RECOIL GROWTH

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MOTIVATION

Although molecular dynamics simulations are extremely useful for studying both the static properties and dynamics behavior of many-body systems, it shows certain limitations. Besides being easier to implement, Monte Carlo simulations present several advantages in systems with discrete degrees of freedom and has become almost always the technique of choice for lattice models. However, when dealing with models of chains, the conventional Monte Carlo techniques fail because the probability of accepting a trial insertion in the box is extremely small, leading to a huge amount of insertion attempts. To address this problem, one can use bias sampling scheme.

The main idea is to bias the initial sampling to enhance the probability of the molecule that is inserted to fit into the existing configuration. When comparing this idea with the unbiased scheme, one can notice that the conventional Monte Carlo technique does not use any information about the existing configuration of the system to generate the trial moves. The existing configuration is only used to either accept or reject the trail moves but no to generate them.

From this subtype of techniques, one of the most popular ones used for modeling chains is Configurational Bias Monte Carlo (CBMC). Even when CBMC represents an improvement to the Rosenbluth scheme, it still has some serious limitations when trying to model polymers (i.e. very large chains). The main problem occurs when during the chain insertion, the growing chain finds itself trapped in what we call a *dead alley*. This is basically the situation where after a given monomer, the chain is unable to find an available position to insert the next monomer to grow. This is a common problem, particularly at high densities, were dead alleys are more likely to occur.

In this matter, the Recoil Growth algorithm emerges as an attempt to solve the dead alley problem by providing the possibility of recoiling back a given number of steps and searching for a new configuration to grow on. In other words, it looks monomers ahead to see whether one could expect dead alleys before permanently adding the monomers to the trial conformation. In Figure 1, we can see a graphical representation of the idea behind the recoil growth algorithm.

Chart, bubble chart

Description automatically generated

Figure 1. Dead alley representation (left) and recoil growth main idea (right).

DEFINITIONS

The first step of the algorithm is to randomly insert the first monomer in the lattice. The next monomer will be inserted in any of possible directions. As an example, in Figure 1, we can see the 4th monomer searches in possible directions to insert the 5th monomer. The value of is user-defined and one can imagine how increasing this number could yield a higher acceptance rate. From this value , one can already determine the maximum total number of possible conformations of a chain of monomers, . This is a very large sampling space. Fortunately, most conformations have vanishing Boltzmann factors and so the sampling space could be reduced to only the most relevant conformations by introducing the concept of OPEN and CLOSED trial directions defined by the probability of the trial position of monomer in a given trial direction (from the possible trial directions) to be open:

To determine whether a trial direction is either OPEN or CLOSED, a random number between and is generated. If the random number is lower than , then that trial direction for monomer is said to be OPEN; else, it would be defined as CLOSED. Notice that many of the possible conformations will be CLOSED so by following only the OPEN trial directions, the algorithm reduces the search space.

ALGORITHM

In general, the algorithm consists of 2 main stages:

1. Growing a new chain conformation using only OPEN directions
2. Decide acceptance of generated trial conformation using the weights of new and old conformations

In Stage I, the energy of monomer , , is computed so that can be calculated. Trial direction is then classified as OPEN or CLOSED according to the criterion described in the section above. For instance, for the first trial direction (from the possible trial directions), the energy and the probability , are computed. If trial direction is OPEN, we move to monomer and repeat the same steps until we reach the last monomer. If trial direction is CLOSED, then we try a second trial direction , compute , calculate and define whether trial direction is OPEN or CLOSED. If is OPEN, we move to monomer and repeat. If is also CLOSED, we retry with .

It may happen that for a given monomer , none of the possible directions are OPEN. If that’s the case, we would proceed to the RECOIL step, where we will go back to monomer and reattempt to insert monomer in any of the available trial directions and repeat the steps described above. If we set the system to recoil back just one single monomer (i.e. ) and no OPEN direction is found, then the whole chain trial conformation is rejected. Depending on the value of , we could still go back down to monomer and reattempt the insertions from there.

In Stage II, we compute the weights of the old and new conformations, and .

We compute the weights of the **new conformation** by exploring from the remaining non attempted trial directions, , where are the number of trial directions found to be closed, which directions could grow monomers. We then define as the number of directions that could grow monomers from monomer (this includes the ones found in and the one that was used for the new trial conformation from stage I). We then compute the weight of monomer for the new conformation using the following equation:

We then repeat this for all monomers until and set to be . We can then compute the weight for the entire chain:

We do the same for the **old conformation** but instead of using trial directions to find , the number of directions that could grow monomers from monomer , we use to do so.

We then accept the new conformation with a probability defined by the weights and the energies of the old and new conformations.

IMPLEMENTATION

The algorithm was first implemented in a 2D lattice using possible trial directions defined with coordinates from monomer located at . The maximum recoil step was first set as and 10 chains with 15 monomers were located in a lattice with 20-by-20 spaces available for insertion using periodic boundary conditions.

The following figure shows the new trial configurations for this system.

Chart, bubble chart

Description automatically generated

A similar 3D implementation was done for a single chain.

Chart, scatter chart, bubble chart

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REFERENCES

Frenkel, D., & Smit, B. (2002). Understanding molecular simulation: From algorithms to applications. *Computational sciences series*, *1*, 1-638.

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