

MOLECULAR SIMULATIONS OF ADSORPTION: FROM ARGON TO LONG CHAIN PARAFFINS

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I INTRODUCTION

It is not surprising that until recently most applications of molecular simulations, utilizing molecular dynamics or the Monte Carlo technique, are to systems containing atoms or small molecules. The reason for this is that for these "ideal" systems the available simulation techniques are very efficient. For example, to obtain reliable thermodynamic and transport properties for a model of methane a simulation of several pico seconds is usually sufficient. However, if one is interested in chain molecules, it may take more than several nano seconds solely to equilibrate the system.

To illustrate the limitations of the conventional techniques, let us consider an example of practical importance: the adsorption of alkanes in the pores of a zeolite. Zeolites are 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 behaviour of the molecules adsorbed in the pores of these zeolites. Since this type of information is extremely difficult to obtain experimentally, simulations appear to be an attractive alternative [1]. Indeed, over the last decade many simulation studies on the behaviour 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, while only a few studies of ethane or propane have been published. The reason why only small molecules have been studied becomes clear from the work of June et al. [3], 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

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significantly with increasing chain length, extrapolation of the results of June et al. suggest that many years of super-computer time would be required to obtain comparable results for the longer alkanes.

In this short review, the example of the adsorption of alkanes in zeolite is used to illustrate the power of some recently developed Monte Carlo techniques to simulate chain molecules efficiently.

II MOLECULAR SIMULATION TECHNIQUES

The example of molecular dynamics simulations of hexane in silicalite illustrates an unavoidable problem of this simulation method. If we succeed in mimicking the behaviour of the molecules accurately, the diffusion would be as slow as is observed in the real systems. This slow diffusion would be reflected in very long simulation times. In the case of long chain alkanes these simulation times turned out to be 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 in which it is attempted to displace a molecule 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. [4] have used such Monte Carlo moves to determine the adsorption isotherm of methane in silicalite. In such a simulation one can observe that on average one needs of the order of 1000 attempts to find one acceptable position, i.e. a position that does not cause an overlap with one of the zeolite atoms. If we were to perform a similar move with an ethane molecule, we would need of the order of 10^6 attempts, and for propane 10^9 . Therefore, also the conventional Monte Carlo scheme is not applicable for long chain molecules.

To make Monte Carlo moves of long chain molecules possible, Siepmann and Frenkel [5] have developed the configurational-bias Monte Carlo technique for lattice models. This technique is based on the early work of Rosenbluth and Rosenbluth [6] and Harris and Rice [7]. This technique has since been extended to continuum models by Frenkel et al. [8] and de Pablo et al. [9].

The starting point for configurational-bias Monte Carlo is the scheme as introduced by Rosenbluth and Rosenbluth in 1954 [6]. At first sight, this may not appear to lead to a new algorithm but to a very old one. The original Rosenbluth scheme itself was designed as a method to sample polymer conformations. The original Rosenbluth scheme, however, suffers from the drawback that it generates an unrepresentative sample of all polymer conformations, i.e. the probability to generate a particular conformation using the Rosenbluth scheme, is **not** proportional to its Boltzmann weight. Rosenbluth and Rosenbluth introduced the weight W to correct for this biasing in the computation of thermal averages. Batoulis and Kremer [10] have shown that this correction procedure only works for relatively short chains. The solution of this problem is to bias the Rosenbluth sampling in such a way that the correct (Boltzmann) distribution of chain conformations is generated in a Monte Carlo sequence. In the configurational-bias scheme to be discussed below, the Rosenbluth weight is used to bias the **acceptance** of trial conformations that are generated with the Rosenbluth procedure. As a consequence, all conformations are generated **with their correct Boltzmann weight**. This removes the main drawback of the original Rosenbluth scheme.

An important aspect of the configurational-bias Monte Carlo scheme is the way a trial conformation of a chain molecule is generated. In a lattice model, the number of trial conformation is dictated by the lattice and the intra-molecular interactions play a minor role. In continuum systems, there are many different models. One can have chains with completely flexible joints or models of polymeric liquid crystals which are extremely stiff. The efficiency of a configurational-bias Monte Carlo algorithm depends to a large extent on the method that is used to generate the trial orientations. For example, a random vector on a sphere would be a perfect trial position for the next segment of a completely flexible chain; for an alkane molecule such a trial position will almost always be rejected because of the intra-molecular interactions. The potential energy of a given conformation has two contributions:

1. The internal potential energy u^{int} , which is equal to the sum of the contributions of the individual joints. For an alkane model, u_i^{int} would account for all local internal potential energy changes due to bending and torsion that act on atom i .

