Entropy Driven Separations in Nanoporous Materials

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Introduction

The current global chemical industry constitutes a 2.6 trillion euros a year businiess with products ranging from cosmetics, health care products, food additives, pesticides, to plastics, pharmaceuticals and fuel products, and is expected to grow to 5.6 trillion euros by 2035 [1]. Most compounds used in the chemical industry are naturally found in an impure state and hence before they can be put in productive use they need to be separated. Separations are not only important in the chemical industry. They are also indispensable in many other industries: the pharmaceutical industry separates and purifies natural and synthetic drugs to meet health needs; the petroleum industry separates crude oil into products used as fuels, lubricants, and chemical raw materials; the mining industry separation is used to purify and recover certain products form natural resources, like the isolation and purification of sugar from sugar beats or canes and the coffee decaffenation.

Separation processes account for 40-90% of capital and operating costs in industry [2]. Distillation, which accounts for more than 90% of all the separation processes in chemical industry [3], is an expensive and energy-inefficient method. Finding alternative separation methods that reduce the energetic and economic costs is very important. Adsorptive separation is an energetically efficient alternative and it is already used in many processes in industry today. Zeolites are for example used to filter sulfur dioxide from other waste gases, to remove water and nitrogen impurities from natural gas and organic chemicals from air streams [4], and to remove ammonia from water [5]. In addition, because some zeolites are highly hydrophilic, they are extensively used as drying agents or desiccants [6].

Zeolites have also revolutionized the oil refining and petrochemical processes. Molecular sieving in zeolites is used to separate organic molecules during oil refinement [4]; zeolite-5A is commercially used for extracting long straight-chain alkanes from hydrocarbon mixtures [7] (used as raw materials in the manufacture of biodegradable detergents) and Ba-X zeolite is commercially used for the



Figure 1: (a) AFI-zeolite: each silicon (brown) is connected to four oxygens (red). This primary units self-assemble in different types of polyhedral building units (second-ary units) that ultimately form a 3-dimensional structure. (b) MIL-47 metal-organic framework: the metals clusters (V^{IIII}) are linked via 1,4-benzenedicarboxylates (BDC) linkers forming 1-dimensional pores of about 10 Å.

separation of xylene isomers [8–11].

Xylene isomers, ortho-, meta- and para-xylene, are mainly produced from petroleum and coal, and are important chemical intermediates: ortho-xylene is used in the production of phthalic anhydride; meta-xylene is used in the production of isophthalic acid and para-xylene, the most valuable of all, is the main precursor for the industrial production of PET (polyethylene terephtalate), which is the raw material for most polyesters used in production of fibers, packing materials and containers. The world wide production of para-xylene in 2001 was near 21.4 million metric tons (approximately 679 kg/s) [12]. Due to their similar boiling points, separating them by fractional distillation or other well established and commercialized technologies is not practical [13]. Their high energy intensity is inherent, regardless of several efforts to optimize, because they require multiple distillations, excessive heating/cooling cycles, and a lot of rotating equipment.

Adsorption processes in general offer a less energy intensive solution and are more economically and environmentally attractive. However, the performance of a suitable adsorption process that can offer these advantages will rely primarily on finding the right adsorption material. Nanoporous materials such as zeolites and metal-organic frameworks (MOFs) offer considerable potential.

0.1 Nanoporous materials

There is large variety of nanoporous materials with a wide range of properties. They are normally characterized by high surface areas, and their different shapes, sizes and pore distributions gives them unique properties to adsorb molecules.

Zeolites and aluminosilicates are materials based on TO_4 tetrahedra primary units (where the central T atom is either aluminum or silicon), which assemble through the oxygens in secondary polyhedral building units such as hexagonal prisms, cubes and octahedra and ultimately arrange in regular 3-dimensional struc-



Figure 2: Metal-organic frameworks have great versatility, there are more than 20,000 MOFs so far. In this figure (adapted from [14]) we show some of the most studied ones. Color code: copper (blue), zinc (cyan), magnesium (green), iron (orange), nitrogen (dark blue), carbon (grey), oxygen (red).

tures, which contain pores or linked cavities of around 3-10 Å in diameter (Figure 1a). Up to date, about 225 different zeolite topologies are know [15]. All-silica zeolites are charge neutral. However, by substituing a silicon ion (Si^{+4}) by an aluminum ion (Al^{3+}) , one negative charge is introduced in the framework. This negative charge has to be balanced by an extra-framework cation. Extra-framework cations play a very important role in the adsorption properties in zeolites. The Si/Al ratio is never smaller than 1.0 (according to Lowenstein's rule [16] no Al-O-Al bridges are allowed), but there is no upper limit. The transition from hydrophilic to hydrophobic zeolites normally occurs around a Si/Al ratio between 8-10. Zeolites have much more open structures than other silicates; between 20 and 50% of the volume of a zeolite structure is void.

MOFs are novel materials made of metal ions or clusters and organic molecules (linkers) that self-assemble into crystalline materials (Figure 1b). The extend to which the metal clusters and linkers geometry, size, and functionality can be varied has led to more than 20,000 different MOFs being reported and studied over the past decade [17–19]. In Figure 2 some of the most well known structures are shown. MOFs have exceptional porosity, typically greater then 50% of the MOF crystal volume, and surface areas ranging from 1000 to 10,000 m²/g, thus exceeding those of traditional porous materials such as zeolites and carbons. These aspects have made MOFs promising candidates for storage of fuels (hydrogen and methane), capture of carbon dioxide, and catalysis applications, to mention a few [20].

0.2 Adsorption

Separation using nanoporous materials relies on adsorption and/or diffusion properties of the mixture components and can be achieved by size/shape exclusion (steric separation), by differences in the adsorbate-adsorbent interactions and/or adsorbate packing interactions (thermodynamic equilibrium effect) or by differences in the diffusion rate of the adsorbates within the adsorbent channels. In this thesis, the focus lies on separations based on adsorption (thermodynamic equilibrium). The amount of adsorbed molecules θ (here after referred to as loading), depends on the pressure P and the temperature T. The variation of the loading with pressure at a chosen temperature is called an adsorption isotherm. Adsorption isotherms are the primary resource of information for an adsorption process and thus for the design of separation processes based on adsorption. In Figure 3, the six main types of adsorption isotherms according to IUPAC [21, 22] are presented.

- Type I is characteristic for microporous solids with pore sizes not much larger than the molecular diameter of the adsorbate or when chemisorption occurs. This isotherm type describes adsorption limited to the completion of a single monolayer of the adsorbate in the adsorbent.
- Type II isotherms are observed in polymolecular adsorption in nonporous or macroporous adsorbents. They do not posses a saturation limit as Type I, but indicate an indefinite multilayer formation. They are found in adsorbents with a wide distribution of pore sizes. Close to the first point of inflection (point B) a monolayer is completed. After this, adsorption occurs in successive layers.
- Type III is characteristic of non-porous adsorbents with small adsorbentadsorbate interactions. They occur when the amount of gas adsorbed increases without limit as its relative saturation approaches unity. In Type III the heat of adsorption is less than the heat of liquefaction. As adsorption occurs, additional adsorption is facilitated because the adsorbate interactions with an adsorbed layer are greater than the interaction with the adsorbent surface [23].



