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## CHAPTER 11

### Some applications of the configurational-bias Monte Carlo technique

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## 1. – Introduction

In the lectures of Frenkel some novel Monte Carlo techniques have been discussed (see Chapter 5). In these notes these techniques are applied to some systems that are of interest in petro-chemical applications. In particular, we focus on phase equilibria of long-chain hydrocarbons and the adsorption and diffusion of hydrocarbons in zeolites. Interesting to note is that without these special Monte Carlo techniques these simulations would have required many (million) years of supercomputer time.

Zeolites are micro-porous materials which are used as catalysts in petro-chemical applications. A prerequisite for an understanding of the catalytic activity of these zeolites is a knowledge of the behavior of the molecules adsorbed in the narrow pores of these zeolites. Since this type of information is extremely difficult to obtain experimentally, simulations appear to be an attractive alternative [1]. Over the last decade many simulation studies on the behavior of molecules in zeolites have been published (for a review see ref. [2]). A more careful look at these studies reveals that most simulations concern the adsorption of noble gases or methane, only a few studies of ethane or propane have been published. In petro-chemical applications of zeolites, however, we are interested in the behavior of much longer alkanes such as octane and decane.

The reason why only small molecules have been studied becomes clear from the work of June *et al.*[3] and Hernández and Catlow [4], in which Molecular Dynamics simulations were used to investigate the diffusion of butane and hexane in the zeolite silicalite. June *et al.* showed that the diffusion of butane from one channel of the zeolite into another channel is very slow compared to diffusion of bulk butane. As a consequence many hours of super-computer time were required to obtain reliable results. In addition, since the diffusion coefficient decreases significantly with increasing chain length, extrapolation of these results suggests that many years of super-computer time would be required to obtain comparable results for the longer alkanes.

The above example illustrates one of the main limitations of Molecular Dynamics. If one tries to mimic the behavior of the molecules as realistically as possible, the diffusion coefficient will be of the same order of magnitude as observed experimentally. Hence the molecules diffuse slowly this will be reflected in very long simulation times and in the case of long chain alkanes in zeolites these simulation times are much longer than we can currently afford. In principle, one can circumvent this intrinsically slow dynamics by using a Monte Carlo technique. In a Monte Carlo simulation one does not have to follow the “natural path” and one can, for example, perform a move a molecule is displaced to a random position in the zeolite. If such a move is accepted, it corresponds to a very large jump in phase space.

Again, utilization of these type of un-natural Monte Carlo moves turned out to be limited to small molecules. For example, Goodbody *et al.*[5] have used grand-canonical Monte Carlo simulations to determine the adsorption isotherms of methane in a zeolite. In such a simulation one can observe that out of the 1000 attempts to move a methane molecule to a random position in the zeolite, 999 attempts will be rejected because the

methane molecule overlaps with a zeolite atom. If we were to perform a similar move with an ethane molecule, we would need of the order of  $1000 \times 1000$  attempts to have one that will be successful. Clearly, this random insertion scheme will break down for any but the smallest alkanes.

Similar difficulties are encountered in the Gibbs-ensemble technique. As explained in the notes of Frenkel (Chapter 5), the Gibbs-ensemble technique is a very elegant method to simulate vapour-liquid equilibria. The accuracy of this method, however, depends on a successful exchange of particles between the liquid and vapour phase. For atoms or small molecules at moderately high densities one can obtain a reasonable number of successful exchanges. For chain molecules (i.e. molecules longer than butane), the probability of a successful insertion in the liquid phase is very small and as a consequence the simulations become prohibitively long.