2. The "external" potential energy u^{ext} . This energy accounts for all interactions with other molecules and for the non-bonded intra-molecular interactions. In addition, interactions with any external field that may be present are also included in u^{ext} .

To perform a configurational-bias Monte Carlo move, we apply the following "recipe" to construct a conformation of a chain of ℓ segments. The construction of chain conformations proceeds segment by segment. Let us consider the addition of one such segment. To be specific, let us assume that we have already grown $i-1$ segments, and that we are trying to add segment i . This is done in two steps. First we generate a trial conformation n , next we consider the old conformation o . A trial conformation is generated as follows (see Fig. 1):

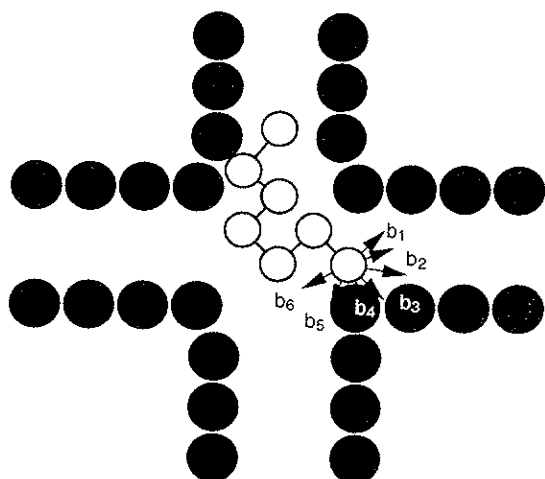


Figure 1

Schematic drawing of the growing of an alkane in a zeolite in a configurational-bias Monte Carlo move. The solid black circles represents the atoms of the zeolite and the white circles the ones of the alkane. The set of k trial orientations $\{\mathbf{b}_1, \mathbf{b}_2, \dots, \mathbf{b}_k\}$ are indicated by arrows.

1. Generate a fixed number (say k) trial segments. The orientations of the trial segments are distributed according to the Boltzmann weight associated with the internal energy of atom i (u_i^{int}). We denote this set of k different trial segments by

$$\{\mathbf{b}\}_k = \{\mathbf{b}_1, \dots, \mathbf{b}_k\}$$

where for each element the probability of being generated is

$$p_i^{\text{int}}(\mathbf{b}) d\mathbf{b} = \frac{\exp[-\beta u_i^{\text{int}}(\mathbf{b})] d\mathbf{b}}{\int d\mathbf{b} \exp[-\beta u_i^{\text{int}}(\mathbf{b})]} = C \exp[-\beta u_i^{\text{int}}(\mathbf{b})] d\mathbf{b}. \quad (1)$$

2. For all k trial segments, we compute the "external" Boltzmann factor $\exp[-\beta u_i^{\text{ext}}(\mathbf{b}_i)]$ and out of these, we select one n , where each has a probability

$$p_i^{\text{ext}}(\mathbf{b}_n) = \frac{\exp[-\beta u_i^{\text{ext}}(\mathbf{b}_n)]}{w_i^{\text{ext}}(n)}, \quad (2)$$

where we have defined

$$w_i^{\text{ext}}(n) = \sum_{j=1}^k \exp[-\beta u_i^{\text{ext}}(\mathbf{b}_j)]. \quad (3)$$

This step ensures that conformations with a low energy have a high probability of being selected.

3. Add this segment as segment i to the chain.

4. When the entire chain is grown, we calculate the Rosenbluth factor of the chain

$$W^{\text{ext}}(n) = \prod_{i=1}^{\ell} w_i^{\text{ext}}(n) \quad (4)$$

where the Rosenbluth factor of the first bead is defined by

$$w_1^{\text{ext}}(n) = k \exp[-\beta u_1^{\text{ext}}(\mathbf{b}_n)] \quad (5)$$

\mathbf{b}_n is the position of the first bead.

For the old configuration, a similar procedure to calculate its Rosenbluth factor is used.

