CHAPTER 7

Configurational-bias Monte Carlo

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Conference Proceedings Vol.49
"Monte Carlo and Molecular Dynamics of Condensed Matter Systems"
K. Binder and G. Ciccotti (Eds.)
SIF, Bologna, 1996

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1. Introduction

The original Metropolis Monte Carlo scheme [1] was designed to perform single-particle trial moves. For most simulations, such moves are perfectly adequate. However, in some cases it is more efficient to perform moves in which the coordinates of many particles are changed. For instance, in the vicinity of a critical point, the Metropolis scheme becomes inefficient due to critical slowing down and it becomes advantageous to perform cluster moves, in which the coordinates (or spins) of particles belonging to the same 'cluster' are changed simultaneously [2, 3].

Similarly, the sampling of equilibrium conformations of polymers is usually time-consuming. The main reason is that the natural dynamics of polymers is dominated by topological constraints (chains cannot cross) and hence any algorithm that is based on the real motion of macromolecules will suffer from the same problem. For this reason, many algorithms have been proposed to speed up the Monte Carlo sampling of polymer conformations (see *e.g.* ref. [4]). For instance, in the elementary trial move of the 'reptation' algorithm for linear homo-polymers [5, 6], an attempt is made to insert a randomly selected end segment at the other end of the chain. For a chain consisting of n monomers, it takes of the order of n^2 moves to remove the correlation between conformations. The Configurational-Bias Monte Carlo (CBMC) method is a dynamic MC scheme that makes it possible to achieve large conformational changes in a single trial move that affects a large number of monomeric units [7, 8, 9, 10].

The CBMC method is based on the Rosenbluth sampling scheme [11, 7, 8] for lattice systems. In this scheme, the molecular conformation is built up step-by-step, in such a way that, at every stage, the next monomeric unit is preferentially added in a direction that has a large Boltzmann weight. This increases the probability of generating a trial conformation that has no hard-core overlaps. As explained below, the probability of acceptance of the trial conformation is given by the ratio of the 'Rosenbluth weights' of the new and the old conformations. Whereas the original Rosenbluth scheme was devised for polymers on a lattice, the CBMC scheme will also work for chain molecules in continuous space. Unlike the reptation algorithm, CBMC can be used in the simulation of grafted chains and ring polymers. Recently, the CBMC method has been integrated with the Gibbs-ensemble technique to simulate liquid-vapour and fluid-fluid phase equilibria of chain molecules [12]. In Gibbs-ensemble simulations of phase coexistence, simulations of the two coexisting phases (e.g. liquid and vapor) are carried out in parallel. In addition to MC trial moves of the molecules within either system, we also allow the two systems to exchange volume and mass. CBMC trial moves are used to swap chain molecules between the two systems. Clearly this requires complete regrowth of the entire chain. For long chains this becomes expensive and, at present, Gibbs-ensemble simulations are limited to chain molecules with less than 50 carbon atoms [13]. For simple CBMC sampling the situation is less serious, because one can choose not to regrow the entire chain but only part thereof. In the limit that only one monomeric unit is regrown, CBMC reduces to the

reptation algorithm, but in general it will be advantageous to regrow a larger number of monomeric units. Of course, the computational cost per trial move is higher for CBMC than for reptation and hence it becomes important to be able to construct the most efficient MC move for a given system.

1.1. Detailed balance

Before explaining the CBMC scheme, it is useful to recall the general recipe to construct a Monte Carlo algorithm. One always starts (or should start) from the condition of detailed balance:

$$P_o \times P_{gen}(o \rightarrow n) \times P_{acc}(o \rightarrow n) = P_n \times P_{gen}(n \rightarrow o) \times P_{acc}(n \rightarrow o) \ , \quad (1)$$

where P_o (P_n) is the Boltzmann weight of the old (new) conformation, P_{gen} denotes the *a priori* probability to generate the trial move from o to n, and P_{acc} is the probability that this trial move will be accepted. From Eqn. 1 it follows that

$$\frac{P_{acc}(o \rightarrow n)}{P_{acc}(n \rightarrow o)} = \exp(-\beta \Delta U) \frac{P_{gen}(n \rightarrow o)}{P_{gen}(o \rightarrow n)} \ , \quad (2)$$

where $\exp(-\beta \Delta U)$ is the ratio of the Boltzmann weights of the new and old conformations. If we use the Metropolis rule to decide on the acceptance of MC trial moves, then Eqn 2 implies

$$P_{acc}(o \rightarrow n) = \min \left(1, \exp(-\beta \Delta U) \frac{P_{gen}(n \rightarrow o)}{P_{gen}(o \rightarrow n)} \right) \ . \quad (3)$$

Ideally, by biasing the probability to generate a trial conformation in the right way, we could make the term on the right-hand side of Eqn. 3 always equal to unity. In that case, every trial move will be accepted. Configurational bias Monte Carlo does not achieve this ideal situation. However it does lead to enhanced acceptance probability of trial moves that involve large conformational changes.