Both examples illustrate the need for more efficient schemes to simulate chain molecules. The configurational-bias Monte Carlo (CBMC) scheme has been developed to make these kind of simulations of chain molecules possible [6, 7, 8, 9, 10]. In this Chapter, the use of the CBMC technique is illustrated with some examples of practical relevance. Important to note is that the CBMC technique is not limited to the simulation of chain molecules, to illustrate this

## 2. – Phase equilibria of n-alkanes

The Gibbs-ensemble technique was introduced by Panagiotopoulos [11] as an efficient tool to simulate vapor-liquid phase equilibria. In the Gibbs-ensemble scheme simulations of the liquid and vapor phases are carried out in parallel. Monte Carlo rules which allow for changes in the number of particles and the volume, ensure that the two boxes are in thermodynamic equilibrium with each other. Since the two boxes are not in 'physical contact', there is no interface and the bulk properties of the two coexisting phases can be obtained directly with a surprisingly small number of particles. This makes the Gibbs ensemble extremely efficient for phase equilibrium calculations. The major limitation of the Gibbs-ensemble technique is that one of the steps involves the exchange of particles between the two boxes. For liquids consisting of small molecules this does not cause serious problems. However, for chain molecules the probability of successful exchanges can become very small. For example, under conditions where it takes approximately  $10^3$  attempts per successful exchange of methane, it takes of the order of  $10^{3n}$  attempts for an  $n$ -alkane. to be limited to systems containing atoms or small molecules. However, by combining the Gibbs-ensemble method with configurational-bias Monte Carlo, the method can be made to work for much longer chain molecules [12, 13].

Siepmann *et al.*[15, 16] have used the combination of the Gibbs-ensemble technique and configurational-bias Monte Carlo to simulate vapor-liquid equilibria of the n-alkanes at conditions where experiments are not (yet) feasible. Alkanes are thermally unstable above approximately 650K, which makes experimental determination of the critical point of alkanes longer than decane ( $C_{10}$ ) extremely difficult. The longer alkanes, however, are present in mixtures of practical importance for the petrochemical industry. In these mixtures, the number of components can be so large that it is not practical to determine all phase diagrams experimentally. One therefore has to rely on predictions made by equations of state. The parameters of these equations of state are directly related to the critical properties of the pure components. Therefore, the critical properties of the long-chain alkanes are used in the design of petrochemical processes, even if they are unstable close to the critical point [14]. Unfortunately, experimental data are scarce and

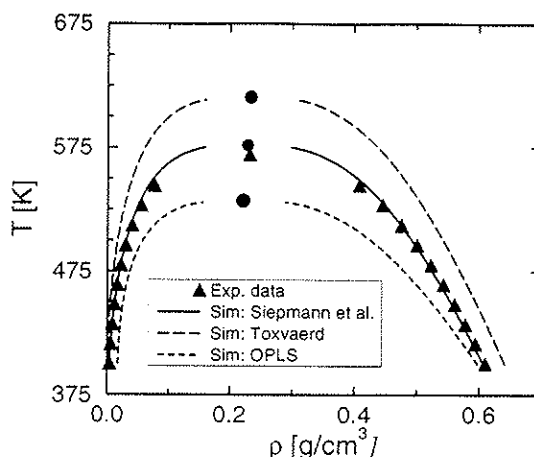


Fig. 1. – Vapor-liquid curve of octane: comparison of Gibbs-ensemble simulations using the OPLS model of Jorgensen and co-workers [17], the model of Toxvaerd [18], and the model of Siepmann *et al.*[15, 16].

contradictory, and one has to rely on semi-empirical methods to estimate the critical properties [14].

Most available models for alkanes have been obtained by fitting simulation data to experimental properties of the liquid at standard conditions. In Figure 1 the vapor-liquid curve of octane as predicted by some of these models is compared with experimental data. This figure shows that the models of refs. [17, 18] which give nearly identical liquid properties, yield estimates of the critical temperature of octane that differ by 100K. Siepmann *et al.*[15, 16] used these vapor-liquid equilibrium data to improve the existing models.

In Figure 2 the critical temperatures and densities as predicted by the model of Siepmann *et al.* are plotted versus carbon number. The simulations reproduce the experimental critical points very well. There is, however, considerable disagreement between the various experimental estimates of the critical densities. Much of our current knowledge of the critical properties of the higher alkanes is based on extrapolations of fits of the experimental data up to  $C_8$ . The most commonly used extrapolations assume that the critical density is a monotonically increasing function of the carbon-number, approaching a limiting value for the very long alkanes [14, 19]. In contrast to these expectations, the experimental data of Anselme *et al.*[20] indicate that the critical density has a maximum for  $C_8$  and then decreases monotonically. The data of Steele (as reported in ref. [19]), however, do not give any evidence for such a maximum (see Figure 2). The simulations indicate the same trend as that observed by Anselme *et al.* In this context, it is interesting to note that Mooij *et al.*[12] and Sheng *et al.*[21] used Monte Carlo simulations to study the vapor-liquid curve of a polymeric bead-spring model for various chain lengths. These studies also show a decrease of the critical density as a function of chain length.

