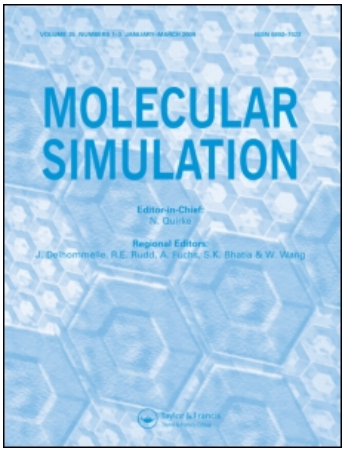

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Mooij, G. C. A. M. and Frenkel, D.(1996) 'A Systematic Optimization Scheme for Configurational Bias Monte Carlo', Molecular Simulation, 17: 1, 41 — 55
To link to this Article: DOI: 10.1080/08927029608024093
URL: http://dx.doi.org/10.1080/08927029608024093

Molecular Simulation, 1996, Vol. 17, pp. 41–55
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A SYSTEMATIC OPTIMIZATION SCHEME FOR CONFIGURATIONAL BIAS MONTE CARLO

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(Received July 1995, accepted August 1995)

We present a simple method that allows us to optimize the efficiency of Monte Carlo schemes that employ trial moves composed of a sequence of elementary steps. One such scheme, namely the Configurational Bias Monte Carlo (CBMC) method, has resulted in great advances in the simulation of phase behavior of chain molecules. Until now the construction of efficient CBMC trial moves was more an art than a science. In this paper we show that there exist simple relations that allow us to design the most efficient CBMC trial moves, for a given temperature and density. The best strategy will vary between random regrowth (in the case of an almost ideal chain) and reptation (in the limit of a dense melt), both of which are special cases of a CBMC trial move. We also show how the same approach can be used to optimize the calculation of the chemical potential of a chain molecule, using the Rosenbluth particle insertion scheme.

KEY WORDS: Configuration Bias Monte Carlo, Monte Carlo optimization, Rosenbluth scheme.

1 INTRODUCTION

Forty years after its introduction, the Metropolis Monte Carlo Method [1] is still expanding. In fact, in recent years we have witnessed the introduction of several schemes that have resulted in a dramatic improvement of the efficiency of sampling method under conditions where, previously, Monte Carlo simulations could hardly (if at all) be applied. The original Metropolis Monte Carlo scheme 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, in the simulation of (long) chain molecules, a trial move that attempts to displace a single monomeric unit in the chain does little to change the conformation of the molecule. For instance, in the elementary trial move of the 'reptation' algorithm for linear homo-polymers [4], an attempt is made to insert a randomly selected end segment at the other end of the chain. For a chain consisting of

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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 [5, 6, 7, 8]. The CBMC method is based on the Rosenbluth sampling scheme [9, 5, 6] 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 hardcore 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-vapor and fluid-fluid phase equilibria of chain molecules [10]. 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 [11]. 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.

In the present paper, we address this question. Although we shall apply our approach to the CBMC scheme, it is in fact 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.

In addition, we consider the extension of the Widom particle-insertion method [12] to compute the excess chemical potential of a molecule. In its original formulation, the Widom method relates the excess chemical potential of a species to the acceptance probability of a virtual trial move in which a molecule of that species is inserted at random in the system under study. This scheme works well for atomic and simple molecular fluids up to approximately twice the critical density. However, for chain molecules, the acceptance probability for a random trial insertion decreases exponentially with chain length. As a consequence, the conventional random insertion scheme can only be used for chains up to 3–4 segments long, for all but the lowest densities. For longer chains the probability of acceptance is so low that the 'measured' excess chemical potential is drowned in the statistical error. Two schemes exist to improve the statistics for longer chains: the first is basically a

thermodynamic integration scheme where the molecule is either inserted monomer-by-monomer [13] or its interaction with the bath is gradually 'switched-on' [14]. The second scheme still attempts a virtual insertion of a chain conformation, but this conformation is no longer random [5, 6, 7]: the trial conformations are generated using the Rosenbluth scheme and the acceptance probability is directly related to the average Rosenbluth weight of the trial conformations. This technique makes it possible to extend the Widom insertion method to longer chain lengths [15].