1.2. Rosenbluth sampling

The Configurational-Bias Monte Carlo scheme for continuously deformable chain molecules [9], is based on Rosenbluth sampling [11, 7, 8] for lattice systems.

Chain configurations are generated by successive insertion of the bonded segments of the chain. When the positions of the segments are chosen at random, it is very likely, that one of the segments will overlap with another particle in the fluid, which results in rejection of the trial move. The Rosenbluth sampling scheme increases the insertion probability by looking one step ahead. On lattices, the availability (i.e. the Boltzmann factor) of all sites adjacent to the previous segment can be tested. In continuous space, there are in principle an infinite number of positions that should be tested (e.g. in the case of a chain molecule with rigid bonds, all points on the surface of a sphere with a radius equal to the bond length). Of course, it is not feasible to scan an infinite number of possibilities. Fortunately, however, it turns out that it is possible to construct a correct Monte Carlo scheme for off-lattice models in which only a finite number of trial segments (k), is selected either at random or, more generally, drawn from the distribution of bond-lengths and bond-angles of the 'ideal' chain molecule.

From here on, the procedure is the same for lattices and continuous space systems. For each of the trial positions, we compute the Boltzmann factor associated with the

non-bonded interactions (more precisely, the contributions of all those interactions that have not yet been accounted for in the generation of the trial positions). One of these trial positions is then selected with a probability proportional to its Boltzmann factor. In this way, regions of high potential energy, such as the hard core of another particle, are avoided and configurations with a non-vanishing Boltzmann weight are generated. To correct for the bias introduced by this very non-random sampling procedure, a weight has to be assigned to each conformation, Γ, called the Rosenbluth weight w_Γ [11]. The contribution of each i^{th} segment to this Rosenbluth weight is equal to the average of the Boltzmann factors of the trial positions for this segment:

$$w_{\Gamma_i} = \frac{1}{k_i} \sum_{j=1}^{k_i} \mathrm{e}^{-\beta U^{\mathrm{nb}}_{\Gamma_{ij}}}, \tag{4}$$

where $\beta = 1/k_B T$ and $U^{\mathrm{nb}}_{\Gamma_{ij}}$ is the non-bonded energy of the j^{th} trial direction for the i^{th} segment. The Rosenbluth weight of the total configuration Γ, is the product of the weights of the individual segments, including the Boltzmann factor of the energy of the first segment, U_{Γ_0}:

$$w_\Gamma = \mathrm{e}^{-\beta U_{\Gamma_0}} \prod_{i=1}^{\ell} w_{\Gamma_i}, \tag{5}$$

where ℓ is the chain length. In the original Rosenbluth scheme, every chain conformation Γ was given a statistical weight proportional to w_Γ. However, as explained in ref. [14], this approach fails when the largest contribution to the equilibrium properties of a chain molecule come from conformations that have a large Rosenbluth weight w, but a very small probability $P(W)$ of being generated in the Rosenbluth sampling scheme. The Configurational-Bias MC scheme was designed to avoid this problem.

1.3. CBMC as 'Dynamic' Rosenbluth sampling

1.3.1. Discrete conformations Consider a trial move from a chain-conformation $\boldsymbol{\Gamma}_1$ with Rosenbluth weight w_1 to some other conformation $\boldsymbol{\Gamma}_2$ with Rosenbluth weight w_2. Let us denote the probability (*i.e* the normalized Boltzmann weight) of finding the chain in conformation $\boldsymbol{\Gamma}_1$ by P_1 and the corresponding probability for $\boldsymbol{\Gamma}_2$ by P_2. In equilibrium, the number of chains in conformation 1(2), N_1 (N_2) is obviously proportional P_1 (P_2). We wish to perform a Monte-Carlo move such that detailed balance is satisfied, *i.e.* the rate K_{12} with which conformations of type 1 are transformed in to type 2 equals the reverse rate:

$$K_{12} = K_{21}. \tag{6}$$

Let us try to compute K_{12} and K_{21}. K_{12} is equal to N_1 times $P_{gen}(\boldsymbol{\Gamma}_2)$, the probability of generating chain 2 by Rosenbluth sampling, times the acceptance probability P_{acc}. We assume that P_{acc} is an, as yet unspecified function of the ratio w_2/w_1, $P_{acc}(w_2/w_1)$. $P_{gen}(\boldsymbol{\Gamma}_2)$ is equal to

$$P_{gen}(\boldsymbol{\Gamma}_2) = \prod_{i=1}^{\ell} \frac{\exp(-\beta u^{(i)}(\boldsymbol{\Gamma}_2(i))}{Z_i}, \tag{7}$$

where, as before, we use the notation $Z_i \equiv \sum_{j=1}^{b} \exp(-\beta u^{(i)}(\boldsymbol{\Gamma}_2(j))$ The sum in Z_i runs over all b possible directions of the i-th segment of the polymer. With this notation, Eq. 6 becomes

$$N_1 P_{gen}(\boldsymbol{\Gamma}_2) P_{acc}(w_2/w_1) = N_2 P_{gen}(\boldsymbol{\Gamma}_1) P_{acc}(w_1/w2) \,. \tag{8}$$

Equation 8 can be simplified by using the result that the Rosenbluth weight w_2 times the generating probability $P_{gen}(\boldsymbol{\Gamma}_2)$ is proportional to N_2 (and similarly for 1). Hence multiplying equation 8 on the left by w_2/w_2 and on the right by w_1/w_1 yields

$$N_1 N_2 \frac{P_{acc}(w_2/w_1)}{w_2} = N_2 N_1 \frac{P_{acc}(w_1/w_2)}{w_1} \tag{9}$$

or

$$\frac{P_{acc}(w_2/w_1)}{P_{acc}(w_1/w_2)} = \frac{w_2}{w_1} \,. \tag{10}$$

There are many choices of P_{acc} that satisfy this condition. One obvious choice is the Metropolis form [1]

$$P_{acc}(w_2/w_1) = \mathrm{Min}(w_2/w_1, 1) \tag{11}$$

In words, the Configurational Bias Monte Carlo (CBMC) scheme works as follows:

(i) Generate a trial conformation by using the Rosenbluth scheme (i.e. eq. 7) to regrow the entire molecule, or part thereof.

(ii) Compute the Rosenbluth weights w_{trial} and w_{old} of the trial conformation *and of the old conformation.*

(iii) Accept the trial move with a probability $\mathrm{Min}(w_{trial}/w_{old},1)$.

1.4. Continuously deformable chain

Next consider Configurational Bias Monte Carlo sampling of flexible chains with or without internal bending energy. Again, we first consider the probability to generate a trial configuration $\boldsymbol{\Gamma}_j$ using the (extended) Rosenbluth scheme. As before, we only consider the expression for one of the ℓ segments, to keep the equations simple.

$$P_{gen}(\{j\}) = d\boldsymbol{\Gamma}_j P_{id}(\boldsymbol{\Gamma}_j) \left[\prod_{j' \neq j}^{k} d\boldsymbol{\Gamma}_{j'} P_{id}(\boldsymbol{\Gamma}_{j'}) \right] \frac{\exp(-\beta u_{ext}(j))}{\sum_{j'=1}^{k} \exp(-\beta u_{ext}(j'))} \tag{12}$$

In order to compute the acceptance probability of this move, we have to consider what happens in the reverse move. Then we start from conformation j and generate a set of k trial directions that includes i. When computing the acceptance probability of the forward move, we have to impose detailed balance. However, detailed balance in this case means not just that in equilibrium the number of moves from i to j is equal to the number of reverse moves, but even that the rates are equal *for any given set of trial directions for the forward and reverse moves.* This condition we will call 'super-detailed balance'. Super-detailed balance implies that we can only decide on the acceptance of the forward move if we also generate a set of $k-1$ trial directions around the old conformation i. We denote the probability to generate this set of $k-1$ trial orientations by $P_{rest}(\{i\})$, where the sub-script 'rest' indicates that this is the set

of orientations around, but excluding, i. This allows us to compute the ratio $w_j^{(t)}/w_i^{(o)}$ of the Rosenbluth weights for forward and reverse moves:

$$w_j^{(t)} = \frac{\exp(-\beta u_{ext}^{(t)}(j) + \sum_{j' \neq j}^{k-1} \exp(-\beta u_{ext}^{(t)}(j'))}{k}$$

and

$$w_i^{(o)} = \frac{\exp(-\beta u_{ext}^{(o)}(i) + \sum_{i' \neq i}^{k-1} \exp(-\beta u_{ext}^{(o)}(i'))}{k}$$

