

## From lattice gases to polymers

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**Abstract.** The modification of a technique that was developed to study time correlations in lattice-gas cellular automata to facilitate the numerical simulation of chain molecules is described. As an example, the calculation of the excess chemical potential of an ideal polymer in a dense colloidal suspension is discussed.

One of the surprising findings of computer simulation studies of very simple model systems, is that a great variety of ordered or partially ordered phases can be induced by pure-excluded volume effects. More than 30 years ago, Alder and Wainwright [1] showed that a system of hard spheres undergoes a first-order phase transition from the fluid to the crystalline solid phase. More recently, it was shown that hard-core interactions could also give rise to a number of liquid crystalline phases. This is not to say that other aspects of the intermolecular interactions in liquid crystals are always unimportant. On the contrary, they are as important as, say, van der Waals forces are for the cohesion of an argon crystal. But the computer simulations strongly suggest that the *structure* of lyotropic nematics [2], smectics [3] and columnar phases [4] is predominantly determined by excluded-volume effects.

It would, however, be a serious mistake to extrapolate this finding and assume that excluded-volume effects are *always* the most important factor determining the structure of a 'non-simple' liquid or liquid crystal, no matter how complex its constituent molecules. A measure for the 'complexity' of a molecule is the number of its internal degrees of freedom. The entropy associated with these degrees of freedom becomes increasingly important as the constituent molecules grow more complex. In the limit of a long polymer chain one may even, to a first approximation, ignore the excluded-volume effects, but never the conformational entropy.

This feature of complex molecules is, of course, well known and it poses a formidable challenge to computer simulators: it is essential that a numerical study of long-chain molecules probes a representative sample of all accessible molecular conformations and positions. Much attention has therefore been paid to the development of efficient numerical schemes to sample polymer conformations. The recent review by Kremer and Binder [5] gives an excellent account of Monte Carlo schemes to study lattice models of macromolecules. Most of the Monte Carlo techniques to sample chain conformations described in that review are based on some kind of *local* rule to rotate, change or break-and-remake bonds between polymer units. Although the existing techniques are quite sophisticated, the local nature of the algorithm results in

slow *global* equilibration. Global equilibration may require large-scale conformational changes of the molecules and, in the case of mixtures, appreciable changes in the local composition of the mixture. Such numerical problems are not limited to Monte Carlo simulations. In fact, although molecular dynamics simulations [6] have the advantage that they allow the molecules to perform collective motions in a natural fashion, the timescale for such diffusive motion is still very long.

The aim of the present paper is to show that a radically different approach to Monte Carlo sampling of polymers is possible, using techniques that have been developed in a very different context, namely for the study of tagged-particle velocity autocorrelation functions in lattice gases [7–9]. The basic idea behind these algorithms is that a ‘brute-force’ sampling of random walks on a lattice is not only very time-consuming but, more importantly, often yields much more information than needed. To give a specific example: if we wish to compute the excess chemical potential of a polymer in a colloidal dispersion, we need to know the total number of polymer conformations that do not intersect a colloidal particle. However, ‘brute-force’ sampling gives us much more than that: from it, we could, in principle, deduce the full  $n$ -body distribution function of a  $n$ -unit polymer. The ‘moment-propagation’ methods of [7–9] allow us to compute certain averages of the  $n$ -body distribution function directly, without attempting to compute the function itself. This approach results in a very appreciable gain in computing speed: for instance, in the case of velocity autocorrelation functions in lattice gases, the method has resulted in a speed-up that varied between  $10^6$  and  $10^{10}$  [7, 8].

Below, I show how these methods, which were developed to study extremely simple fluids, can help us with the study of a very complex fluid, namely a polymer system. To this end, let us consider a specific example of some practical interest, namely a system of *ideal* non-interacting polymers in the external potential provided by a dispersion of ‘hard-sphere’ colloidal particles.