The efficiency of the Rosenbluth sampling technique depends on the choice of a set of parameters, namely the number of trial insertions for a given segment i, k_i. As described in the next section, k_i can, in principle, be chosen freely. However, the choice of k_i affects the efficiency of the sampling scheme. In this article we show how this efficiency can be optimized with respect to k_i. In section 3, we explain how the k_i-values that optimize the efficiency are determined, and in section 4 we present the results of an efficiency analysis and discuss the range of applicability of CBMC-type sampling techniques.

2 CONFIGURATIONAL-BIAS MONTE CARLO

2.1 Rosenbluth sampling

In Configurational-Bias Monte Carlo 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 [9]. 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:

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

where $\beta = 1/k_B T$ and $U^{nb}_{\Gamma_{ij}}$ 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}:

$$W_\Gamma = \mathrm{e}^{-\beta U_{\Gamma_0}} \prod_{i=1}^{l} W_{\Gamma_i}, \tag{2}$$

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. [16], 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 that we discuss below, was designed to avoid this problem.

2.2 *Rosenbluth sampling of μ*

First, however, we discuss how the Rosenbluth sampling scheme can be used to calculate the chemical potential of a chain molecule. This method is based on the 'Widom' expression that relates the excess chemical potential μ^{ex} of a species to the potential energy, U, of a ghost particle that is added to the system at a random position,

$$\beta\mu^{ex} = \ln\langle \exp[-\beta U] \rangle. \tag{3}$$

The angular brackets denote ensemble averaging over all configurations of the system and over all conformations of the test-molecule. When the conformation of the test molecules are generated using the Rosenbluth scheme, we obtain an expression for $\beta\mu^{ex}$ that is similar to the one given in equation 3, but for the fact that the Boltzmann weight is replaced by the Rosenbluth weight [7, 9],

$$\beta\mu^{ex} = -\ln\langle W \rangle. \tag{4}$$

This expression is valid irrespective of the choice of k_i, the number of trial directions for each segments i. However, the statistical error in $\beta\mu^{ex}$ depends strongly on k_i. Below, we shall discuss how to arrive at an optimal choice for k_i. Note also that equation 4 suffers from the same drawback as the original Rosenbluth scheme: for long isolated chains, or not-so-long chains in dense media, the largest contributions to $\langle W \rangle$ come from conformations that are sampled infrequently [16]. It is however, easy to detect this problem when it occurs: this point is discussed in more detail in reference [17].

2.3 *CBMC: 'Dynamic' Rosenbluth sampling*

The Configurational-Bias Monte Carlo procedure for generating a new conformation of a chain is as follows. First, a chain is chosen at random. Next, a trial conformation for this chain is generated by means of the Rosenbluth sampling scheme and a Rosenbluth weight for this new conformation is calculated. Next, we should decide if we accept the proposed 'move'. To this end, we must compare the Rosenbluth weight W_{new} of the trial conformation with W_{old}, the weight of the old conformation. In fact, the computation of the latter quantity is a bit subtle. In case of a lattice system it is obvious what the trial directions for the old conformation are, and hence its Rosenbluth weight can be evaluated unambiguously. In contrast, for continously deformable chains the trial directions are chosen at random for every new conformation, and it is not immediately obvious what choice should be made for the calculation of the Rosenbluth weight of the old conformation. As shown in ref. [7], it can be proven that the following simple procedure satisfies detailed balance, and thereby fulfills a sufficient condition to ensure that all chain conformations are generated with a probability proportional to their Bolzmann weight: around every segment i of the old chain, $k_i - 1$ trial directions are drawn from the same probability distribution as the one from which the directions for the trial conformation are chosen. The old Rosenbluth weight is calculated, by treating the $k_i - 1$ trial directions *plus the direction in which the segment of the old chain is situated*, as the set of 'trial' directions for the existing conformation. Finally, we compute the ratio of the Rosenbluth weights of the new and the old conformations. We use a Metropolis-like criterion to decide on the acceptance of the trial move, i.e. the trial move is accepted with a probability P_{acc},