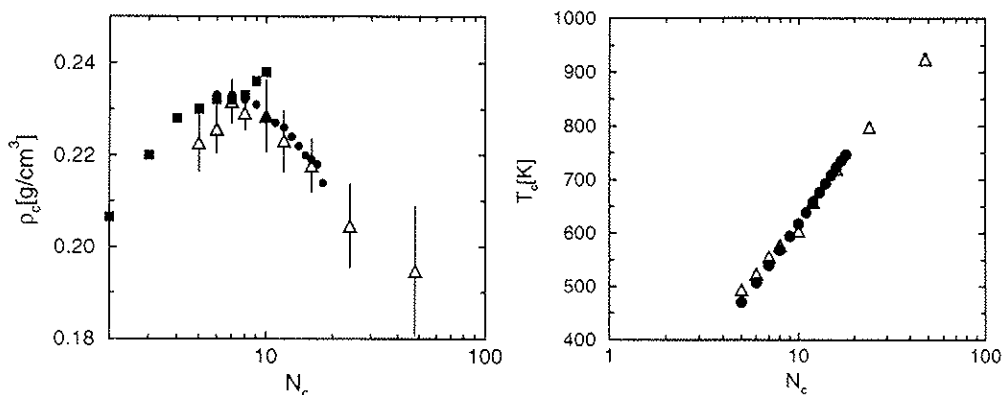


Fig. 2. – Critical temperature  $T_c$  (left figure) and density  $\rho_c$  (right figure) as a function of carbon number  $N_c$ . The open symbols are the simulation data and the closed symbols are experimental data.

### 3. – Adsorption and diffusion of alkanes in zeolites

In the introduction we have used the adsorption of molecules as an example to illustrate the type of problem one can encounter in simulating systems that exhibit slow diffusion. Smit and Siepmann have used the configurational-bias Monte Carlo technique to study the energetics and siting of alkanes in the zeolites silicalite and mordenite [22, 23]. In these simulations alkane molecules are modelled with a united atom model, i.e., a  $\text{CH}_3$  and a  $\text{CH}_2$  group are considered as a single interaction centre and the zeolite is modelled as a rigid crystal. The zeolite-alkane interactions are assumed to be dominated by dispersive interaction with the oxygen atoms, which are described with a Lennard-Jones potential. A closely related technique was used by Maginn *et al.* [24]. The simulations of Smit and Siepmann and Maginn *et al.* predict heats of adsorption of the longer chain alkanes in silicalite that are in good agreement with the experimental data and the simulations of Bigot and Peuch [25].

Simulations can also be used to determine adsorption isotherms. Adsorption isotherms are of practical importance since they give information on the number of molecules adsorbed in the pores of a zeolite as a function of the pressure of the reservoir. Adsorption isotherms are also of fundamental interest since they may signal phase transitions, such as capillary condensation or wetting, of the fluid inside the pores [26]. For example, if a system exhibits capillary condensation, one would measure a stepped adsorption isotherm with hysteresis. Steps or kinks without hysteresis are occasionally observed on flat substrates [27]. Since the pores of most zeolites are of molecular dimensions, adsorbed alkane molecules behave like a (pseudo) one-dimensional fluid. In a one-dimensional system phase transitions do not occur and therefore one would expect that for alkanes the adsorption isotherms are of type I, i.e., do not show kinks or steps. If steps occur they are usually attributed to capillary condensation in the exterior secondary pore system formed by the space between different crystals [28]. For silicalite, adsorption isotherms have been determined for various  $n$ -alkanes: for the short chain alkanes (methane—pentane) the isotherms are indeed of type I [29, 28], also for decane a type I isotherm is observed [30, 28]. For hexane and heptane, however, a kink or step is observed [29, 31].



