

Figure 7.9 The possible transformations of chains *a* and *b*. One of the two possible transformations of chain *b* violates the self-intersection restriction, and the head and tail are interchanged.

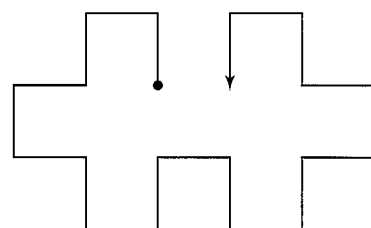


Figure 7.10 Example of a double-ended cul-de-sac configuration for the self-avoiding walk that cannot be obtained by the reptation method.

- (b) Modify the reptation model so that the bond angle can also be 180° . This modification leads to a maximum of three directions for a new bond. Compare your results with those from part (a). ■

In principle, the dynamics of a polymer chain undergoing collisions with solvent molecules can be simulated by using a molecular dynamics method. However, in practice, only relatively small chains can be simulated in this way. An alternative approach is to use a Monte Carlo model that simplifies the effect of the random collisions of the solvent molecules with the atoms of the chain. Most of these models (cf. Verdier and Stockmayer) consider the chain to be composed of beads connected by bonds and restrict the positions of the beads to the sites of a lattice. For simplicity, we assume that the bond angles can be either $\pm 90^\circ$ or 180° . The idea is to begin with an allowed configuration of N beads ($N - 1$ bonds). A possible starting configuration can be generated by taking successive steps in the positive y and positive x directions. The dynamics of the Verdier–Stockmayer algorithm is summarized by the following steps:

1. Select at random a bead (occupied site) on the polymer chain. If the bead is not an end site, then the bead can move to a nearest neighbor site of another bead if this site is empty and if the new angle between adjacent bonds is either $\pm 90^\circ$ or 180° . For example, bead 4 in Figure 7.11 can move to position $4'$, while bead 3 cannot move

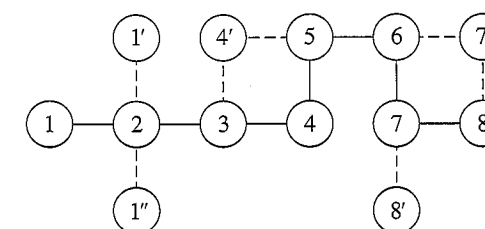


Figure 7.11 Examples of possible moves of the simple polymer dynamics model considered in Problem 7.31. For this configuration, beads 2, 3, 5, and 6 cannot move, while beads 1, 4, 7, and 8 can move to the positions shown if they are selected. Only one bead can move at a time. This figure is adopted from the article by Verdier and Stockmayer.

if selected. That is, a selected bead can move to a diagonally opposite unoccupied site only if the two bonds to which it is attached are mutually perpendicular.

2. If the selected bead is an end site, move it to one of two (maximum) possible unoccupied sites, so that the bond to which it is connected changes its orientation by $\pm 90^\circ$ (see Figure 7.11).
3. If the selected bead cannot move, retain the previous configuration.

The physical quantities of interest include $\langle R^2 \rangle$ and the mean square displacement of the center of mass of the chain $\langle r^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 + \langle y^2 \rangle - \langle y \rangle^2$, where x and y are the coordinates of the center of mass. The unit of time is the number of Monte Carlo steps per bead; in one Monte Carlo step per bead, each bead has one chance on the average to move to a different site.

Another efficient method for simulating the dynamics of a polymer chain is the bond fluctuation model (see Carmesin and Kremer).

Problem 7.31 The dynamics of polymers in a dilute solution

- (a) Consider a two-dimensional lattice and compute $\langle R^2 \rangle$ and $\langle r^2 \rangle$ for various values of N . How do these quantities depend on N ? (The first published results for three dimensions were limited to 32 Monte Carlo steps per bead for $N = 8, 16$, and 32 and only 8 Monte Carlo steps per bead for $N = 64$.) Also compute the probability density $P(R)$ that the end-to-end distance is R . How does this probability compare to a Gaussian distribution?
- (b) Two configurations are strongly correlated if they differ by the position of only one bead. Hence, it would be a waste of computer time to measure the end-to-end distance and the position of the center of mass after every single move. Ideally, we wish to compute these quantities for configurations that are approximately statistically independent. Because we do not know *a priori* the mean number of Monte Carlo steps per bead needed to obtain configurations that are statistically independent, it is a good idea to estimate this time in our preliminary calculations. The correlation time τ is the time needed to obtain statistically independent configurations and can be obtained by computing the equilibrium averaged time-autocorrelation function for a chain of fixed N :

$$C(t) = \frac{\langle R^2(t' + t)R^2(t') \rangle - \langle R^2 \rangle^2}{\langle R^4 \rangle - \langle R^2 \rangle^2} \quad (7.48)$$