$$P_{acc} = \text{Min}\left(1, \frac{W_{\text{new}}}{W_{\text{old}}}\right). \tag{5}$$

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 homo-polymers). It should be stressed that there are many possible ways to generate a trial conformation. For instance, one can generalize the 'pivot' algorithm [18]. 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 continously deformable chain molecules to CBMC and chemical potential

calculations, namely the choice for the number of trial directions 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.

3 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.

Two opposing trends determine the 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

$$\text{Eff}(l) = \frac{\langle P(l) \rangle}{\langle \text{Cost}(l) \rangle}, \tag{6}$$

where $\langle P(l) \rangle$ 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. $\langle \text{Cost}(l) \rangle$ 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 $l+1$ is given by

$$\langle \text{Cost}(l+1) \rangle = \langle \text{Cost}(l) \rangle + 2k_{l+1} \times \langle P(l) \rangle. \tag{7}$$

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_{l+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 $l+1^{th}$ segment, $\langle P_{\text{add}}(k_{l+1}) \rangle$, also increases with k_{l+1}. If we assume that subsequent insertions of segments are independent, $\langle P(l+1) \rangle$ is given by

$$\langle P(l+1) \rangle = \langle P(l) \rangle \times \langle P_{\text{add}}(k_{l+1}) \rangle. \tag{8}$$

Equations 7 and 8 can be combined with equation 6 to yield the following very simple recursive relation

$$\frac{\text{Eff}(l+1)}{\text{Eff}(l)} = \frac{\langle P_{\text{add}}(k_{l+1}) \rangle}{1 + 2k_{l+1} \times \text{Eff}(l)}. \tag{9}$$

Together with a 'boundary' condition for $\text{Eff}(l=1)$, equation 9 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 9. 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 sucessfully 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 Eff(1), we must know $\langle P_{\text{add}}(k_{l+1}) \rangle$ for all l. $\langle P_{\text{add}}(k_{l+1}) \rangle$ can be determined numerically by calculating

$$\langle P_{\text{add}}(k_{l+1}) \rangle = 1 - \langle (1 - P_{\text{add}}(1)^{k_{l+1}} \rangle. \tag{10}$$

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_{l+1} attempts. In equation 10, $P_{\text{add}}(1)$ is the probability that the insertion of a single trial segment willl be sucessful. It should be noted that this probability is a fluctuating quantity: the angular brackets in equation 10 denote averaging over the equilibrium configurations of the fluid. Of course, we can make a crude estimate of $\langle P_{\text{add}}(k_{l+1}) \rangle$ by ignoring all fluctuations, in which case we get the 'mean-field' estimate

$$\langle P_{\text{add}}(k_{l+1}) \rangle = 1 - (1 - \langle P_{\text{add}}(1) \rangle)^{k_{l+1}}. \tag{11}$$

Although equation 11 is useful for order-of-magnitude estimates, we shall not use it in what follows. Rather, we shall compute $\langle P_{\text{add}}(k_{l+1}) \rangle$ by simulation. Instead of

computing $\langle P_{\text{add}}(k_{l+1})\rangle$ for all l, we measured it for $l \leqslant 2$, and assume that for $l > 2$, the values for $l = 2$ can be used as an estimate. We verified this assumption under various conditions by calculating $\langle P_{\text{add}}(k_{l+1})\rangle$ 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 9, 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 5), the overall acceptance probability is determined by the ratio of the new and the old Rosenbluth weights: $W_{\text{new}}/W_{\text{old}}$. The decrease in efficiency that is attended with this acceptance criterion is estimated by $(W_{\text{new}}/W_{\text{old}})$, and the efficiency is thus defined as

$$\text{Eff}(l) = \frac{\langle P(l)\rangle}{\langle \text{Cost}(l)\rangle}\left\langle \frac{W_{\text{new}}}{W_{\text{old}}}\right\rangle. \tag{12}$$