The superscript (t) and (o) distinguish the trial conformation from the old conformation. Again, we shall devise a Metropolis criterion to determine the acceptance probability of a trial move from i to j. As before, this acceptance probability is determined by the ratio $x \equiv w_j^{(t)}/w_i^{(o)}$ (actually, for a molecule of ℓ segments, we should compute a product of such factors). Let us assume that $w_j^{(t)} < w_i^{(o)}$. In that case, $P_{acc}(i \to j) = x$ while $P_{acc}(j \to i) = 1$. Next, let us check whether detailed balance is satisfied. To do so, we write down the explicit expressions for K_{ij} and K_{ji}.

$$K_{ij} = N_i P_{gen}(\{j\}) P_{rest}(\{i\}) w_j^{(t)}/w_i^{(o)}$$

and

$$K_{ji} = N_j P_{gen}(\{i\}) P_{rest}(\{j\}) 1$$

In addition, we use the fact that

$$P_{gen}(\{j\}) P_{rest}(\{i\}) w_j^{(t)} \sim N_j P_{rest}(\{j\}) P_{rest}(\{i\})$$

and

$$P_{gen}(\{i\}) P_{rest}(\{j\}) w_j^{(t)} \sim N_i P_{rest}(\{i\}) P_{rest}(\{j\})$$

In then follows immediately that

$$\begin{aligned} K_{ij} w_i^{(o)} &= N_i P_{gen}(\{j\}) P_{rest}(\{i\}) w_j^{(t)} \qquad (13) \\ &= \text{constant} \times N_i N_j P_{rest}(\{i\}) P_{rest}(\{j\}) \\ &= N_j P_{gen}(\{i\}) P_{rest}(\{j\}) w_i^{(o)} \\ &= K_{ji} w_i^{(o)} \qquad (14) \end{aligned}$$

Hence, K_{ij} is indeed equal to K_{ji}. This completes the proof that the above Configurational Bias MC scheme satisfies detailed balance. Note that, in this derivation, the number of trial directions, k, was arbitrary.

The CBMC scheme for completely flexible molecules has been applied Frenkel et al. [9] to study conformational changes of chain molecules in solution. The method was found to be particularly efficient in generating large conformational changes of such a molecule. More interestingly, the CBMC scheme makes it possible to perform direct simulations of phase equilibria in polymer mixtures, using the Gibbs-ensemble method [12, 15, 16].

The procedure sketched above is valid for a complete regrowth of the chain, but it is also possible to regrow only part of a chain, i.e. to cut a chain at a (randomly

chosen) point and regrow the cut part of the chain either at the same site or at the other end of the molecule. Clearly, if only one segment is regrown and only one trial direction is used, CBMC reduces to the reptation algorithm (at least, for linear homopolymers). It should be stressed that there are many possible ways to generate a trial conformation. For instance, one can generalize the 'pivot' algorithm [17]. In the pivot algorithm a new conformation is generated by rotating a molecule over a random angle around a randomly selected 'pivot' segment. The pivot algorithm is very efficient for isolated chains, but becomes inefficient for molecules in dense media. However, with CBMC, one can introduce a larger number of pivots in a chain molecule, in such a way that the acceptance of the trial moves is enhanced (at the expense of additional computation). Of course, when CBMC is combined with Grand Canonical and Gibbs-ensemble MC simulations, where entire molecules are exchanged, it is necessary to include moves that attempt to (re)grow chains completely.

One choice remains to be made before applying the Rosenbluth sampling scheme for continuously deformable chain molecules to CBMC and chemical potential calculations, namely the choice for the number of trial directions at the $i-th$ regrowth step, k_i. Too many trial directions increase the cost of a simulation cycle, but too few trial directions lower the acceptance rate, and increase the simulation length. Clearly, we wish to have simple guidelines that allow us to select k_i for every segment such that it optimizes the efficiency of the simulation. In the following section we show how the optimal values for the set $\{k_i\}$ and the maximum efficiency achievable can be estimated.

Although we apply our analysis to optimize the efficiency to the CBMC scheme, it is in fact much more general, and can be used to optimize the efficiency of any MC trial move that can be decomposed into a sequence of elementary steps.