Relative pressure p/p°

Figure 3: Isotherm types according to IUPAC.

- Types IV and V are similar to types II and III, but refer to porous adsorbents where capillary condensation can occur. Type IV only occurs in pores ranging from 15-1000 Å. Type IV isotherm are a variation of Type II, but with a finite multi-layer formation corresponding to complete filling of the pores. The adsorption terminates close to a relative pressure of one.
- Type VI isotherms are characteristic of non-porous adsorbents with homogeneous surface (e.g. Graphite/Kr and NaCl/Kr).

Various functional forms are available to describe the different types of isotherms: Langmuir [24], Freundlich [25], Langmuir-Freundlich (Sips) [26], Brunauer-Emmett-Teller [27], Temkin [28], Toth [29], Dubinin-Radushkevich [30], Sips [26], and Hill [31], among others, as well as their dual and triple site variations.

Experimentally, adsorption isotherms are obtained by measuring the amount of adsorbed substance (gas or liquid) on the adsorbing surface using volumetric or gravimetric methods. In the volumetric techniques, a known amount of adsorbent mass (m_s) is introduce into a sample cell of calibrated volume (V_t) . Once the adsorbent has been activated and the system has reached the desired temperature, a measure dose of the adsorbates (Δn) is introduce in the sample cell. After equilibrium is reached, the temperature (T) and pressure (P) are measured and the amount adsorbed (n_e) is defined by a mass balance:

$$n_e = \frac{n_t - \rho_g(T, P)V_d}{m_s} \tag{1}$$

where V_d is the helium dead space of the sample cell, $\rho_g(T, P)$ is the density of



Figure 4: Mass transfer zone moving through the adsorbent bed as time goes on. The shape of the mass transfer zone changes as it moves through the bed. It depends on the adsorption isotherm (thermodynamic equilibrium), flow rate, and the diffusion properties. Once all the adsorbent crystallites are saturated, the adsorbates will start to emerge until the concentration at the outlet is the same as in the inlet ($C/C_0=1$). Breakthrough (t_{break}) occurs when 0.01-0.05 of the adsorbent concentration appears in the outlet.

the bulk gas obtained from the equation of state and $n_t = \sum_j \Delta n_j$ is the total amount of adsorbates in the sample cell. In gravimetric techniques, a mass (m_s) of adsorbent is loaded into a bucket attached to a microbalance and weighed. Once the adsorbent has been activated and the desired temperature is reached, adsorbates are admitted into the sample. After the adsorption is completed, the temperature and pressure are measured and the amount adsorbed is determined from the weight of the bucket containing the adsorbent and adsorbates. The weight of the adsorbates equals the weight of the bucket containing the adsorbent and adsorbates minus the degassed tare weight under full vacuum. The amount adsorbed is defined by:

$$n_e = \frac{\Delta m}{Mm_s} + \rho_g v_{st} \tag{2}$$

where M is the molecular weight of the gas and v_{st} is the volume of the structure (adsorbent) not accessible to the gas molecules. The second term in the Eq. 2 is the buoyancy correction, due to the fact that the adsorbent is weighed immersed in a gas. The correction is equal to the weight of the bulk gas displaced. In both, gravimetric and volumetric methods, the measured amount adsorbed is the *excess adsorption*, that is, the difference between the number of moles of adsorbate present in the system (sample cell containing porous solid) and the number of moles that would be present if all the accessible volume in the system were occupied by the adsorbate fluid in its bulk state at the same temperature and pressure.

0.3 Breakthrough curves

Although isotherms give a good indication of the efficiency of an adsorbent for a particular adsorbate, designing separation technologies requires the transient nature of the adsorption procedure (still by far the most common procedure for bulk high volume processing operations) to be taken into account.

Separation based on adsorption usually involves passing a fluid over a static fixed bed of adsorbent. As the fluid enters the bed, it comes in contact with the first few layers of adsorbent and becomes adsorbed, filling up the available sites until all the adsorption sites near the entrance are saturated. When this occurs, the fluid moves farther into the adsorbent bed. Thus the active region (mass transfer zone) shifts down through the bed as time goes on until it "breaks through" (Figure 4). The fluid emerging from the bed has initially little or no adsorbates. After the bed becomes saturated, the concentration of adsorbates rises to the feed concentration. The break point occurs when the concentration of the fluid leaving the bed spikes as unadsorbed fluid begins to emerge. At this point the adsorbent bed becomes ineffective, the flow is stopped and the bed is replaced or regenerated. The adsorbate can thus be recovered and the adsorbent reused. Regeneration can be accomplished in several ways, and these lead to the "cycle type": temperature swing (TSA), pressure swing (PSA), inert/purge stripping and displacement purge.

Ideally, a separation process is isothermal [32], but in reality the process operates under adiabatic conditions, since heat is generated across the adsorbent bed as adsorption occurs. The heat of adsorption or enthalpy of adsorption determines the extent of the adsorbent temperature changes during the adsorption (exothermic) and desorption (endothermic). It is a quantitative measure of the strength of the adsorbates binding to the adsorbent. In physicorption, typical values range from 10 to 40 kJ/mol and in chemisorption the enthalpy of adsorption is normally between 40 and 800 kJ/mol. The desired enthalpy of adsorption depends on the application. For example for hydrogen storage, Bhatia and Myers [33] estimate an optimum adsorption enthalpy of 15.1 kJ/mol at ambient temperature and delivery between 30 and 1.5 bar and Bae et al. [34] showed that in order to attain the H_2 storage targets by the US Department of Energy (DOE) at ambient temperatures, the heat of adsorption of several MOFs should be around 20 kJ/mol. For separation processes, where in general the adsorbent needs to be regenerated for further use, a very high enthalpy of adsorption is not desirable. Although it might improve the selectivity, it also makes the regeneration step energy costly. For example in PSA, after the material has reached saturation, the process swings to low pressures for desorption. If the enthalpy of adsorption is too high, even at low pressures molecules will be adsorbed and additional methods are required. In TSA (where regeneration is achieved by increasing the temperature) if the enthalpy of adsorption is too high, then the necessary temperature to desorb will be very high. For MOFs, their thermal (in)-stability should be taken into account.



Figure 5: Relationship between the heat of adsorption, the surface area, the void fraction and the deliverable capacity for methane. Taken from ref [35]

0.4 Selectivity vs. Capacity

The primary requirement for an economic separation process is an adsorbent with (1) sufficiently high selectivity, (2) large capacity, (3) appropriate heat of adsorption, (4) favorable adsorption kinetics, (5) thermal, mechanical and chemical (especially water) stability. An appropriate heat of adsorption is necessary to ensure adsorption occurs at a reasonable pressure range. If the heat of adsorption is too low, the adsorption process requires very high pressures. If the heat of adsorption is too high, the regeneration (desorption) step becomes energetically expensive. Favorable adsorption kinetics (high surface area and relatively large pore sizes) are necessary to allow adsorbates to diffuse to the interior surface. Thermal, mechanical and chemical stability are necessary since most of the practical applications are carried out at high temperatures (TSA), high pressures (PSA) or under conditions where moisture can be a problem. Also, for catalysis, most practical applications are done in acidic or basic conditions.