Below, we shall use this crude estimate of the reduction of efficiency. It should be noted, however, that this estimate is quite conservative, because it assumes that the decision to accept or reject a trial move is only taken after the complete trial configuration has been generated. In practice, it is possible to reject trial moves at any stage during their growth (see [3]). This will result in a lower computational cost per trial move, and hence a higher efficiency.

When calculating the excess chemical potential for a chain of l segments from the average Rosenbluth weight through $\beta\mu^{\text{ex}} = -\ln\langle W(l)\rangle$ (see equation 4), it is appropriate to use a slightly different definition of the efficiency. The relevant quantity here is $\sigma(l)$, the error in $\ln\langle W(l)\rangle$ which should be minimized. Therefore, we choose to define the efficiency by

$$\text{Eff}^{\mu}(l) = \frac{1/\sigma^2(l)}{\text{Cost}(l)}, \tag{13}$$

which is independent of run length. The average Rosenbluth factor of a chain of $l+1$ segments is given by

$$\langle W(l+1)\rangle = \langle W(l) \times W(l+1|l)\rangle, \tag{14}$$

where $W(l+1|l)$ is the Rosenbluth factor for adding an extra segment to a chain of l segments. If we assume that there is no correlation between insertion of subsequent segments, then this means that the error in $\ln\langle W(l+1)\rangle$ is given by

$$\sigma^2(l+1) = \sigma^2(l) + \sigma^2_{k_{l+1}}(l+1|l) + \sigma^2(l)\sigma^2_{k_{l+1}}(l+1|l), \tag{15}$$

where $\sigma_{k_{l+1}}(l+1|l)$ is the error in $\ln\langle W(l+1|l)\rangle$. Equations 6, 7, and 15 can be combined with equation 13 to give for the efficiency

$$\frac{\text{Eff}^{\mu}(l)}{\text{Eff}^{\mu}(l+1)} = \left(1 + \sigma^2{}_{k_{l+1}}(l+1|l) + \frac{\sigma^2_{l+1}(l+1|l)}{\sigma^2(l)}\right)(1 + \text{Eff}(l) \times k_{l+1}). \tag{16}$$

The starting values $\text{Eff}(1)$ and $\text{Eff}^{\mu}(1)$ can be calculated from the insertion of one segment into the system. Repeated use of equation 16 yields the efficiencies at larger l,

for which at every l, $\sigma_{k_{l+1}}(l+1|l)$ is needed, given by

$$\sigma^2_{k_{l+1}}(l+1|l) = \frac{\langle W^2_{k_{l+1}}(l+1|l)\rangle - \langle W^2(l+1|l)\rangle^2}{\langle W^2(l+1|l)\rangle^2} \tag{17}$$

$\langle W^2_{k_{l+1}}(l+1|l)\rangle$ can be determined numerically and tabulated. Again we assumed that the values for $l=2$ can be used to estimate the values for larger l, and verified that this assumption made no significant difference for the optimization of the efficiency. $\langle W^2_{k_{l+1}}(l+1|l)\rangle$ decreases with increasing k_{l+1}, and in the limit of large k_{l+1} it is equal to $\langle W(l+1|l)\rangle^2$, which reduces the error $\sigma_{k_{l+1}}(l+1|l)$ to zero. The decrease in the error competes with the increase in the cost and the set of k_i-values can be determined, which optimize the efficiency of calculating the chemical potential with Rosenbluth sampling.