2. Efficiency of Configurational-Bias Monte Carlo

In order for the Rosenbluth sampling scheme to work, it is essential to generate, on average, at least one trial position that has a non-negligible Boltzmann weight for every segment. If all trial positions have a small Boltzmann weight, the Rosenbluth weight of the new conformation is virtually zero, while the Rosenbluth weight of the existing conformation is necessarily finite, and the trial move will be rejected. The probability of finding at least one trial position with a non-negligible Boltzmann weight, depends on the choice for the value of k_i, i.e. the number of trial directions that are scanned when looking for an acceptable position of the next, i^{th}, segment. In discussing the efficiency of the CBMC scheme, it is convenient to consider monomeric units with a hard repulsive core because in that case the Boltzmann weight associated with conformations that have hard-core overlaps is strictly zero. Below, we indicate how to generalize our results to molecules interacting through 'soft' potentials (for more details, see [18]).

Two trends determine this choice for optimal k_i-values, k_i^{opt}. On the one hand, the probability of a successful chain insertion grows with increasing k_i. There is an upper limit to that, because when the space to insert another segment is simply not available, there is no point in generating more and more trial directions. Moreover, the computational cost also rises with increasing k_i. The optimal choice for k_i depends on density, temperature and the nature of the intermolecular interactions. For instance, at high densities a larger number of trial directions is needed to regrow a given number

of segments than at low densities. It can also be expected that k_i^{opt} varies along a chain. After successful insertion of part of the chain, a larger number of trial directions should be chosen for the next segment, in order to minimize the probability that we waste the computational effort that has already been invested in this trial move.

Below, we show how we can arrive at an estimate of the optimal values k_i^{opt}. To do so, we should first define what we mean by the 'efficiency' of a given CBMC trial move. Loosely speaking, we expect the efficiency to be proportional to the probability that a given trial conformation is successfully generated and inversely proportional to the computational cost of that trial move. For a chain of ℓ segments

$$\text{Eff}(\ell) = \frac{\langle P(\ell) \rangle}{\langle \text{Cost}(\ell) \rangle}, \tag{15}$$

where $\langle P(\ell) \rangle$ is the probability to find for every segment at least one trial direction with a non-negligible Boltzmann weight, in which case the chain can be inserted successfully. $\langle \text{Cost}(\ell) \rangle$ is the average cost for trying to insert the chain, measured in the number of times the energy of a trial direction is calculated. The extra cost for trying to insert a chain which is one segment longer, depends linearly on the number of trial directions and on the probability to insert ℓ segments successfully. So, the average cost for one trial insertion of a chain of length $\ell + 1$ is given by

$$\langle \text{Cost}(\ell + 1) \rangle = \langle \text{Cost}(\ell) \rangle + 2k_{\ell+1} \times \langle P(\ell) \rangle \,. \tag{16}$$

where we have introduced, as our unit of computational cost, the amount of computation needed to compute the energy for one trial segment. In the computational cost of a trial move in the CBMC scheme, we have included the cost of the energy calculations for the $k_{\ell+1}$ 'trial' directions of the old conformation, needed to compute the 'old' Rosenbluth weight w_{old}. The probability to find at least one acceptable position for the $\ell+1^{\text{th}}$ segment, $\langle P_{\text{add}}(k_{\ell+1}) \rangle$, also increases with $k_{\ell+1}$. If we assume that subsequent insertions of segments are independent, $\langle P(\ell + 1) \rangle$ is given by

$$\langle P(\ell + 1) \rangle = \langle P(\ell) \rangle \times \langle P_{\text{add}}(k_{\ell+1}) \rangle \,. \tag{17}$$

Equations 16 and 17 can be combined with equation 15 to yield the following very simple recursive relation

$$\frac{\text{Eff}(\ell + 1)}{\text{Eff}(\ell)} = \frac{\langle P_{\text{add}}(k_{\ell+1}) \rangle}{1 + 2k_{\ell+1} \times \text{Eff}(\ell)}. \tag{18}$$

Together with the 'boundary' condition $\text{Eff}(\ell = 1)$, equation 18 allows us to compute the efficiency of a trial move for a given set of k_i-values. The values of the set $\{k_i\}$ affect both the numerator and the denominator of equation 18. Our aim is to vary all k_i-values until the optimum efficiency is reached.