For a binary mixture, the selectivity of component i relative to j is defined as

$$S_{i,j} = \frac{q_i/q_j}{f_i/f_j} \tag{3}$$

where q_i is the loading of component *i*, q_j the loading of component *j*, f_i the partial fugacity of component *i* and f_j the partial fugacity of component *j* and the capacity is defined as the amount of component *i* in the adsorbed phase

$$Capacity = q_i \tag{4}$$

A high selectivity, makes the separation process easier by preferential adsorption of component i over component j (less cycles will be needed to achieve a high degree of purity in the separation). A large capacity (associated with high pore volumes) implies that more material can be adsorbed before the adsorbent gets saturated (the regeneration time is longer). Unfortunately not all of these requirements can be easily combined. In Figure 5 (taken from ref. [35]), the relationship of some of these quantities for methane storage is shown. We can see that, if the volume surface increases, the deliverable capacity increases but the heat of adsorption decreases.

When selectivity arises from the interactions between the adsorbates and the adsorbent, it is inherently hard to combine high selectivity with high pore volumes because only the surface-adsorbed molecules "feel" the framework, but the rest of the molecules behave like a fluid inside the pores [36]. In this case, high selectivity can only be achieved with small pores or at low loading regimes. In order to combine high selectivity with high capacity and appropriate heats of adsorption, the selectivity has to be inherently present in the saturation regime. Separation mechanisms that are effective at saturation conditions have (in general) to be *entropic* in nature.

At saturation conditions, the success in the separation process is strongly dependent on the difference in saturation capacities of the mixture components. The latter in turn, is strongly influenced by the underlying entropic mechanisms occurring in the nanoporous materials. For molecules that have a bulky size and shape (relative to the framework) such as alkanes and aromatics, during my PhD I discovered two new entropic effects that can be used for separations:

- commensurate stacking [37], which favors molecules with stacking arrangements that are commensurate with the dimensions of one-dimensional channels;
- *face-to-face stacking* [38], which favors molecules that, when reoriented, significantly reduce their footprint in one-dimensional channels.

In addition to these effects, other effects have previously been reported:

- configurational entropy [39, 40], which favors molecules that efficiently pack in intersecting channels structures;
- size entropy [41, 42], which favors the smallest molecules;
- *length entropy* [41, 43–45], which favors the molecules with the shortest effective length (footprint) in one-dimensional channels.

Exploiting and understanding separation mechanisms that are effective at pore saturation conditions is of crucial importance to design and develop next-generation nanoporous materials for industrial separation applications, especially separations in the liquid-phase such as the separation of xylene isomers.

0.5 Molecular simulations

In order to improve the separations using nanoporous materials, it is important to have the best material for the desired application. Molecular simulations play a very important role in the characterization of structures. They allow us to obtain knowledge of the mechanisms taking place inside the materials, and therefore are a great tool to improve the properties of the materials, to predict material's properties and to screen materials for specific end-uses [46–50].

In molecular simulations a system is modeled by describing the interactions between the atoms (either classically or quantum mechanically (QM)) and an appropriate molecular simulation technique is used to link these interactions at the molecular level to macroscopic quantities that are accessible experimentally. In adsorption research, classical Monte Carlo (MC) simulations are commonly used. In MC simulations, instead of following the system through time (and computing properties as averages over time), properties are computed as averages over ensembles (a collection of microstates that are compatible with a given macrostate). These states are generated randomly and accepted depending on an *acceptance* criteria that ensures that the probability of being in a given state is equal to its Boltzmann factor. Thus, states with low energy are accepted with high probability and states with high energy are accepted with low probability. In Monte Carlo simulations we are interested in static properties (there are no dynamics). Static properties are obtained as averages over the system configurations. The freedom with which the configurations are generated makes the method very powerful. More details of this methodology are given in chapter 1 and 2.

The main quantity in the study of adsorptive separations is the adsorption isotherm. Adsorption isotherms can be obtained by performing Monte Carlo simulations in the grand canonical ensemble (GCMC), where the temperature, volume and chemical potential are kept fixed. In these simulations, the number of adsorbed particles varies during the simulation and the equilibrium conditions are obtained by setting the temperature and the chemical potential inside and outside of the gas to the same values. The volume is fixed by the crystallographic positions of the adsorbent. In nanoporous materials, most simulation studies follow the assumptions pioneered by Kiselev and co-workers [51] in which the frameworks are assumed to be rigid with atoms fixed at their crystallographic positions. In this case, the framework-framework interactions are not needed and the potential energy of the framework is described only by the non-bonded terms between the framework and the adsorbates. The adsorbates are considered either rigid or flexible. Both the adsorbate and framework are modeled using well-established force fields such as TraPPE [52–54], DREIDING [55], UFF [56] and OPLS [57–60].

Because inserting and deleting molecules in confined systems is not easy, most adsorption studies make use of Configurational-Bias Monte Carlo (CBMC) method [61–63]. In this method, molecules insertions and deletions are biased by growing them atom by atom towards favorable configurations. The CBMC method starts to have problems at medium densities and fails at high densities. In my work, I studied systems under confinement and at saturation conditions. In order to study these systems, I first developed (in collaboration with Delft University of Technology) the Configurational-Bias Continuous Fractional Monte Carlo (CB/CFCMC) [64]. This method is a combination of the above mention CBMC method and the Continuous Fractional Component Monte Carlo (CFCMC) method proposed by Shi and Maginn [65, 66]. In the CFCMC method, the system is expanded with a fractional molecule, which interactions with the surrounding molecules are scaled using a coupling parameter λ . Molecules are inserted and deleted in the system by performing a random walk in λ -space using the Monte Carlo method. When $\lambda = 0$ the fractional molecule is deleted and when $\lambda = 1$ a molecule is inserted. Together with the random walk in λ -space, normal Monte Carlo moves such as translations, rotations and reinsertions are employed. The method basically is gradually inserting and deleting molecules (much like inflating and deflating balloons), while allowing the surroundings to adapt to its presence, therefore reducing the energy penalty of insertion and deletion. One of the problems of CFCMC is that the fractional molecule is inserted randomly with configurations taken from the ideal gas distribution. These configurations are not always "appropriate", especially under confinement and at saturation conditions, where the available space for insertions is very limited. The method developed during my PhD combines the ideas of CFCMC and CBMC. This method not only allows studying saturated systems but also to study any system where insertions and deletions are difficult, for example ionic liquids [67, 68].

Besides adsorption isotherms, other important quantities to describe the systems can be obtained from molecular simulations like the heat of adsorption, diffusion constants, mechanical stability, etc. Molecular simulations are therefore an ideal complement to experimental investigations of adsorption and diffusion in nanopores. They can provide detailed information on molecular mechanisms; they can be used to explore the effect of changes in the composition and crystallographic structure on the material's properties (allowing to intelligently design materials), and they can predict observables such as X-ray, vibrational spectra, isotherms and heats of adsorption [69].