Without much loss of generality, we can assume that the ideal polymer conformations correspond to random walks on a lattice. Suppose that every lattice site has  $b$  neighbours, that the polymer consists of  $p$  segments and that there are  $N$  lattice sites. Clearly, for an ideal polymer in the absence of any obstacles, the total number of allowed conformations is  $\Omega_{\text{id}} \equiv N \times b^p$ . If obstacles are present, some random walks are blocked, and the total number of allowed conformations,  $\Omega_{\text{T}}$ , is less than  $\Omega_{\text{id}}$ . The ‘brute-force’ method to determine the ratio  $\Omega_{\text{T}}/\Omega_{\text{id}}$  would be to attempt a large number of insertions of chains with arbitrary conformation at random points on the lattice. The ratio of the number of ‘accepted’ trial moves to the total number of attempted insertions can be used to compute the excess chemical potential of an ideal polymer chain in this system:

$$\mu_{\text{excess}} = -k_{\text{B}}T \log(P_{\text{acceptance}}) \quad (1)$$

This is the usual ‘Widom’ expression for the excess chemical potential [10]. However, unless the density of obstacles is quite low, the relative statistical error in the insertion probability will be quite large (see [11]). Next, consider the ‘moment-propagation’ approach. To this end, let us first compute all  $N$  Boltzmann factors associated with the insertion of a point particle at any lattice site. Clearly, the sum of these Boltzmann factors is simply the partition function of a point particle on a lattice in an external potential. Let us denote the Boltzmann factor associated with site  $i$  as  $f_i^{(0)} \equiv \exp(-u(r_i)/k_{\text{B}}T)$ . The partition function for a one-segment polymer (2 points)

is computed as follows. Starting from site  $i$ , we have  $b$  ways to grow one segment. But all  $b$  directions will, in general, have different Boltzmann weights  $f_j^{(0)}$ , where  $j$  denotes one of the nearest neighbours of  $i$ . The total Boltzmann weight associated with the addition of a one-segment polymer at site  $i$  is then:

$$f_i^{(1)} \equiv f_i^{(0)} \times \left( \sum_j^b f_j^{(0)} \right) \quad (2)$$

where the sum runs over the nearest neighbours of  $i$ . The partition function of a one-segment polymer on a lattice is then simply:

$$Z_1 = \sum_{i=1}^N f_i^{(1)} \quad (3)$$

(where, for convenience, I have assumed that the polymer 'head' and 'tail' are distinguishable). Repeating the same argument  $p$  times, it is clear that the Boltzmann factor associated with *all possible conformations* of a  $p$ -segment polymer starting at site  $i$  is given by:

$$f_i^{(p)} = f_i^{(0)} \times \left( \sum_j^b f_j^{(p-1)} \right). \quad (4)$$

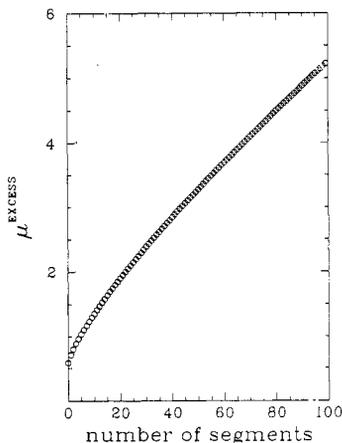
And the total partition function is given by:

$$Z_p = \sum_{i=1}^N f_i^{(p)}. \quad (5)$$

The important fact to note is that the computation of  $Z_p$ , a quantity that depends on  $N \times b^p$  conformations, requires only  $p$  iterations of  $b \times N$  local 'propagations' of real numbers. For a fixed external potential, the partition function thus computed is *exact*.