The computational cost of the insertion of the first monomer of the chain is zero if we simply start regrowing part of an existing chain. However, if we must succesfully insert one monomer before we can continue growing the rest of the chain, then the computational cost of the first insertion is non-negligible and this, in turn, will affect (increase) the optimal values for all subsequent k_i's. In addition to $\text{Eff}(1)$, we must know $\langle P_{\text{add}}(k_{\ell+1}) \rangle$ for all ℓ. $\langle P_{\text{add}}(k_{\ell+1}) \rangle$ can be determined numerically by calculating

$$\langle P_{\text{add}}(k_{\ell+1}) \rangle = 1 - \langle (1 - P_{\text{add}}(1))^{k_{\ell+1}} \rangle \,. \tag{19}$$

In words: the probability to generate at least one acceptable trial segment is equal to one minus the probability that not a single acceptable trial segment is generated in $k_{\ell+1}$ attempts. In equation 19, $P_{\mathrm{add}}(1)$ is the probability that the insertion of a single trial segment will be successful. It should be noted that this probability is a fluctuating quantity: the angular brackets in equation 19 denote averaging over the equilibrium configurations of the fluid. Of course, we can make a crude estimate of $\langle P_{\mathrm{add}}(k_{\ell+1})\rangle$ by ignoring all fluctuations, in which case we get the 'mean-field' estimate

$$\langle P_{\mathrm{add}}(k_{\ell+1})\rangle = 1 - (1 - \langle P_{\mathrm{add}}(1)\rangle)^{k_{\ell+1}}. \tag{20}$$

Although equation 20 is useful for order-of-magnitude estimates, we shall not use it in what follows. Rather, we shall compute $\langle P_{\mathrm{add}}(k_{\ell+1})\rangle$ by simulation. Instead of computing $\langle P_{\mathrm{add}}(k_{\ell+1})\rangle$ for all ℓ, we measured it for $\ell \leq 2$, and assume that for $\ell > 2$, the values for $\ell = 2$ can be used as an estimate. We verified this assumption under various conditions by calculating $\langle P_{\mathrm{add}}(k_{\ell+1})\rangle$ for all ℓ and we found no significant difference in the answers.

The procedure described above allows us to determine numerically the values for the set $\{k_i\}$ that maximize equation 18, and thereby the efficiency to generate an acceptable trial conformation for a chain in a CBMC move.

Thus far we have ignored the fact that this trial conformation, although acceptable in principle, may be rejected in practice. As stated before (equation 11), the overall acceptance probability is determined by the ratio of the new and the old Rosenbluth weights: $w_{\mathrm{new}}/w_{\mathrm{old}}$. The decrease in efficiency that is attended with this acceptance criterion is estimated by $\langle w_{\mathrm{new}}/w_{\mathrm{old}}\rangle$.

2.1. Remark

For molecules interacting through 'soft' potentials, the same efficiency analysis can be performed. The main difference with systems with hard core potentials is, that it is never impossible to insert a segment which interacts through soft potentials, it can at most be very difficult. An insertion is difficult, if all trial segments have a high energy. The Rosenbluth weight of a segment selected from such a set of trial segments is very low, and if it is not compensated by the other segments in the chain, the conformation will hardly contribute to the averaging. Therefore, it is more efficient if, at the point where a segment has to be selected from a set of trial directions that all have a high energy, the conformation is discarded. This can be done by defining a lower limit for the Rosenbluth weight of a segment, $w_{\mathrm{low}} \ll 1$, below which it has to be decided whether it is worth while to continue growing the chain conformation. Of course this introduces a bias in the sampling procedure, but this can be corrected for if the proper criterion are used for the decision. A way to solve this is by discarding a conformation with a Rosenbluth weight lower than w_{low} with a probability

$$P_{\mathrm{discard}} = \mathrm{Min}\left[1, w_\Gamma/w_{\mathrm{low}}\right]. \tag{21}$$

Chains with a Rosenbluth weight below w_{low} have now a probability $w_\Gamma/w_{\mathrm{low}}$ to contribute to the averaging. In the original scheme they were given a weight w_Γ, so in this scheme they must have a weight w_{low}. The procedure for chains with a Rosenbluth weight larger than w_{low} does not change. The scheme mentioned here has been described in more detail elsewhere [3].