In Section 4 we show our results for the dependence of the efficiency of the chemical potential calculations on the values of $\{k_i\}$.

3.1 *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 always possible 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, $W_{\text{low}} \ll 1$, below which it has to be decided whether it is worthwhile 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

$$P_{\text{discard}} = \text{Min}[1, W_\Gamma / W_{\text{low}}]. \tag{18}$$

Chains with a Rosenbluth weight below W_{low} have now a probability W_Γ/W_{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 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}.

4 RESULTS

As an example we studied a system with only hard core interactions, but, as we explained 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 10 for a range of k_2-values. The efficiency for successfully adding another segment, Eff(2), is calculated from equation 9, 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} that is higher than k_2^{opt}. As already mentioned, k_l^{opt} is expected to increase with l, because more and more effort is invested previously in the insertion of $l-1$ segments, which will be wasted if all the trial directions result in a hard core overlap with spheres in the fluid. In Table 1 the optimal k-values are listed for insertion of chains up to 12 segments long into a fluid at various densities. For adding a fifth segment or more in a fluid at the highest density, $\rho\sigma^3 = 0.5$, the optimal k-values fell out of the range of values that we considered. However, here the efficiency is already close to its optimal value for the highest k-values in our range. In Figure 2 we show the corresponding

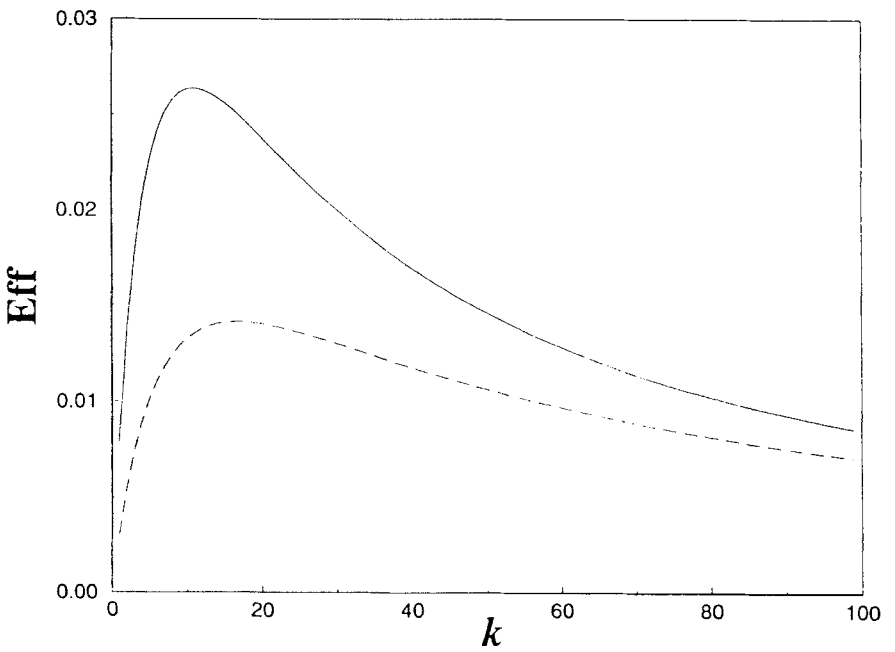

Figure 1 The efficiency, as defined by equation 6, for inserting a hard dimer (—) and a fully flexible trimer of hard spheres (- - -) into a fluid of hard spheres at density $\rho\sigma^3 = 0.3$, over a range of k-values.