In a practical situation, as with the addition of polymer to a colloidal dispersion, the external potential is not fixed, but depends on the (continuous) coordinates of all  $M$  colloidal particles,  $\{\mathbf{r}^M\}$ . Hence, the total partition function of the polymer also depends on these coordinates:  $Z_p = Z_p(\mathbf{r}^M)$ . As a simple demonstration of the approach sketched above, figure 1 shows the result of a computation of the excess chemical potential of an ideal polymer with a number of segments varying from 0 to 100, in a system of 108 hard spheres at a density that corresponds to 60% of regular close packing. The hard-sphere coordinates were generated in a standard Monte Carlo procedure. Polymer insertion probabilities (i.e.  $Z_p/(Nb^p)$ ) were computed every 500 MC cycles, during a run of some  $4 \times 10^4$  cycles.

The approach sketched above is not limited to completely random polymer conformations. In fact, it is simple to exclude  $180^\circ$  reversals or to account for the different weight of gauche and trans conformations [12]. An interesting application of the above scheme is that it allows us to perform simulations of a polymer system *at constant osmotic pressure*, II. This corresponds to a very common experimental condition. To



**Figure 1.** Excess chemical potential of an ideal polymer with 0–100 segments in a fluid of hard spheres at a density corresponding to 60% of close packing (see text). The statistical errors are smaller than the symbols.

see how this can be achieved, let us consider the partition function of  $n$  ideal polymers of length  $p$  in an external field. Clearly,

$$Z_p^{(n)}(\mathbf{r}^M) = [Z_p^{(1)}(\mathbf{r}^M)]^n / n! \quad (6)$$

where  $Z^{(1)}$  ( $Z^{(n)}$ ) denotes the partition function for one ( $n$ ) polymer(s). Now let us transform to an ensemble where the polymer chemical potential,  $\mu$ , is held constant. To be specific, let us again consider the polymer colloid mixture. For convenience, we assume that the total number of colloid particles is held constant. The potential energy function that describes the direct interaction between the colloid particles is denoted by  $U(\mathbf{r}^M)$ . The partition function for this constant  $M, V, T, \Pi$  ensemble is

$$\Xi = \text{constant} \times \int d\mathbf{r}^M \exp(-U(\mathbf{r}^M)/k_B T) \sum_{n=0}^{\infty} \exp(n\mu/k_B T) [Z_p^{(1)}(\mathbf{r}^M)]^n / n!. \quad (7)$$

Clearly, the summation in equation (7) yields an exponential,  $\exp(z Z_p^{(1)}(\mathbf{r}^M))$ , where we have used the shorthand notation  $\exp(\mu/k_B T) \equiv z$ . Equation (7) is the starting point for Monte Carlo simulations at constant  $\Pi$  [13]. In such simulations, the relative probability of different colloid configurations is proportional to

$$P(\mathbf{r}^M) = \exp[-U(\mathbf{r}^M)/k_B T + z Z_p^{(1)}(\mathbf{r}^M)]. \quad (8)$$

Note that  $Z_p^{(1)}$ , which describes the polymer-induced interaction between colloidal particles, can be calculated exactly for every colloid configuration. Of course, such constant- $\Pi$  simulations are not limited to polymer colloid mixtures. Another interesting application is the simulation of polymer-induced forces between two surfaces. It is worth pointing out that in constant- $\Pi$  simulations we have no direct knowledge of the actual polymer positions and conformations (although some averages can be computed easily). This demonstrates clearly that great gains in computational efficiency can be made by throwing away ‘irrelevant’ information.

Thus far, I have only discussed non-interacting polymers. However, the techniques described above can be used to perform very efficient sampling of the conformations of mutually interacting, self-avoiding polymers [12]. It should be stressed that, although the techniques described in this paper require that the polymer backbone should fit on a lattice, the actual polymer position and, surprisingly, even orientation can be described by continuous coordinates. For the simulation of more realistic models for chain molecules, the present approach can be conveniently combined with the 'configurational bias' Monte Carlo scheme that was recently developed by Siepmann [11].

In summary: a numerical technique that was used to study long-time tails in extremely simple fluids (namely lattice-gas models) has been modified to speed up the simulation of extremely complex fluids. This opens the way to the numerical study of a class of problems that have, thus far, defied simulation.

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