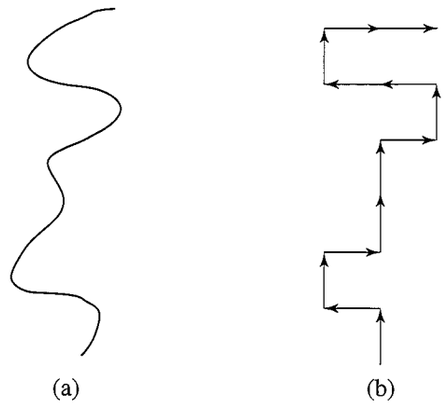

Figure 7.6 (a) Schematic illustration of a linear polymer in a good solvent. (b) Example of the corresponding self-avoiding walk on a square lattice.

in the rubber chain is essential. However, if we are interested in the global properties of the polymer, the details of the chain structure can be ignored.

Let us consider a familiar example of a polymer chain in a good solvent: a noodle in warm water. A short time after we place a noodle in warm water, the noodle becomes flexible, and it neither collapses into a little ball or becomes fully stretched. Instead, it adopts a random structure as shown schematically in Figure 7.6. If we do not add too many noodles, we can say that the noodles behave as a dilute solution of polymer chains in a good solvent. The dilute nature of the solution implies that we can ignore entanglement effects of the noodles and consider each noodle individually. The presence of a good solvent implies that the polymers can move freely and adopt many different configurations.

A fundamental geometrical property that characterizes a polymer in a good solvent is the mean square end-to-end distance $\langle R_N^2 \rangle$, where N is the number of monomers. (For simplicity, we will frequently write R^2 in the following.) For a dilute solution of polymer chains in a good solvent, it is known that the asymptotic dependence of R^2 is given by (7.13) with $\nu \approx 0.5874$ in three dimensions. If we were to ignore the interactions of the monomers, the simple random walk model would yield $\nu = 1/2$, independent of the dimension and symmetry of the lattice. Because this result for ν does not agree with experiment, we know that we are overlooking an important physical feature of polymers.

We now discuss a random walk that incorporates the global features of dilute linear polymers in solution. We have already introduced a model of a polymer chain consisting of straight line segments of the same size joined together at random angles (see Problem 7.13). A further idealization is to place the polymer chain on a lattice (see Figure 7.6). A more realistic model of linear polymers accounts for its most important physical feature; that is, two monomers cannot occupy the same spatial position. This constraint is known as the *excluded volume* condition, which is ignored in a simple random walk. A well-known lattice model for a linear polymer chain that incorporates this constraint is known as the *self-avoiding* walk (SAW). This model consists of the set of all N-step walks starting from the origin subject to the global constraint that no lattice site can be visited more than once in each walk; this constraint accounts for the excluded volume condition.

Self-avoiding walks have many applications, such as the physics of magnetic materials and the study of phase transitions, and they are of interest as purely mathematical objects.

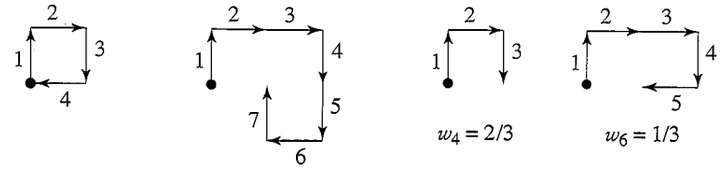

Figure 7.7 Examples of self-avoiding walks on a square lattice. The origin is denoted by a filled circle. (a) An $N = 3$ walk. The fourth step shown is forbidden. (b) An $N = 7$ walk that leads to a self-intersection at the next step; the weight of the $N = 8$ walk is zero. (c) Two examples of the weights of walks in the enrichment method.

Many of the obvious questions have resisted rigorous analysis, and exact enumeration and Monte Carlo simulation have played an important role in our current understanding. The result for ν in two dimensions for the self-avoiding walk is known to be exactly $\nu = 3/4$. The proportionality constant in (7.13) depends on the structure of the monomers and on the solvent. In contrast, the exponent ν is independent of these details and depends only on the spatial dimension.

We consider Monte Carlo simulations of the self-avoiding walk in two dimensions in Problems 7.28–7.30. Another algorithm for the self-avoiding walk is considered in Project 7.41.

Problem 7.28 The two-dimensional self-avoiding walk

Consider the self-avoiding walk on the square lattice. Choose an arbitrary site as the origin and assume that the first step is "up." The walks generated by the three other possible initial directions only differ by a rotation of the whole lattice and do not have to be considered explicitly. The second step can be in three rather than four possible directions because of the constraint that the walk cannot return to the origin. To obtain unbiased results, we generate a random number to choose one of the three directions. Successive steps are generated in the same way. Unfortunately, the walk will very likely not continue indefinitely. To obtain unbiased results, we must choose at random one of the three steps, even though one or more of these steps might lead to a self-intersection. If the next step does lead to a self-intersection, the walk must be terminated to keep the statistics unbiased. An example of a three-step walk is shown in Figure 7.7a. The next step leads to a self-intersection and violates the constraint. In this case we must start a new walk at the origin.

(a) Write a program that implements this algorithm and record the fraction $f(N)$ of successful attempts at constructing polymer chains with N total monomers. Represent the lattice as a array, so that you can record the sites that already have been visited. What is the qualitative dependence of $f(N)$ on N? What is the maximum value of N that you can reasonably consider?

(b) Determine the mean square end-to-end distance $\langle R_N^2 \rangle$ for values of N that you can reasonably consider with this sampling method. ■

The disadvantage of the straightforward sampling method in Problem 7.28 is that it becomes very inefficient for long chains; that is, the fraction of successful attempts decreases exponentially. To overcome this attrition, several "enrichment" techniques have