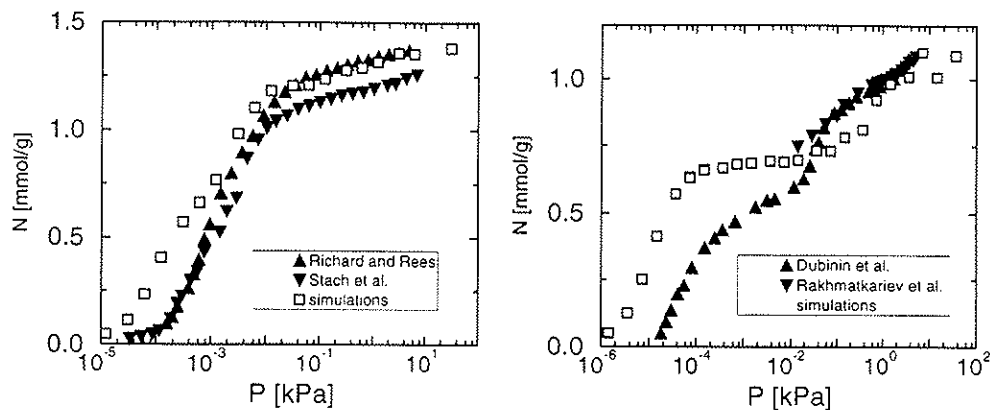


Fig. 3. – Adsorption isotherms of hexane (left), and heptane (right), the closed symbols are experimental data and the open symbols the results from simulations at  $T = 298$  [K].

Adsorption isotherms are conveniently determined from simulations in the grand-canonical ensemble. In this ensemble the temperature and chemical potential are imposed, but the number of particles is allowed to fluctuate. Adsorption isotherms of alkanes in silicalite have been simulated by Smit and Maesen [32]. The simulated adsorption isotherms for hexane and heptane are shown in Figure 3. The agreement of the simulation results with the experimental data is good at high pressures, but at low pressures deviations exist which indicate that the zeolite-alkane model may be further improved. It is interesting to note that for heptane both the experiments and the simulations show a step at approximately half the loading. Also for hexane detailed inspection of the calculated adsorption isotherm shows a kink at this loading. Since the simulations are performed on a perfect single crystal, these deviations from the type I isotherm must be due to a transition of the fluid inside the pores and can not be attributed to the secondary pore system. Smit and Maesen attribute this transition to a commensurate ‘freezing’ in the channels of a zeolite. The length of a hexane molecule is of the order of the length of the period of the zig-zag channel. At low chemical potential, the hexane molecules move “freely” in these channels and the molecules will be part of their time in the intersections. If part of the intersection is occupied, other molecules can not reside in the straight channels at the same time. At high pressures, almost all hexane molecules are exactly fitting into the zig-zag channel, they do no longer move freely and keep their nose and tail out of the intersection. In such a configuration the entire straight channel can now be tightly packed with hexane molecules. This may explain the plateau in the adsorption isotherm; in order to fill the entire zeolite structure neatly, the hexane molecules located in zig-zag channels have first to be “frozen” in these channels. This “freezing” of the positions of the hexane molecules implies a loss of entropy and will therefore only occur if the pressure (or chemical potential) is sufficiently high to compensate for this loss. Further experimental evidence for this commensurate freezing of hexane and heptane has been found by van Well *et al.* [33].

It is interesting to compare the siting of linear alkanes with the siting of branched alkanes in zeolites. Figure 4 compares the distribution of the CH group of the head of 2-methyl-butane with the distribution of the middle segment of pentane in the pores of

silicalite at  $T=498\text{K}$  [34]. This figure shows that the distribution of the linear alkanes is very different from the distribution of the branched alkanes. Whereas pentane has an equal probability to be in the straight channels, zig-zag channels, or intersections, the branched alkanes have a strong preference to be with the head group in the intersections. These results are in very good agreement with the Monte Carlo integration results of June et al. [35] Also for the other branched alkanes a similar preference of the head group for intersections.