For this scheme the efficiency analysis we have presented above can be applied with some minor modifications to systems with soft potentials. The probability to

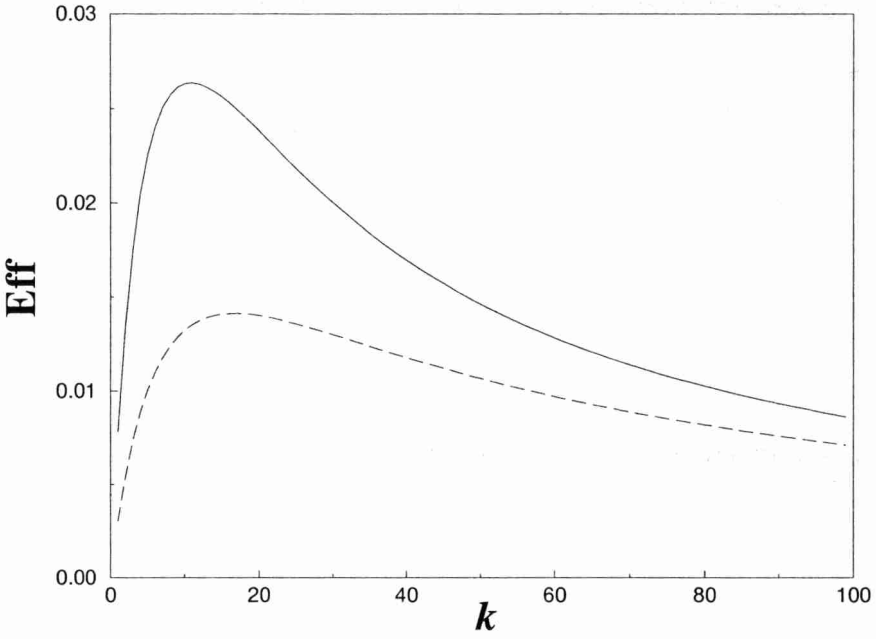

Figure 1. The efficiency, as defined by equation 18, for inserting a hard dimer (———) and a fully flexible trimer of hard spheres (– – –) into a fluid of hard spheres at several densities $\rho\sigma^3$, over a range of k-values.

find at least one trial segment which does not overlap with a particle in the fluid is now replaced by the probability to find at least one trial direction with a Boltzmann factor that is higher than about $k_i \times w_{\text{low}}$, so that the Rosenbluth weight is higher than w_{low}.

3. Results

As an example we studied a system with only hard core interactions, but, as we showed above, the efficiency analysis can also be applied to energetic interactions. In a fluid of hard spheres with diameter σ at number density $\rho\sigma^3$, we insert a fully flexible chain of ℓ hard spheres with the same diameter, attached at a fixed bond length σ.

The insertion probability of one segment (which for this particular system is given by the Carnahan-Starling equation [19]) gives Eff(1) and by inserting a second segment $\langle P_{\text{add}}(k_2) \rangle$ is calculated from equation 19 for a range of k_2-values. The efficiency for successfully adding another segment, Eff(2), is calculated from equation 18, and the result is shown in Figure 1 for a fluid at density $\rho\sigma^3 = 0.4$. The maximum determines the value of k_2^{opt}. Eff(3) for a fluid at the same density is plotted in the same Figure, which shows a shift of the maximum to a value for k_3^{opt} which is higher than k_2^{opt}. As already mentioned, k_ℓ^{opt} is expected to increase with ℓ, because more and more