Table 1 Optimal k_l-values, for both the CBMC and for calculating the chemical potential, μ, by Rosenbluth sampling for a chain of l hard spheres in a hard sphere fluid of density $\rho\sigma^3$.

l	*CBMC*			μ		
	$\rho\sigma^3 = 0.3$	*0.4*	*0.5*	$\rho\sigma^3 = 0.3$	*0.4*	*0.5*
2	5	10	29	4	9	25
3	9	18	55	5	12	31
4	12	27	86	6	15	37
5	15	35	> 100	8	17	43
6	18	43	> 100	9	20	48
7	20	51	> 100	10	23	57
8	22	59	> 100	11	26	64
9	25	66	> 100	13	29	69
10	27	73	> 100	14	32	79
11	29	80	> 100	15	35	84
12	30	87	> 100	17	38	90

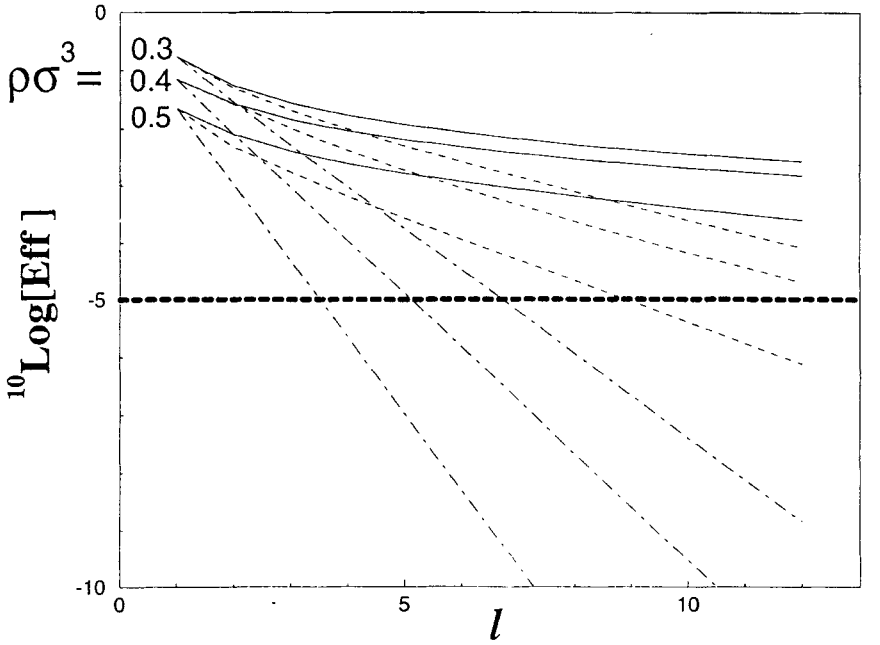

Figure 2 The efficiency (equation 12) of accepting insertion of a fully flexible chain of ℓ hard spheres into a fluid of hard spheres at several densities $\rho\sigma^3$. Both the efficiency of a random insertion (- · - · -), i.e. $k_\ell = 1$ for all ℓ, and the maximal efficiency (—), obtained by choosing the optimal k-values listed in Table 1, are shown. In the same Figure we show the efficiency for acceptance of a CBMC move (- - -) by the acceptance criterion 5. The dashed horizontal line shows the minimal efficiency needed for a simulation of typical length.

maximal values of Eff(l), and in the same Figure we compare these efficiencies with the efficiencies of a random insertion, i.e. the limit $k_l = 1$ for all l. It 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 5. This decrease is estimated by $\langle W_{new}/W_{old} \rangle$, 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 effficiency needed is of the order of 10^{-5}. Figure 2 shows, that random insertion does not fulfill 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 $l = 12$ 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 $l = 9$.