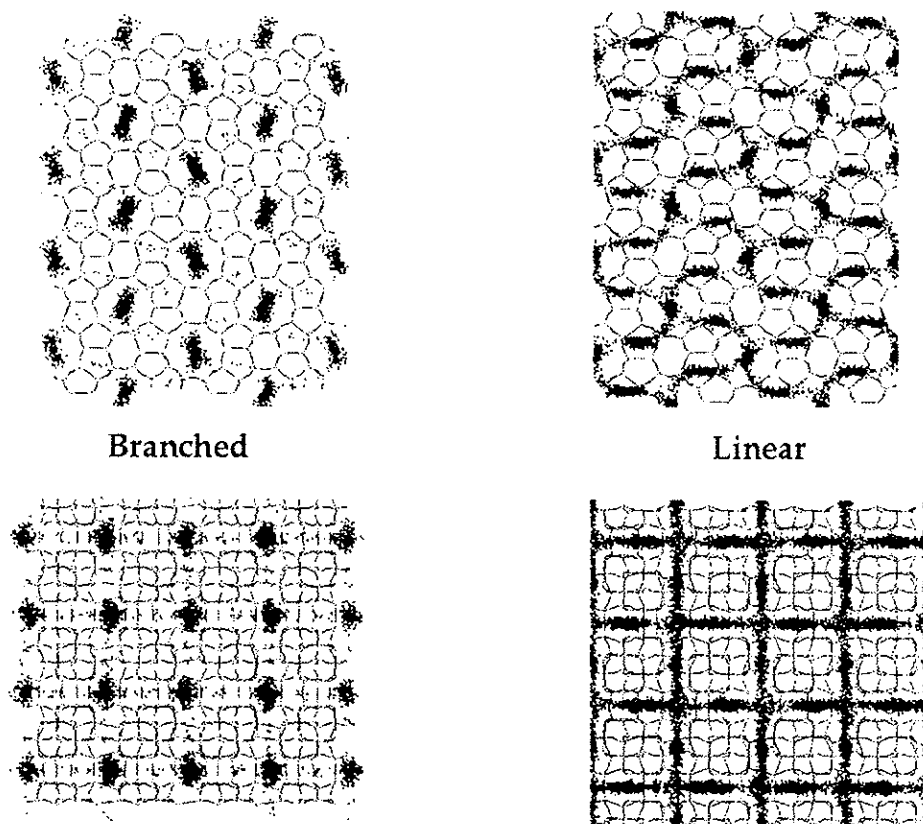


Fig. 4. - Distribution of the alkanes in the channels of silicalite [34]. The lines represent the zeolite lattice. At regular intervals a dot representing the position of the CH pseudo atom of the head group in the case of the branched alkane (2-methyl-butane) or the  $\text{CH}_2$  middle segment in the case of a linear alkane (pentane) is drawn. The density of the dots is a measure of the probability of finding a molecule in a particular section of the zeolite. The top figures give a projection along the straight channels (i.e., the  $z$ - $x$  plane), the bottom figures along the zig-zag channel (i.e., the  $x$ - $y$  plane).

It is interesting to discuss the consequences of these results for the diffusion of these molecules in the pores of the zeolite. Comparison of the siting of the linear alkanes with the siting of the branched alkanes shows that the (short chain) linear alkanes have a uniform distribution whereas the branched alkanes have a preference to be at the intersection. This suggests that these linear alkanes can move "freely" in the channels and therefore their diffusion coefficient can be obtained from a molecular dynamics simula-

tions within a reasonable amount of cpu time. The branched alkanes, however, are pinned with their head group at the intersections and have a very small probability to be in the channels connecting the intersections. These straight and zig-zag channels therefore form a barrier for the diffusion. If this barrier is much higher than  $k_B T$ , the diffusion of such an alkane is an activated process; most of the time the molecule resides at an intersection and occasionally a molecule hops from one intersection to another.

If the diffusion of these branched alkanes is an activated process, we can use the simulation techniques developed by Bennett and Chandler [36, 37] to simulate rare events [38]. The basic idea behind these calculations is that the rate at which a barrier crossing proceeds is determined by the product of a static term, namely the probability of finding the system at the top of the barrier and a dynamic term that describes the rate at which systems at the top of the barrier move to the other valley.