Outline of thesis

The main objective of this thesis was to study the separation of mixtures at saturation conditions using molecular simulations. In chapter 1 the basic molecular methods are described. This chapter is a summary of a recent review we published. In chapter 2, the Configurational-Bias Continuous Fractional Component Monte Carlo method is presented. This method was used in most of the simulations presented throughout the thesis. Chapter 3 further explores the CB/CFCMC method, and highlights its application to study other types of systems where insertion and deletion of particles is a problem, for example the vapor-liquid equilibrium of strong and directionally interacting liquids such as water and N,Ndimethylformamide. In chapter 4, it is shown that the CB/CFCMC method can be used to compute the enthalpy of adsorption (using the energy/particle fluctuation method in the grand-canonical ensemble) close to saturation conditions, where normal Monte Carlo and even Configurational-Bias Monte Carlo fail.

The remainder of the thesis are applications of the method to industrially relevant separations. In chapter 5, the adsorption and selectivity of the BTEX mixture in different adsorbents is studied. A new entropic effect, commensurate stacking, responsible for the high para-xylene selectivity of MAF-X8 (a zinc based metalorganic framework) is presented. In chapter 6 a new entropic effect, responsible for the high selectivity of ortho-xylene in AFI and MAZ zeolites is explored: faceto-face stacking. In chapter 7 the separation of styrene/ethylbenzene mixtures in different adsorbents is studied. The observed selectivity's are analyzed based on entropic mechanisms and the negative correlation between selectivity and capacity is highlighted. And finally, chapter 8, reviews the known entropic mechanisms so far and studies the previously known effects (size-entropy, length-entropy and configurational-entropy) to higher detail than before. By doing so, it is concluded that all entropy effects are derived from size-entropy. The difference between the effects is which size is regulating the process.

Except for chapter 5, the figures and tables referred to in the original papers in the SI, have been included in the text. For chapter 5 the Supporting Information can be found online http://dx.doi.org/10.1002/anie.201402894

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CHAPTER 1

Molecular simulation techniques*

1.1 Introduction

To study thermodynamic properties at the molecular level one needs to collect averaged information on the positions of atoms over long times. In Molecular Dynamics (MD) simulations [1–3], the system evolves according to Newton's equations of motion. This generates a trajectory that describes the positions, velocities and forces on the molecules as they vary over time. Monte Carlo (MC) takes a similar approach, but focuses on static properties. There is therefore no requirement that the system evolves in time. In MD, each state of the system depends on the previous one, related in time as a trajectory. But in MC there is no such connection between "snapshots" (states) of the system. Similar to MD, average properties are computed as averages over all the states of the system [4]. The MC method can easily be adapted to ensembles other than just the canonical ensemble, as long as each state can be generated with the proper weight. In principle each molecular state can be created independently. However, for efficiency reasons, most MC algorithms base a new snapshot on modification of the current one by performing changes called *moves*. Common moves are to translate and/or rotate a molecule. Such an attempt can be *accepted* (in which case the state of the system is changed) or *rejected* (in which case the state of the system is equal to the old one) by an *acceptance rule*. All these snapshots form a chain, called a Markov chain, and averages are computed as averages of this Markov chain. Only static properties can be computed in MC, because there is no time involved in an MC move. This might seem nonphysical or unnatural, but is in fact where the

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real power of MC lies. There are no constraints on MC moves other than that they generate the appropriate ensemble. This is guaranteed by the form of the acceptance rules. The MC algorithm should in principle allow the sampling of all relevant states of the system (*ergodic sampling*) but, in addition to the moves required for the ergodic sampling, there is an enormous opportunity to device clever and efficient MC algorithms, sampling techniques, and MC moves. For example, MC moves that change the composition or connectivity of the atoms can be devised. The biggest limitation of MC methods is that they are considerably harder to apply to chemically complex molecules than MD. The application of MC used to be limited to reasonably small molecules, but the range of systems sizes, molecules, and algorithms is rapidly advancing. For more details, Vitalis *et al.* published an overview of the state-of-the-art MC methods designed for efficient sampling of biomacromolecules [5].

1.2 Molecular simulations

1.2.1 Force fields

The basic ideas behind Molecular Mechanics (MM) date back to the 1930's and 1940's [6–8]. MM assumes that matter consists of atoms and for every set of positions of the atoms the potential energy surface (PES) can be defined [9]. The classical molecular energy U can be expressed as an expansion in bonds, bends, torsions, etc. [10, 11]

$$U = \sum_{\text{bonds}} u_b(r) + \sum_{\text{bends}} u_\theta(\theta) + \sum_{\text{torsions}} u_\phi(\phi) + \sum_{\substack{\text{out-of-plane} \\ \text{bends}}} u_\chi(\chi) + \sum_{\substack{\text{non-bonded}}} u_{nb}(r) + \sum_{\substack{\text{bond-bond}}} u_{bb'}(r,r') + \sum_{\substack{\text{bond-bend}}} u_{b\theta'}(r,\theta) + \sum_{\substack{\text{bond-bend}}} u_{\theta\theta'}(\theta,\theta') + \sum_{\substack{\text{bond-torsion}}} u_{r\phi}(r,\phi,r') + \sum_{\substack{\text{bend-torsion}}} u_{\theta\phi}(\theta,\phi,\theta') + \dots$$
(1.1)

This expansion captures all familiar entities such as atoms, bonds, angles and physical properties like equilibrium structures, vibrational spectra, etc. The cross terms arise naturally from this expansion and are not *ad hoc* functions. For example, bonds and bends interact, as the bend angle becomes smaller the bond lengths tend to increase. Their inclusion leads to two advantages: (1) they increase the accuracy of the simulations (especially the vibrational frequencies), and (2) they increase the transferability of the diagonal terms $u_r(r)$, $u_\theta(\theta)$, $u_\phi(\phi)$, $u_\chi(\chi)$. In addition to the terms in Eq. 1.1, one can add *ad hoc* terms, such as hydrogen bonding, that are not adequately accounted for otherwise. Just because a model lacks certain key elements does not mean all results are wrong; similarly, a more sophisticated force field does not necessarily give better results. A well calibrated simplistic model can often produce better results than a generic, elaborated model. The more parameters a model has to optimize, the harder it becomes. There have been a number of approaches to parameterize a force field directly from the quantum chemical calculations (see Ref. [12] and references therein). Since the true PES can be approximated using quantum mechanical methods, a force field can be directly fitted to a calculated QM PES by numerically matching the gradients or energy. Although it is theoretically possible to include non-bonded interactions in the fitting, it is more common to obtain charges and van der Waals parameters separately and use these as input.