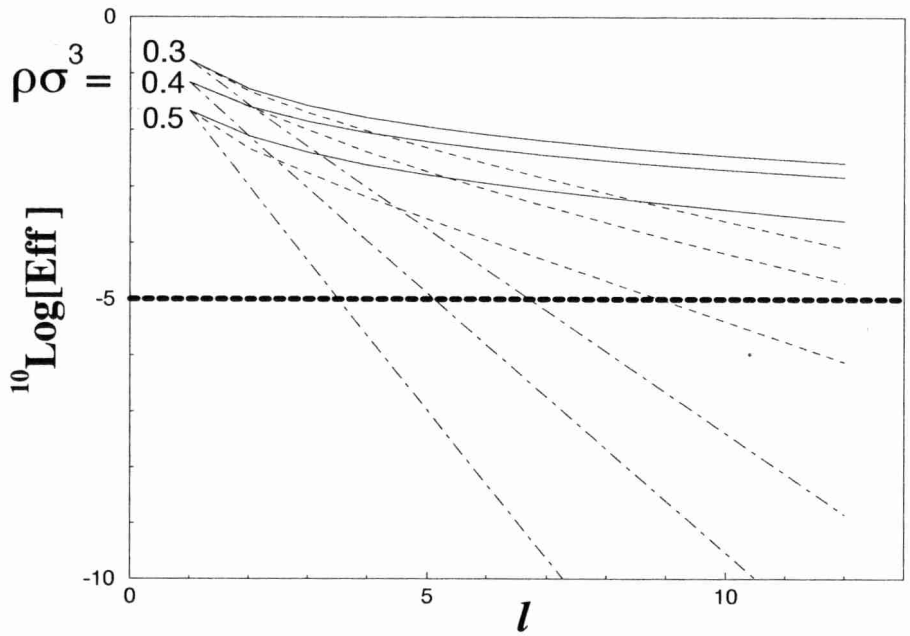

Figure 2. The efficiency (equation 18) for inserting a fully flexible chain of ℓ hard spheres into a fluid of hard spheres at several densities $\rho\sigma^3$. Both the efficiency of a random insertion ($- \cdot - \cdot -$), i.e. $k_\ell = 1$ for all ℓ, and the maximal efficiency (———), obtained by choosing the optimal k-values, are shown. In the same Figure we show the efficiency for acceptance of a CBMC move ($- - -$) by the acceptance criterion 11. The dashed horizontal line shows the minimal efficiency needed for a simulation of typical length.

effort is invested previously in the insertion of $\ell - 1$ segments, which will be wasted if all the trial directions result in a hard core overlap with spheres in the fluid.

In Figure 2 we show the maximal values of Eff(ℓ), compared these efficiencies with the efficiencies of a random insertion, i.e. the limit $k_\ell = 1$ for all ℓ. The figure shows a considerable increase of efficiency using CBMC, and much longer chain lengths are feasible. We also show the decrease in efficiency due to the acceptance probability given by equation 11. This decrease is estimated by $\langle w_{\text{new}}/w_{\text{old}} \rangle$, where w_{new} is only averaged over chains already inserted successfully. It is possible to give a rough estimate of the maximum chain length that can be reached: if the maximum simulation length feasible is estimated at 10^8 energy calculations and if the minimum number of successful insertions needed is of the order of 10^3, then the minimal efficiency needed is of the order of 10^{-5}. Figure 2 shows, that random insertion does not fullfill this requirement for chains longer than three segments at $\rho\sigma^3 = 0.5$, five segments at $\rho\sigma^3 = 0.4$ or seven segments at $\rho\sigma^3 = 0.3$. The CBMC scheme can be used at least up to $\ell = 12$ for $\rho\sigma^3$=0.3 and 0.4, and at the higher density $\rho\sigma^3 = 0.5$ it can be used up to $\ell = 9$.

Acknowledgments

The work of the FOM Institute is part of the research program of FOM and is supported financially by the Netherlands Organization for Research (NWO).

References

[1] Metropolis N., Rosenbluth A.W., Rosenbluth M.N.,Teller A.H. and Teller E., *J.Chem. Phys.* **21**, 1087 (1953).
[2] Swendsen R.H. and Wang J.S., *Phys. Rev. Lett.* **58**, 86 (1987).
[3] Frenkel D., in *Computer Simulation in Chemical Physics*, edited by M.P. Allen and D.J. Tildesley (Kluwer, Dordrecht, 1993).
[4] Kremer K. and Binder K., *Computer Physics Reports* **7**, 259 (1988).
[5] Kron A.K., *Polymer Sci. USSR* **7**, 1361 (1965).
[6] Wall F.T. and Mandel F., *J. Chem. Phys.* **63**, 4529 (1975).
[7] Harris J. and Rice S.A., *J. Chem. Phys.* **88**, 1298 (1988).
[8] Siepmann J.I. and Frenkel D., *Mol.Phys.* **75**, 59 (1992).
[9] Frenkel D., Mooij G.C.A.M. and Smit B., *J.Phys. Condensed Matter* **4**, 3053 (1992).
[10] dePablo J.J., Laso M. and Suter U.W., *J. Chem. Phys.* **96**, 2394 (1992).
[11] Rosenbluth M.N. and Rosenbluth A.W., *J.Chem. Phys.* **23**, 356 (1955).
[12] Mooij G.C.A.M., Frenkel D. and Smit B., *J. Phys. Condensed Matter* **4**, L255 (1992).
[13] Siepmann J.I., Karaborni S. and Smit B., *Nature* **365**, 330 (1993).
[14] Batoulis J. and Kremer K., *J. Phys. A: Math. Gen.* **21**, 127 (1988).
[15] Siepmann J.I., Karaborni S. and Smit B., *J. Am. Chem. Soc.* **115**, 6454 (1993).
[16] Siepmann J.I., Karaborni S. and Smit B., *Nature* **365**, 330 (1993).
[17] Lal M., *Mol. Phys.* **17**, 57 (1969).
[18] Mooij G.C.A.M. and Frenkel D., *Mol. Simulation* (in press).
[19] Carnahan N.F. and Starling K.E., *J. Chem. Phys.* **51**, 635 (1969).