To compute the diffusion coefficients of a branched alkane in a zeolite we have to determine a reaction coordinate for which we can compute the free energy. For diffusion a natural reaction coordinate is the position of one of the atoms of the adsorbed molecules. In case of branched alkanes it is convenient to take, for example, the position of the CH group (i.e., the group for which the distribution is shown in Figure 4). Let us assume the concentration of hydrocarbons is sufficiently low such that the probability that two hydrocarbons are in neighbouring intersections is very small. In this limit, the jumps from one intersection to another are independent. In silicalite we can jump from one intersection to another via the straight channel or zig-zag channel. Of each of these paths the jump rates can be calculated. Because of the symmetry of the crystal the two different paths via the straight channels (jumping up or down) and the paths via the zig-zag channels are equivalent. The calculation can therefore be limited to computing the jump rates via these two paths.

In practice, the computation of a rate constant consists of two steps. The expression of the rate constant is given by [38]

$$(1) \quad k_{A \rightarrow B}(t) = \frac{\langle \dot{q}(0) \delta(q^* - q(0)) \theta(q(t) - q^*) \rangle}{\langle \delta(q^* - q(0)) \rangle} \times \frac{\langle \delta(q^* - q) \rangle}{\langle \theta(q^* - q) \rangle}.$$

Where we assume that  $A$  is one intersection and  $B$  a neighbouring intersection,  $q(t)$  is the reaction coordinate,  $\theta(x)$  is the Heavyside step-function,  $\theta(x) = 1$  for  $x > 0$  and  $\theta(x) = 0$  otherwise, and  $q^*$  is the top of the free energy barrier separating the states  $A$  and  $B$ . Let us focus on the second term on the right-hand side of equation (1), i.e.,  $\langle \delta(q^* - q) \rangle / \langle \theta(q^* - q) \rangle$ , the probability density to find the system at the top of the barrier, divided by the probability that the system is on the reactant side of the barrier. This ratio, can be calculated from the free energy as a function of the order parameter. We can use the CBMC algorithm to compute this free energy as a function of the order parameter.

A typical result is presented in Figure 5, in which the free energy of 2-methylhexane as a function of order parameter in the straight and zig-zag channels is shown. This figure indicates that in the straight channel there are three barriers. The height of the first barrier ( $q = 0.29$ ) is approximately  $14 k_B T$ , which demonstrates that a jump over this barrier is indeed a rare event. In addition this figure shows two additional barriers one at  $q = 0.5$  and one at  $q = 0.68$ . Because of the symmetry of the crystal the barrier at  $q = 0.68$  and  $q = 0.29$  have an equal height. Within the accuracy of the calculation, the barrier at  $q = 0.5$  has the same height as the other two. For the zig-zag channel we observe 4 barriers, the highest barrier has a height of  $18 k_B T$ . If we assume that

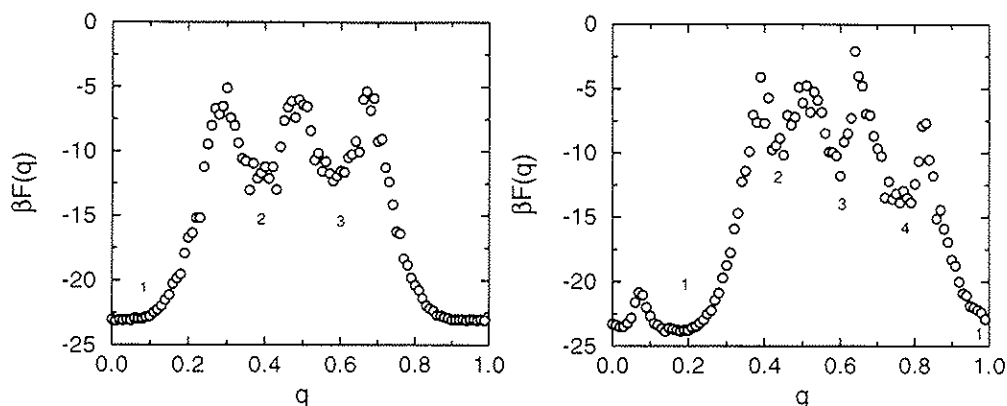


Fig. 5. – Free energy of a branched alkane as a function of the position of the head group in the straight channel (left) and zigzag channel (right). For  $q = 0$  and  $q = 1$  the head group is in the intersections. The results are for 2-methylhexane in silicalite at  $T = 398$  K.