It can be convenient to think of the parametrization process as bottom-up (left-to-right in Eq. 1.1):

- Bonds/angles/torsion: can be obtained from gas phase quantum mechanics and spectroscopy.
- Point charges: by minimizing the difference of the classical electrostatic potential and a quantum mechanical electrostatic potential over many spatial grid points (ChelPG methods) [13–15]; REPEAT method [16, 17]; Partial Equalization of Orbital Electronegativity (PEOE) or the Gasteiger method [18]; charge equilibration methods [19–21].
- Polarizabilities: from gas-phase quantum mechanical calculations or from experiment.
- Van der Waals interactions: from Vapor-Liquid Equilibrium (VLE) curves; inflections in isotherms [22, 23]; small noble gases like Argon from second virial coefficients; in general, from comparison with experiments (*e.g.* density, heat capacity, compressibility).

Eq. 1.1 is historically referred to as a *force field*. The name arose from the lowest order approximation using only springs with *force constants*. Over the last years force fields have matured. Therefore, given a force field, many different parameters exist for a wide range of structures. These parameters are crucial and determine the quality of the force field. A few examples of popular generic force fields are AMBER [24–28], OPLS [29–32], AMBER/OPLS [33–36], CHARMM [37–39], GROMOS [40–42], CVFF [43], CFF [44–46], MM2 [47–49], MM3 [50, 51], MM4 [52–57], MMFF94 [58–63], DREIDING [64], COMPASS [65], PCFF [65], and UFF [66].

1.2.2 The simulation cell and boundary conditions

Modeling materials by computer simulations has some practical limitations. One is related to the number of molecules that can be efficiently stored in memory. Although simulations of hundreds of thousands of atoms have been reported and will likely increase by orders of magnitude in the future, this number is still far removed from the thermodynamic limit. In order to enhance the convergence of the finite-size system results to macroscopic bulk values one usually employs periodic boundary conditions [1]. Importantly, this also eliminates unwanted surface effects. When using periodic boundary conditions, the central simulation box is artificially replicated throughout space, including all the atoms within it [67]. For every atom in the central cell, the periodic image positions can be calculated using translation operators. Therefore, only the positions in the central cell need to be stored. If a molecule leaves the central box, one of its images will enter the box through the opposite face. To calculate the interactions between particles, usually the minimum-image convention is used. The minimum-image is defined as the shortest distance between two particles or any of their images. Only the shape and orientation of periodic box have physical significance (not the boundary itself) [3]. The use of periodic boundary conditions inhibits the occurrence of longwavelength fluctuations. It is for example not possible to simulate a liquid close to the gas-liquid critical point where the range of critical density fluctuations can extend to macroscopic length scales [3].

In general the unit cell is defined by the length of the cell edges a, b, c, the angles between the cell edges α , β , γ , and by the fractional coordinates \mathbf{s} of the atoms within the unit cell. These coordinates are defined in an orthonormal dimensionless space. The transformation from fractional space to Cartesian space can be carried out by the matrix \mathbf{h} :

$$\mathbf{h} = \begin{pmatrix} a & b\cos\left(\gamma\right) & c\cos\left(\beta\right) \\ 0 & b\sin\left(\gamma\right) & c\zeta \\ 0 & 0 & c\sqrt{1 - \cos^2\beta - \zeta^2} \end{pmatrix}$$
(1.2)

with

$$\zeta = \frac{\cos \alpha - \cos \gamma \cos \beta}{\sin \gamma} \tag{1.3}$$

This aligns the *a* cell vector along the *x* axis, *b* in the *xy*-plane. Conversely, \mathbf{h}^{-1} transforms Cartesian coordinates **r** to fractional coordinates **s**. Using **h** the scaled box has unit length. Force fields are defined in Cartesian space, therefore it is convenient to store position in Cartesian space, transform them to fractional space, apply periodic boundary conditions in **s**-space, and transform back to Cartesian space to compute distances within the simulation box

$$\mathbf{s} = \mathbf{h}^{-1}\mathbf{r}$$

$$\mathbf{s}' = \mathbf{s} - \operatorname{rint}(\mathbf{s})$$

$$\mathbf{r}' = \mathbf{h}\mathbf{s}'$$

$$r = \sqrt{(\mathbf{r}'_x)^2 + (\mathbf{r}'_y)^2 + (\mathbf{r}'_z)^2}$$
(1.4)

where the "rint"-function is defined as the rounded integer value of its argument. The spherical cutoff (radius after which intermolecular interactions are truncated) in Cartesian space has to be consistent with the minimum image convention [3]. For this, the smallest perpendicular width of the simulated periodic box must be at least twice the spherical cutoff.

1.3 Long-range interactions

1.3.1 Van der Waals

The most common repulsion/dispersion functional forms are the Lennard-Jones potential (see Figure 1.1)

$$u^{\text{VDW}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$
(1.5)

and the Hill (also known as Buckingham) potential function,

$$u^{\text{VDW}}(r) = a \exp\left(-br\right) - \left(\frac{c}{r}\right)^{6}$$
(1.6)

The Hill potential, having 3 adjustable parameters vs. 2 for Lennard-Jones (the *strength* parameter ϵ and the *size*-parameter σ), might be slightly more accurate. However, the Lennard-Jones potential is most commonly used for convenience. The parameters for generic force fields are usually self-parameters and a *mixing-rule* is needed to compute the interaction between different types of atoms *i* and *j*. Common mixing rules are:

arithmetic (or Lorentz-Berthelot)
$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$
 $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$ (1.7)

geometric (or Jorgensen)

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$
 $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$ (1.8)

sixth-power (or Waldman-Hagler)
$$\epsilon_{ij} = \frac{2\sigma_i^3\sigma_j^3}{\sigma_i^6 + \sigma_j^6}\sqrt{\epsilon_i\epsilon_j} \quad \sigma_{ij} = \left(\frac{\sigma_i^6 + \sigma_j^6}{2}\right)^{1/6}$$
(1.9)

Many more mixing rules are given in ref. [68]. A downside of the Hill potential is it's divergence to large negative energies at $r \to 0$. In MD, assuming that all atoms initially do not overlap, the repulsive part of the potential avoids this issue. However, in MC a move may choose a new random position near another particle's position. Therefore, the potential needs to be "blocked" (such a move would be explicitly considered an overlap and rejected) or changed to a polynomial repulsion (*e.g.* MM2) at short distances. To make the simulations tractable, the Van der Waals potentials are truncated at a certain distance where the interactions are considered sufficiently small. In MC the truncated potential can be used, and the energy-correction due to this truncation, called the *tail-correction*, can be approximated (see Figure 1.1). The truncation distance and whether or not to use tail-correction should be considered as part of the force field. For molecular dynamics the truncation in the energy leads to a divergence in the forces. Common approaches include to shift the Van der Waals potential to zero at the cutoff and the use of a switching function where the energy is adjusted to smoothly go to zero [69–71]

$$u(r) = \begin{cases} u(r) & < r_{\rm on} \\ u(r) \times \frac{(r_{\rm off}^2 - r^2)(r_{\rm off}^2 + 2r^2 - 3r_{\rm on})}{(r_{\rm off}^2 - r_{\rm off}^2)^3} & r_{\rm on} \le r \le r_{\rm off} \\ 0 & r > r_{\rm off} \end{cases}$$
(1.10)



Figure 1.1: The Lennard-Jones has two parameters: the "strength" parameter ϵ and the "size"-parameter σ . Energy and force evaluations only take place within the cutoff distance. It is possible to estimate the neglected energy (called the "tail-correction, green area in the picture). For MD is customary to use "smoothing" which makes the potential smoothly go to zero at the cutoff (red line). Alternatively, the whole potential can be "shifted" to be zero at the cutoff. The latter leads to continuous forces but remains divergent for higher derivatives. The tail-correction calculation assumes that the RDF is approximately unity after the cutoff. The right figure shows that for methane-methane interactions an arbitrary methane sees an idealgas of other methane molecule at distance greater than about 12-14 Å for this system. The RDF/tail-correction formulation breaks down inside nanoporous materials (here methane in ERI-type zeolites) where the particles are located at adsorption sites in a heterogeneous environment. The RDFs of methane in the fluid and in the pore of ERI are computed at the same density (102 kg/m³).