From this it can be seen that in cases where it is needed to grow large parts of a chain in one move, the CBMC technique allows for simulation of much longer chains than could be handled up to now. For instance, constant chemical potential simulations and the Gibbs ensemble technique for simulating two coexisting phases both involve inserting full molecules in a system and can now be applied to chain molecules [10,11]. However, for a normal Monte Carlo move needed to calculate ensemble averages by sampling different configurations of chain molecules, an alternative approach is possible and is commonly used in existing algorithms. Instead of trying to achieve changes as large as possible in one costly move, many cheap moves are performed that each yield small configurational changes. Most existing techniques follow the latter approach by wiggling or slithering a molecule. As mentioned before, one such a technique, the reptation algorithm, can be viewed as the limit of growing only one segment per move by the CBMC technique. The number of accepted moves that are needed to create a completely new configuration from an existing one can be estimated from random walk statistics to be inversely proportional to the square of the number of segments regrown in one move. However, the acceptance decreases as well. The result is that there will be an optimum for the number of segments to be regrown which will be large for high acceptance rates and reduce to one, i.e. reptation, for low acceptance rates. This means that it is expected that at higher densities the reptation algorithm is most efficient and that at low densities CBMC becomes more efficient.

Similarly, we used equation 16 to determine the efficiency of chemical potential calculations by Rosenbluth sampling. In general, $\mathrm{Eff}^{\mu}(1)$ can be calculated numerically from the error in the insertion probability of the first segment, $\sigma(1)$. Because there are only hard core interactions in our system we have binomial statistics, and $\mathrm{Eff}^{\mu}(1)$ is given directly by the insertion probability of the first segment,

$$\mathrm{Eff}^{\mu}(1) = \frac{P_{ins}(1)}{1 - P_{ins}(1)}, \tag{19}$$

where the insertion probability for one segment, $P_{ins}(1)$, for this particular hard sphere system is given by the Carnahan-Starling equation [19]. We calculated

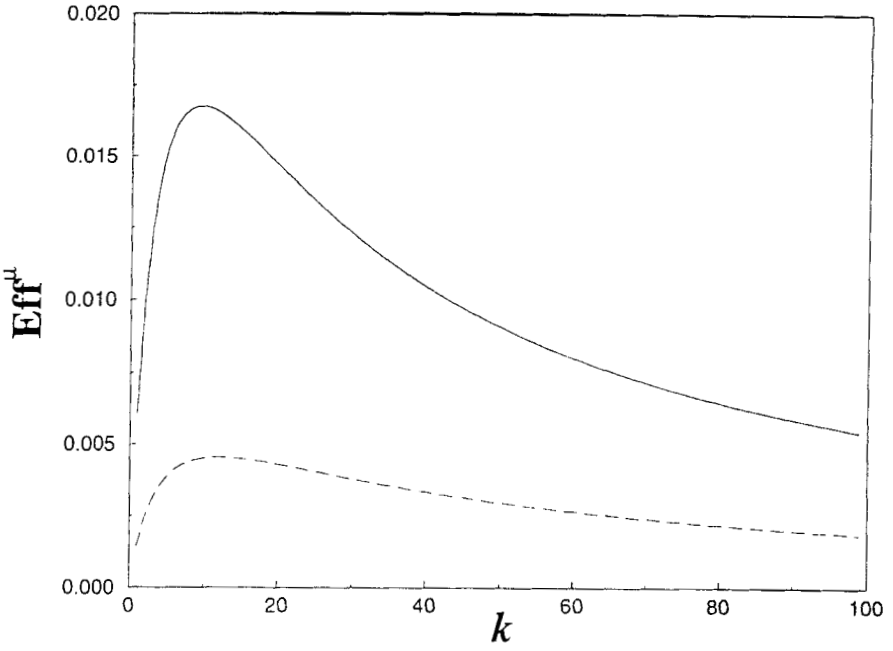

Figure 3 The efficiency, as defined by equation 13, for calculating the chemical potential of a hard dimer 9(—) and a fully flexible trimer of hard spheres (- - -) in a fluid of hard spheres at several densities $\rho\sigma^3$, over a range of k-values.