1. One of the chains is selected at random. This chain is denoted o and the position of one of its beads is denoted by \mathbf{b}_o .

2. The external energy of the first bead is calculated. This energy involves only the external interactions and hence the contributions from the other segments of the chain are excluded. The Rosenbluth weight of the first segment is given by

$$w_1^{\text{ext}}(o) = k \exp[-\beta u_1^{\text{ext}}(o)]. \quad (6)$$

3. The Rosenbluth factors of the other $\ell - 1$ beads are calculated as follows. We consider the calculation of the Rosenbluth factor of atom i . We generate a set of $k - 1$ orientations with a distribution prescribed by the internal interactions (1). These orientations together with the actual position form the set of k orientations

($\mathbf{b}_o, \mathbf{b}'^*$). These orientations are used to calculate the external Rosenbluth factor

$$w_i^{\text{ext}}(o) = \sum_{j=1}^k \exp[-\beta u_i^{\text{ext}}(\mathbf{b}_j)]. \quad (7)$$

4. For the entire chain the Rosenbluth factor of the old conformation is defined by

$$W^{\text{ext}}(o) = k \prod_{i=1}^{\ell} w_i^{\text{ext}}(o) \quad (8)$$

After the new configuration has been generated and the Rosenbluth factor of the old configuration has been calculated the move is accepted with a probability

$$\text{acc}(o \rightarrow n) = \min[1, W^{\text{ext}}(n)/W^{\text{ext}}(o)]. \quad (9)$$

Important to note is that the growing procedure used in the algorithm above introduces a bias, such that only the most favourable configurations are being generated. If one were to use the ordinary Metropolis acceptance rule, such a bias in the configurations of the molecules would lead to an incorrect distribution of configurations. Frenkel et al. [8] have shown that by using acceptance (9) this bias can be removed exactly. Various details on the implementation of this technique in various ensembles can be found in Refs. [8, 9, 11-15].

At this point it is important to emphasize this is a Monte Carlo technique and therefore cannot be used directly to determine transport properties. One may consider using the configurational-bias Monte Carlo technique to enhance the equilibration, but to determine the transport properties one has to do a molecular dynamics simulation. For cases in which the interest is primarily in the thermodynamic properties, the configurational-bias Monte Carlo technique can be extremely useful since it can be many orders of magnitude more efficient than the conventional techniques.

III ADSORPTION 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 [13, 16]. In these simulations

alkane molecules are modelled with a united atom model, i.e. a CH_3 and a 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. [17]. Fig. 2 shows that 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 [18].

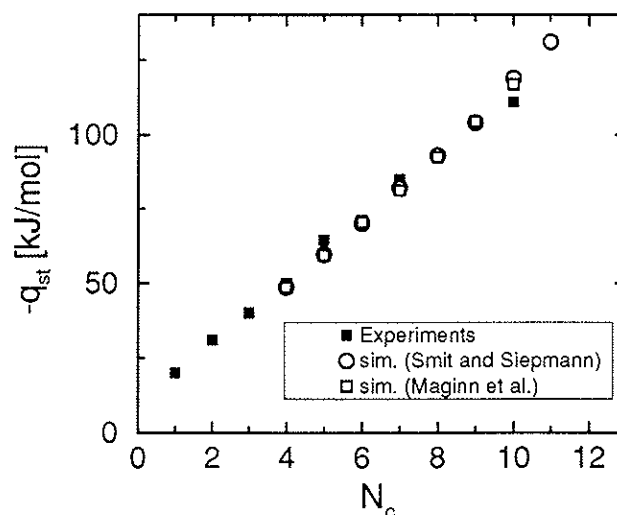


Figure 2

The heats of adsorption of the alkanes in silicalite as a function of the total number of carbon atoms. The experimental data are compiled from Refs [24, 27-30, 21] and the simulation data are from Maginn et al. [17] and Smit and Siepmann [16, 13].

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 [19]. 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 [20]. Since the pores of most zeolites are of molecular dimensions, adsorbed alkane molecules behave like a (pseudo) one-di-

mensional 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 [21]. 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 [22, 21], also for decane a type I isotherm is observed [23, 21]. For hexane and heptane, however, a kink or step is observed [22, 24].