The cutoff is usually chosen as the distance where the RDF approaches unity. The requirements that the smallest perpendicular distance of the simulation cell has to be larger than twice the cutoff distance r_c determines the minimum amount of crystallographic unit cells to be used in *e.g.* adsorption simulations. If we assume

the RDF g(r) = 1 for $r > r_c$, we can write

$$U \approx \sum_{i < j} u^{\text{VDW}}(r) + \frac{N\rho}{2} \int_{r_c}^{\infty} 4\pi r^2 u^{\text{VDW}}(r) \, \mathrm{dr}$$
(1.11)

where N is the number of particles and $\rho = N/V$ is the average number density. The last term in Eq. 1.11 is a *tail-correction*, *i.e.* the systematic contribution to the energy due to truncation of the potential. Similar expressions have been derived for the pressure and chemical potential [1]. Note that this is only possible for potentials decaying faster than $1/r^3$, like the van der Waals potentials. Another point worth mentioning is that for molecules adsorbed in a porous material the RDF does not approach unity, not even at long distances, because it is no longer an homogeneous system (see Figure 1.1). Analytical tail-corrections therefore do not apply in nanoporous systems [72] and they are usually just omitted.

1.3.2 Coulombic interactions

The total electrostatic potential energy of interaction between point charges q_i at the positions \mathbf{r}_i is given by

$$U = \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|} = \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(1.12)

where ϵ_0 is the electric permittivity of free space (8.8541878176 10^{-12} F/m). The first form in this expression, explicitly counts all pairs of atoms, the second form counts all interactions. In the later to compensate for double counting one needs to divide by two.

This expression can be evaluated directly for finite systems but for a large or periodic system, the expression is exceedingly time consuming, but more importantly, does *not* converge to the proper value. Dedicated procedures must be used to evaluate the energy.

For a charged infinite periodic system, the energy of interaction is undefined but for neutral systems a meaningful interaction energy can be defined by using an Ewald summation [73–75]. The basic idea of this approach is to replace a single divergent summation by two convergent summations. This is done by noting that

$$\frac{1}{r} = \frac{\operatorname{erf}\left(\alpha r\right)}{r} + \frac{\operatorname{erfc}\left(\alpha r\right)}{r} \tag{1.13}$$

where the error function $\operatorname{erf}(x)$ and its complement $\operatorname{erfc}(x)$ are defined as:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \qquad \operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt \qquad (1.14)$$

The error function goes to a constant $\left(\frac{2\alpha}{\sqrt{\pi}}\right)$ as $r \to 0$, but slowly converges as $r \to \infty$. Its complement has a singular behavior as $r \to 0$, but vanishes exponentially as $r \to \infty$.

Using this, the potential energy of interaction between point charges can be expressed as:

$$U = \frac{1}{8\pi\epsilon_0} \sum_{i\neq j} q_i q_j \frac{\operatorname{erf}(\alpha|\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i\neq j} q_i q_j \frac{\operatorname{erfc}(\alpha|\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(1.15)

The first summation is convergent and conveniently computed in Fourier space and the second summation is convergent and usually computed in real space. More details can be found in [1, 3].

1.4 Ensembles

To describe the microscopic state of a system, classically, at some instant of time, we need 6N variables; for each of the N atoms we have 3 positions and 3 velocities. This state is a point in a 6N-space, called phase-space. The state evolves through phase-space according to the laws of mechanics. The measurements of macroscopic variables like temperature T, volume V, pressure p involve taking time averaging over the phase-space trajectory of the system. This is in fact the basis of the molecular dynamics technique.

Around 1900 Gibbs introduced the concept of "ensembles", were the timeaveraging is replaced by averaging over a group of microstates with the same macroscopic state (e.g. N, V, T). The ergodic principle states that this ensemble averaging and time averaging is equivalent (when simulated infinitely long). By employing the ergodic principle, the problem is moved from solving high dimensional differential equations (classical) or eigen value equations (quantum) to formulating the probability density ρ of finding the system in a specific microstate. This is the basis of Monte Carlo simulations.

Molecular simulations are conducted under well defined thermodynamic conditions, such as the number of particle, volume and temperature. These conditions determine the "ensemble" of the system, which in turn determines the functional form of the probability density. Each ensemble is associated with a thermodynamic state function from which all the thermodynamic properties of the system can be derived.

For systems with just one type of components (single components) there is one fundamental thermodynamic function

$$dU(V, S, n) = -p \, dV + T \, dS + \mu \, dn \tag{1.16}$$

from which three others can be derived by a Legendre transformation [76]

$$dH(p, S, n) = V dp + T dS + \mu dn$$
(1.17)

$$dA(V,T,n) = -p \, dV - S \, dT + \mu \, dn \tag{1.18}$$

$$dG(p,T,n) = V dp - S dT + \mu dn$$
(1.19)
where the entropy is denoted by S, the chemical potential by μ , n is the number of moles, U is the internal energy, H the enthalpy, A the Helmholtz function, and G the Gibbs function, respectively. A system where the number of moles n varies is called an *open system*. In the thermodynamic limit, all ensembles are equivalent and it is possible to change between them by a Legendre transformation of the chemical work term μdn .

1. Transformation of the internal energy U

$$L = U - \mu n \quad ; \quad dL = -p \, dV + T \, dS - n \, d\mu \tag{1.20}$$

where the function $L(V, S, \mu)$ is known as the *Hill energy*.

2. Transformation of the enthalpy H

$$R = H - \mu n$$
; $dR = V dp + T dS - n d\mu$ (1.21)

where the function $R(p, S, \mu)$ is known as the *Ray energy*.

3. Transformation of the Helmholtz function A

$$J = A - \mu n \quad ; \quad dJ = -p \, dV - S \, dT - n \, d\mu \tag{1.22}$$

where the function $J(T, V, \mu)$ is known as the grand function.

4. Transformation of the Gibbs function G

$$Z = G - \mu n = 0 \quad ; \quad dZ = V \, dp - S \, dT - n \, d\mu = 0 \tag{1.23}$$

where the function $Z(p,T,\mu)$ is known as the *Guggenheim function*.