transition state theory can be applied to this system, Figure 5 is sufficient to compute the crossing rate. For the straight channel we find that the highest barrier is crossed  $1 \cdot 10^5$  times per second. This implies that a molecule resides in the intersection approximately 7 micro seconds, which is very long on the time scale of a Molecular Dynamics simulation. This shows that the diffusion of branched alkanes is indeed an activated process.

#### 4. – Beyond chain molecules

Thus far, the configurational-bias scheme has been presented exclusively as a method to generate conformations of chain molecules. In fact, the method is more general than that. For example, it can be used as a scheme to perform collective rearrangements of any set of labeled coordinates. In fact, the scheme can be used to carry out Monte Carlo moves to swap  $n$  small particles within a volume  $\Delta V$  with one large particle that occupies the same (excluded) volume. This application of the CBMC scheme has been exploited by Biben [39] to study mixtures of large and small hard spheres. Gibbs-ensemble simulations of mixtures of spherical colloids and rod-like polymers were performed by Bolhuis [40] using CBMC-style particle swaps and a closely related approach was employed by Dijkstra to study phase separation in [41, 42] mixtures of large and small hard-core particles on a lattice. Another application is to perform Monte Carlo simulations on a parallel computer.

**4.1. Mixtures of colloids and polymers.** – Bolhuis and Frenkel are interested in simulating the properties of colloidal solutions. Examples of such solutions are milk, paint, or mayonnaise. Since a single colloidal particle may contain over  $10^9$  atoms, it is not possible to model such a particle as a collection of atoms. However, it is possible to describe colloidal solutions using coarse grained models. For example, a suspension of silica spheres can be described surprisingly accurately with a hard-sphere potential. Similarly to the hard-sphere fluid, such a colloidal suspension has a fluid-solid transition, but not a liquid-gas transition. Experimentally, it is observed that a liquid-gas transition can be induced by adding polymers to the suspension.

The effect of adding polymers is like having attractive interactions between the colloidal particles. These effective interactions occur even in systems that have only excluded volume interactions and are therefore called entropic interactions. To see this, consider a system of two colloidal particles to which we add a polymer. We assume that this polymer behaves like an ideal polymer except that it cannot overlap with the colloidal particle, that is, the polymer and colloid have excluded volume interactions. If the distance between the colloids is large, the total entropic contribution of the polymer is related to the total number of configurations of the polymer minus those configurations that overlap with the first colloidal particle and those which overlap with the second. When the distance of the two colloidal particles is smaller than the length of the polymer, the total entropy *increases*. If for such a system, we were to compute the entropy by subtracting those configurations of the polymer that overlap with the two colloids, we would count those configurations twice which overlap with both colloids at the same time. This increase of the entropy as two colloidal particles approach each other gives rise to an effective attractive force between the particles. Similar effects can be expected in mixtures of infinitely thin hard rods and hard spheres. If these rods are sufficiently long, they may induce a vapor-liquid like transition for the hard-spheres.

Bolhuis and Frenkel have studied the phase behavior of a mixture of hard spheres and hard rods. In particular, Bolhuis and Frenkel used Gibbs-ensemble simulations to determine the "vapor-liquid" coexistence curve. In a Gibbs-ensemble simulation one simulates two boxes that are kept in equilibrium with each other via Monte Carlo rules. In this case the "gas" box has as a low density of hard spheres and the "liquid" box has a high density of spheres. Similarly, to the phase equilibrium calculation of linear alkanes, the exchange step, in which particles are exchanged between the two boxes is the bottle neck of the simulation. For example, the insertion of a sphere into the "gas-phase" would almost always fail because of overlaps with some of the rods. Bolhuis and Frenkel have used the following scheme to make this exchange possible;

1. Select a sphere in one of the boxes at random and insert this sphere at a random position in the other box.
2. Remove all the rods that overlap with this sphere. These rods are inserted in the other box. If these rods would be inserted at random, almost always one of the rods would overlap with a sphere and such a move would be rejected. However, if one tries several orientations and positions of the rods and select an acceptable configuration using the configurational-bias Monte Carlo scheme one can make such a move possible. During the insertion of the rods one has to be careful that detailed balance is obeyed (for details see [40]).