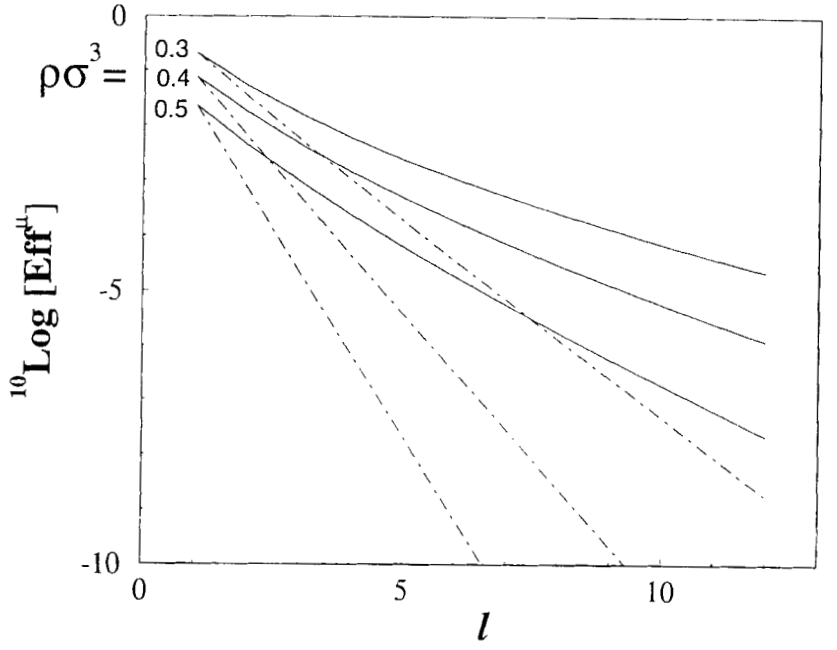

Figure 4 The efficiency (equation 13) for calculating the chemical potential of a fully flexible chain of ℓ hard spheres into a fluid of hard spheres at density $\rho\sigma^3 = 0.3$. Both the efficiency of a random insertion (-·-·-), i.e $k_\ell = 1$ for all ℓ, and the maximal efficiency (—), obtained by choosing the optimal k-values listed in Table 1, are shown.

$\langle W^2_{k_{l+1}}(l+1|l)\rangle$ and from Equation 16 we determined the optimal k_l-values and the maximum efficiency for calculating the chemical potential for chains of lengths ranging from $l = 1$ to $l = 12$. In Figure 3 we show $\mathrm{Eff}^u(2)$ and $\mathrm{Eff}^u(3)$ as a function of k, for a fluid of hard spheres at density $\rho\sigma^3 = 0.4$. For the same reason as before, the efficiency is optimized for k_3^{opt} larger than k_2^{opt}. Figure 4 shows the maximum feasible efficiencies $\mathrm{Eff}^u(l)$, which turn out to be smaller than for successfully inserting a chain. The reason for this is, that a successfully inserted chain may have a very small Rosenbluth weight, and contribute little to the average Rosenbluth weight. For the same reason, the optimar k_l-values, listed in Table 1, for the chemical potential calculations are smaller than for the CBMC. Increasing k_l may increase the probability to find free space for another segment, but for high k_l the Rosenbluth weight can be very low, which accordingly gives a low contribution of a conformation. In Figure 4 we compare again with random insertion, and we see a considerable increase in efficiency if the Rosenbluth sampling is used.

5 CONCLUSIONS

In this article we have shown how to optimize the efficiency of both the Configurational-Bias Monte Carlo scheme and chemical potential calculations with Rosenbluth sampling, with respect to the choice for k, the number of trial directions to insert a segment. Many effects influence the efficiency, and we find that all can be taken into account in a single numerical analysis. For the specific example of a fully flexible chain of hard spheres in a hard sphere fluid, the choice for k is optimized and the limits of both techniques are indicated.

Acknowledgements

The investigations reported in this paper were supported in part by 'Scheikundig Onderzoek Nederland' (SON) with financial aid from NWO ('Nederlandse Organisatie voor Wetenschappelijk Onderzoek'). The work of the FOM Institute is part of the research program FOM and is supported by NWO.

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