All seven functions H(p, S, n), A(V, T, n), G(p, T, n), L(V, S, n), R(p, S, n), J(V, T, n) and Z(p, T, n) are derivable from a Legendre transformation of the fundamental law of the energy conservation expressed in the internal energy function U(V, S, n) (see Eq. 1.16). Figure 1.2, taken from Ref. [77], shows the ensembles and their connection to the reservoirs (or the constraints of the system).

All eight ensembles (for a single component system) may be simulated using either MD or MC simulations. The choice of ensemble for a simulation is entirely a matter of convenience. For MD, the natural ensemble is NVE. This is because Newtons equations lead naturally to the conservation of energy. For Monte Carlo simulations the different ensembles determine different functional forms of the probability density (this will be discussed further in the next section).



Figure 1.2: Representation of the eight ensembles for a single component system. The systems interact through a combined temperature, pressure and chemical potential reservoir. The ensembles on the left are adiabatically insulated from the reservoir while those on the right are in thermal contact with the reservoir. Pistons and porous walls allow for volume and particle exchange. Adiabatic walls are shown cross-hatched while diathermal walls are shown as solid lines. Ensembles on the same height are related by Laplace and inverse Laplace transformations. The pressure stands for the pressure and the tension. Picture taken from Ref. [77].

1.5 Methodology

1.5.1 Monte Carlo

Monte Carlo simulations are based on statistical mechanics. Statistical mechanics formulates the following postulates [78]:

1. Postulate of ensemble averaging.

The average behavior of a macroscopic system in equilibrium is given by the average taken over a suitable ensemble consisting of an infinite number of randomized mental copies of the system of interest.

- 2. Postulate of equal a priori probabilities. In a state of macroscopic equilibrium, all stationary quantum states of equal energy have equal a priori probability (in the micro-canonical ensemble).
- 3. Postulate of equilibrium state. Equilibrium state is the one that occupies the maximum volume in phasespace.

The implications are:

- 1. The method of calculation is *statistical* in nature.
- 2. The predictions are to be regarded as true on average rather than precisely expected for any particular system.
- 3. The probability of finding a system in a given state is proportional to the phase space volume associated with it, the most probable state would be one that occupies the maximum volume in phase space. It follows that the equilibrium state is the state of maximum probability.

In its simplest form, the MC method is nothing more than a computer-based exploitation of the Law of Large Numbers to estimate a certain probability or expectation. At the heart of the algorithm lies the "random numbers generator" and therefore it is advisable to use a high quality generator like the "Mersenne Twister" [79, 80]. To estimate the average properties of systems with many accessible states, the Markov Chain Monte Carlo method (MCMC) can be used [81, 82].

In MC simulations, the system evolves from state to state (possibly the same state) and averages of a property are computed as the average over the elements of the Markov chain. This expression is exact for an infinite Markov chain. It uses the fact that not the absolute probabilities of the states are needed, but only the relative probability. To guarantee that states are visited with the correct frequency, random trial moves are generated that take the system from the current ("old") state (o) to the new state (n).

The condition of detail balance (as is used in the original Metropolis scheme [81]), is normally applied to ensure that any arbitrary initial distribution eventually relaxes to the equilibrium distribution. If $P_{eq}(o)$ and $P_{eq}(n)$ denote the probability of finding the system in state (o) and (n), respectively, and $\alpha(o \to n)$ and $\alpha(n \to o)$ denote the conditional probability to perform a trial move from $o \to n$ and $n \to o$, respectively, then the condition called "detailed balance" can be written as

$$P_{\rm eq}(o)\,\alpha(o\to n)P_{\rm acc}(o\to n) = P_{\rm eq}(n)\,\alpha(n\to o)P_{\rm acc}(n\to o) \tag{1.24}$$

In equilibrium the flow from the old state o to any other state n is exactly equal to the reverse flow. In the Metropolis algorithm α is chosen as a symmetric matrix

$$\alpha(o \to n) = \alpha(n \to o) \tag{1.25}$$

For a symmetric transition matrix

$$P_{\rm eq}(o) P_{\rm acc}(o \to n) = P_{\rm eq}(n) P_{\rm acc}(n \to o)$$
(1.26)

which leads to

$$\frac{P_{\rm acc}(o \to n)}{P_{\rm acc}(n \to o)} = \frac{P_{\rm eq}(n)}{P_{\rm eq}(o)}$$
(1.27)

Metropolis *et al.* choose the following acceptance rule [81]

$$P_{\rm acc}(o \to n) = \min\left(1, \frac{P_{\rm eq}(n)}{P_{\rm eq}(o)}\right) \tag{1.28}$$

Each ensemble has a characteristic probability distribution. Thus, the acceptance criteria will vary depending on the ensemble we are working with. The general approach in deriving the MC method for a given ensemble is:

- 1. Determine the microstate probability distribution for the ensemble of interest.
- 2. Determine the Monte Carlo moves to accomplish changes in the fluctuating quantities in the ensemble.
- 3. Find the acceptance criteria.

Some of the most commonly used ensembles are the canonical ensemble, the isothermal-isobaric ensemble, the grand-canonical ensemble, the Gibbs ensemble, and the $\mu_1 N_2 pT$ -ensemble. In Table 1.1 the probability densities associated to some of these ensembles are presented.

In MC simulations we are only interested on the positions, as the momenta can be analytically integrated out by making use of $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$

$$\int e^{-\beta \left(\sum_{i} \frac{p_{i}^{2}}{2m_{i}}\right)} \mathrm{d}\mathbf{p} = \left(\int e^{-\beta \frac{p^{2}}{2m}} \mathrm{d}p\right)^{3N} = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}N}$$
(1.29)

The de Broglie wavelength Λ is the quantum mechanical wavelength of a gas particle with momentum determined by the average thermal kinetic energy per degree of freedom $k_B T$. If we use the de Broglie relation $p_x = h/\Lambda$, then from $\frac{1}{2}p_s^2/m = \frac{1}{2}k_B T$ we have $\Lambda = h/\sqrt{m k_B T} = \sqrt{h^2/(m k_B T)}$. The condition for the applicability of classical or Boltzmann statistics is equivalent to the condition $\Lambda^3/V \ll 1$ where Λ represents the critical length scale at which interactions are neglected. Closely related to h divided by the momentum, the de Broglie wavelength is defined as

$$\Lambda \equiv \left(\frac{h^2 \beta}{2\pi m}\right)^{1/2} \tag{1.30}$$

The differences between the partition functions with and without explicit momentum integration are $h \leftrightarrow \Lambda$ and $H(\mathbf{p}^N, \mathbf{r}^N) \leftrightarrow U(\mathbf{r}^N)$. For example, for the canonical partition function

$$\frac{1}{h^3 N!} \iint e^{-\beta H(\mathbf{p},\mathbf{r})} d^N \mathbf{p} d^N \mathbf{r} = \frac{1}{\Lambda^3 N!} \int e^{-\beta U(\mathbf{r})} d^N \mathbf{r}.$$
 (1.31)

For ensembles where the simulation cell is allowed to change it is more convenient to redefine the positions in fractional coordinates using $\mathbf{s} = \mathbf{h}^{-1}\mathbf{r}$ [83]. The partition function in fractional coordinates is related to the Cartesian version by a factor V^N where $U(\mathbf{s}^N; \mathbf{h})$ means that the Hamiltonian depends on the Cartesian **Table 1.1:** Most common ensembles partition function and probability density functions. The momenta have already been integrated out and fractional coordinates are used in all cases.