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 [25]. In Fig. 3

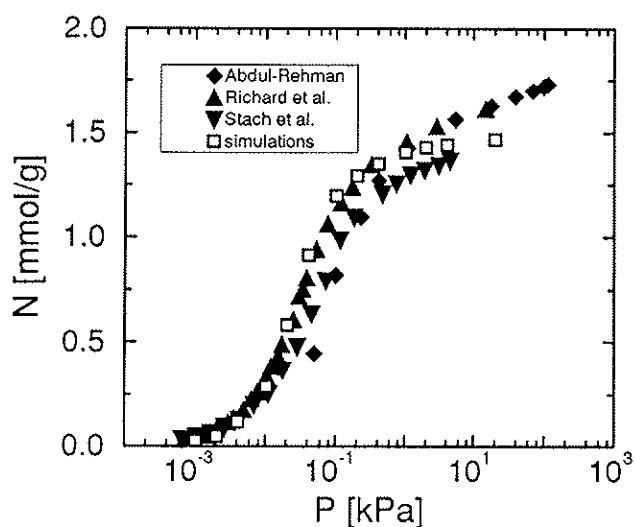


Figure 3

Adsorption isotherms of butane the closed symbols are experimental data [21, 29, 22] and the open symbols the results from simulations at $T = 298$ K.

the experimental adsorption isotherms of butane in silicalite are compared with the results from simulations. The scatter in the experimental data illustrates that measurements of adsorption isotherms on well-defined silicalite samples turned out to be difficult. The simulation data are in good agreement with the experimental data.

For hexane and heptane (see Fig. 4) 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. [26].

IV CONCLUDING REMARKS

Industrial applications of molecular simulations to determine thermodynamic properties usually involve systems containing complex fluids. For these type of systems, in particular for systems containing long chain alkanes, the conventional simulation techniques are not sufficiently efficient. It is shown that the recently developed configurational-bias Monte Carlo technique is particularly suited to simulate the thermodynamic properties of these complex fluids. The use of this novel technique is illustrated with simulations on the adsorption of long chain alkanes in zeolites.

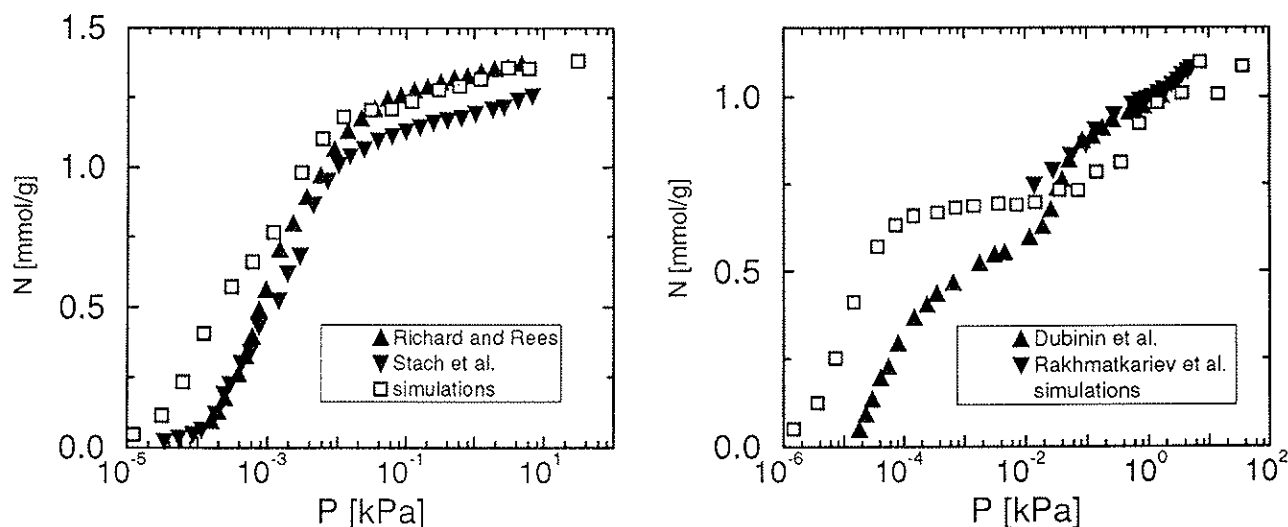


Figure 4

Adsorption isotherms of hexane (left), and heptane (right). The closed symbols are experimental data [22, 24, 31] and the open symbols the results from simulations at $T = 298$ K.

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