Because of this redistribution scheme of the rods during the insertion step using the CBMC one can generate configurations that do not have overlap. This allowed Bolhuis and Frenkel to exchange spheres between the two boxes and obtain the coexistence densities. The result of these Gibbs-ensemble simulations is shown in Figure 6. The figure shows that if one increase the fugacity (chemical potential) of the rods and hence the concentration of rods, a demixing occurs in a phase with a low density of spheres and a phase with a high density of spheres. If the rods are longer, this demixing occurs at a lower concentration. Important to note is that in this system the particles interact with hard-core interactions only. Therefore this demixing is driven by entropy.

An interesting extension of this technique used by Bolhuis and Frenkel would be to biological systems. For example, if one would like to make a large displacement

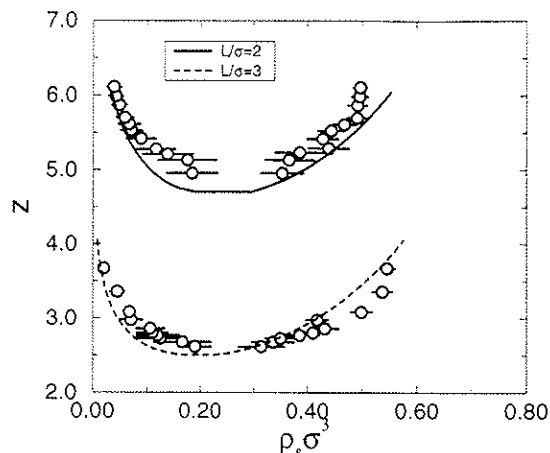


Fig. 6. – Coexistence curves for a mixtures of hard spheres and rods as obtained by Bolhuis and Frenkel. The x-axis gives the density and the y-axis the fugacity (chemical potential) of the rods.  $L/\sigma$  is the ratio of the length of the rod and the diameter of the hard-sphere.

of a part of a protein, in vacuum this would be relatively easy to do. In an aqueous solution, however, one has to remove the water molecules that overlap with that part of the protein that has been moved and the water molecules need to be redistributed. This redistribution can be done with the scheme of Bolhuis and Frenkel.

**4.2. Parallel Monte Carlo simulations.** – A different application of the CBMC ideas is used by Esselink *et al.*[43] to develop an algorithm to perform Monte Carlo moves in parallel. Parallel Monte Carlo appears to be a contradiction in terms, since the Monte Carlo procedure is an intrinsically sequential process. One has to know whether the current move is accepted or rejected before one can continue with the next move. The conventional way of introducing parallelism is to distribute the energy calculation over various processors, or to farm out the calculation by performing separate simulations over various processors. Although the last algorithm is extremely efficient and requires minimum skills to use a parallel computer, it is not a truly parallel algorithm. For example, farming out a calculation is not very efficient if the equilibration of the system takes a significant amount of cpu time. In the algorithm of Esselink *et al.* several trial positions are generated in parallel and out of these trial positions the one with the highest probability of being accepted is selected with the highest probability. This selection step introduces a bias which is removed by adjusting the acceptance rules. The generation of each trial move, which includes the calculation of the energy (or Rosenbluth factor in the case of chain molecules), is distributed over the various processors. Loyens *et al.* have used this approach to perform phase equilibrium calculation in parallel using the Gibbs-ensemble technique [44].

## 5. – Concluding remarks

In this Chapter, we have discussed various applications of the configurational-bias Monte Carlo technique. For example, it is illustrated how this technique can be com-

bined with the Gibbs-ensemble method to simulate vapour-liquid equilibria of long-chain alkanes. This combination results in an algorithm that is many orders of magnitude more efficient compared to the conventional algorithms. Similar gains in efficiency have been obtained in the simulations of hydrocarbons adsorbed in the pores of a zeolite.

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