen. After thermalization, measurements for the mean squared end-to-end length were started. Measurements are done for several persistence lengths in the range of 1.5 to 26 and polymer lengths from 10 to 5×10^4 monomers.

4 Results

There are several ways to plot the results of the measurements. Here we chose to plot the ratio of the mean squared end-to-end length of the self avoiding walk with persistence length l_p, and that of a random walk with the same persistence length (equation (10)) against the length of the polymer. This is done in a double-logarithmic plot, to be able to get useful information from the slopes of the lines (figure 3).

In a plot like this a horizontal line comes from a polymer that behaves like a random walk. The line with persistence length 1.5 is a normal self avoiding walk.

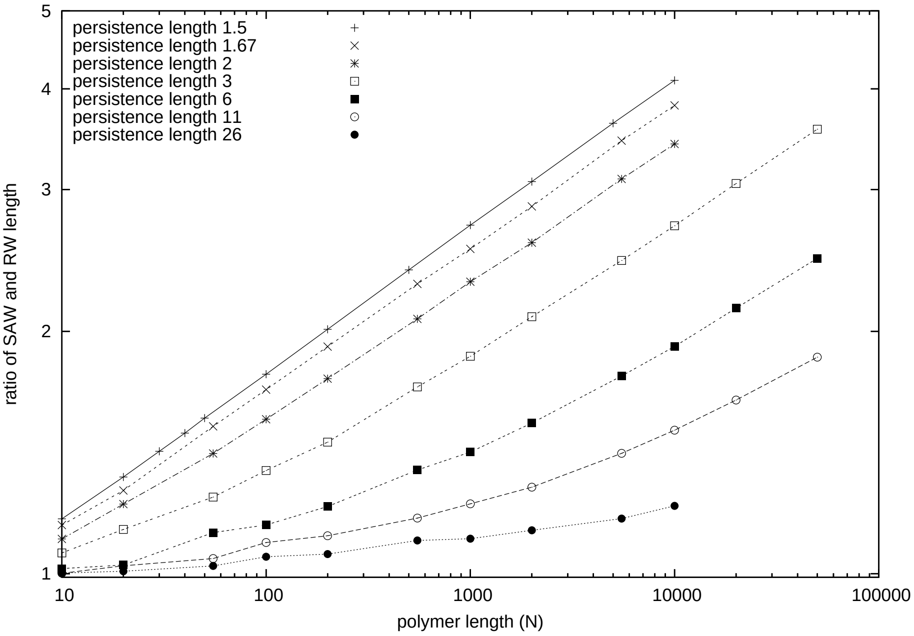

Figure 3: *Ratio of the mean squared end-to-end length of a self avoiding walk with persistence length l_p, and that of a random walk with the same persistence length, for several values of l_p. The top curve is a normal self avoiding walk.*

All curves seem to approach a line with the same slope as the top curve for longer polymers. The larger the persistence length, the longer the polymer has to be, before it behaves like a self avoiding walk.

Knowing this we can look for a way to collapse all the curves onto one curve. It turns out that this can be done by dividing the length of the polymer by its persistence length to the power three on the horizontal axis (figure 4).

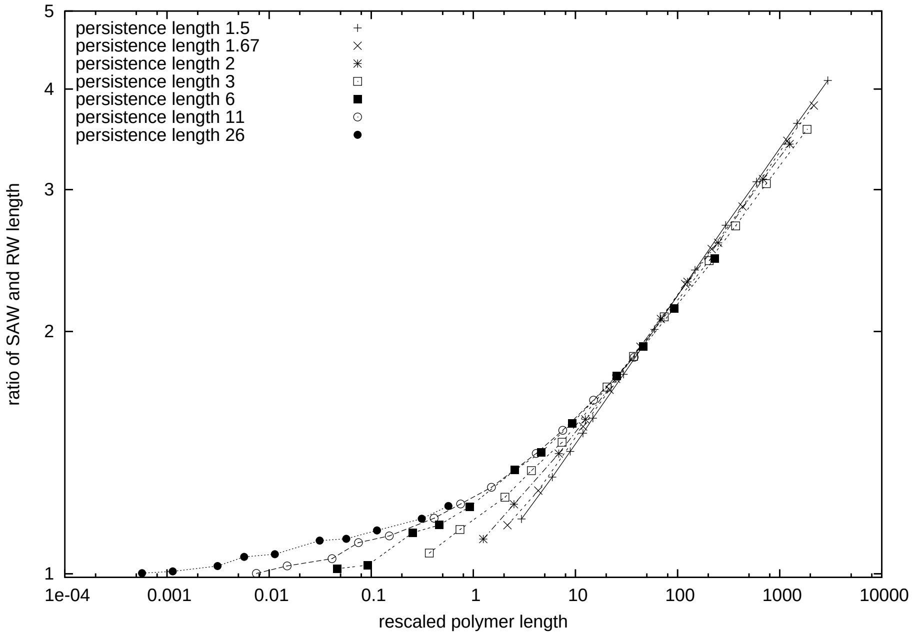

Figure 4: *Same as figure 3, except that the polymer length is divided by* l_p^3. *Note that all graphs are close to one general curve.*

5 Conclusion

From figure 3 we see that the behavior of stiff polymers depends on their length. Short, very stiff polymers behave almost like a random walk. But the longer they become, the more they behave like self-avoiding walks.

From the collapse in figure 4 and equations (1) and (2) the following relation can be derived for $\langle r_e^2(N)\rangle_{SAW}/\langle r_e^2(N)\rangle_{RW}$:

$$\langle r_e^2(N)\rangle_{SAW}/\langle r_e^2(N)\rangle_{RW} = ([(N/l_p^3)^{2\nu-1}]^\alpha + 1^\alpha)^{1/\alpha}, \tag{13}$$

in which the part between straight brackets on the right hand site of the equation describes self avoiding walk behavior and the other part the random walk behavior. The parameter α says something about the way the curve changes from random to self avoiding behavior; this parameter has not been studied here. For $(N/l_p^3)^{2\nu-1} \ll 1$ the random walk behavior will dominate and for bigger values of $(N/l_p^3)^{2\nu-1}$ the behavior will be mainly self avoiding.

References

[1] *Monte Carlo Simulation of Lattice Polymer Models*, G.T. Barkema, unpublished.

[2] *Scaling properties of stiff polymers in a good solvent*, G.T. Barkema, unpublished.

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[4] N. Madras and A.D. Sokal, J. Stat. Phys. **50**, 109 (1988). The pivot algorithm was invented in 1969 by Lal.

[5] `http://en.wikipedia.org/`