Ensemble	Partition function (Z) and probability density $\left(P\left(\mathbf{s}^{N},V\right)\right)$
Canonical	$\mathbf{Z} = Q\left(N, V, T\right) = \frac{V^{N}}{\Lambda^{3N} N!} \int e^{-\beta U\left(\mathbf{s}^{N}; \mathbf{h}\right)} d^{N}\mathbf{s}$
	$P\left(\mathbf{s}^{N},V ight) \propto e^{-eta U\left(\mathbf{s}^{N};\mathbf{h} ight)}$
Isothermal-isobaric	$\mathbf{Z} {=} \Delta\left(N, P, T\right) = \tfrac{\beta P}{\Lambda^{3N} N!} \int V^{N+1} e^{-\beta p V} \left(\int e^{-\beta U\left(\mathbf{s}^{N}; \mathbf{h}\right)} \mathrm{d}^{N} \mathbf{s} \right) \mathrm{d} V$
	$P\left(\mathbf{s}^{N},V\right) \propto V^{N+1}e^{-\beta pV}e^{-\beta U\left(\mathbf{s}^{N};\mathbf{h}\right)}$
Grand canonical	$\mathbf{Z} = \Xi\left(\mu, V, T\right) = \sum_{N=0}^{\infty} \frac{V^N e^{\beta \mu N}}{\Lambda^{3N} N!} \int e^{-\beta U\left(\mathbf{s}^N; \mathbf{h}\right)} \mathrm{d}^N \mathbf{s}$
	$P\left(\mathbf{s}^{N},V ight) \propto rac{V^{N}e^{eta\mu N}}{\Lambda^{3N}N!}e^{-eta U\left(\mathbf{s}^{N};\mathbf{h} ight)}$

positions [83], *i.e.* potentials are usually defined in Cartesian space as opposed to fractional space. For example, for the canonical partition function

$$\frac{1}{\Lambda^{3N}N!} \int e^{-\beta U\left(\mathbf{r}^{N}\right)} \mathrm{d}^{N}\mathbf{r} = \frac{V^{N}}{\Lambda^{3N}N!} \int e^{-\beta U\left(\mathbf{s}^{N};\mathbf{h}\right)} \mathrm{d}^{N}\mathbf{s}.$$
 (1.32)

The two most common MC moves are rigid translation and rotation in which a molecule is displaced or rotated by a small modification. The modification is usually scaled to achieve around 50% acceptance. In a strongly interacting fluid (e.q. water) the acceptance ratio of the rigid rotation becomes low and it might be better to do a full random rotation. The "reinsertion"-move removes a randomly selected molecule and reinserts it at a random position. For rigid molecules it uses orientational biasing, and for chains the molecule is fully regrown (the internal configuration is modified). This will be discussed in detail in the configurational-bias method. The reinsertion-move by passes (free) energy barriers and is particularly useful to redistribute molecules in cages of nanoporous materials. At high densities the acceptance ratio of the reinsertion move becomes vanishingly low. To properly sample the internal structure (i.e. bond/bend/torsions) the "partial reinsertion" move is useful. Several atoms of the molecules are kept fixed, while others are regrown. Because there is already space for the atoms the acceptance ratios are high. For mixtures, especially at higher density, the "identity-switch" move becomes crucial. The identity-change trial move [84–87] is called semi-grand ensemble, but it can also be seen as a special case of the Gibbs ensemble. One of the components is selected at random and an attempt is made to change its identity. To sample concerted motions of atoms the hybrid MC/MD can be used. To obtain a new configuration a short NVE molecular dynamics of M time steps is run and accepted or rejected [88, 89]. The starting velocities are chosen from a Maxwell-Boltzmann distribution at the desired temperature.

In Monte Carlo simulations the quantities of interest are the averages of properties over an ensemble:

$$\langle A \rangle = \frac{\int A(\mathbf{r}^N) P(\mathbf{r}^N) d^{N}\mathbf{r}}{\int P(\mathbf{r}^N) d^{N}\mathbf{r}}$$
(1.33)

where $P(\mathbf{r}^N)$ is the probability of finding configuration \mathbf{r}^N (and thus depends on the ensemble). In general Monte Carlo simulations are divided in an initial equilibration part, where the system is relaxed towards the states we are interested in sampling, and a subsequent production part, where the average of properties are computed. In both cases, the duration is measured in "MC steps" or "MC cycles". An MC *step* is one performed MC move, either accepted or rejected. The MC moves are chosen in random order with preset probabilities. An MC *cycle* takes the number of particles into account and in each cycle on average one MC move has been attempted *per particle*. The reasoning behind this is that one needs to sample longer if there are more molecules in the system. Therefore the number of cycles is less dependent on the system size. To avoid poor sampling at low densities the number of steps per cycle can have a set lower limit of *e.g.* 20. A cycle is then for example defined as [90]: $N_{cycles} = \max(20, N)N_{steps}$.

1.5.2 Adsorption simulation

In adsorption studies one would like to know the amount of material adsorbed as a function of pressure and temperature of the reservoir with which the adsorbent is in contact. Adsorption simulations can be performed in the Gibbs-ensemble [86] (Figure 1.3b), the $\mu_1 N_2 pT$ ensemble (Figure 1.3c) when flexible frameworks are used and the grand-canonical ensemble [91] (Figure 1.3d). In our research we computed the adsorption isotherms using the grand-canonical ensemble.

grand-canonical ensemble or μVT ensemble In this ensemble, the chemical potential μ , the volume V and the temperature T are fixed. This is simulated by coupling the system under study to an infinite reservoir which has the same μ and T, and keeping the volume of the system fixed. The partition function is given by

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \frac{V^N e^{\beta \mu N}}{\Lambda^{3N} N!} \int e^{-\beta U\left(\mathbf{s}^N; \mathbf{h}\right)} d^N \mathbf{s}$$
(1.34)

where \mathbf{s}^N ; \mathbf{h} refer to the fractional positions. The probability of a particular configuration is

$$P\left(\mathbf{s}^{N}, V\right) \propto \frac{V^{N} e^{\beta \mu N}}{\Lambda^{3N} N!} e^{-\beta U\left(\mathbf{s}^{N}; \mathbf{h}\right)}$$
(1.35)



a Two fluid phases with fixed total volume V and temperature T.



c An adsorbent with fixed particle number N_1 under a constant pressure p in contact with a reservoir that imposes constant temperature T and chemical potential μ_2 .

Adsorption in the Gibbs ensemble (flexible framework)



b An adsorbed phase and a fluid phase with fixed pressure p and temperature T.



Fixed number of framework atoms and volume

d An adsorbent with a fixed volume in contact with a reservoir that imposes constant temperature T and chemical potential μ .

Figure 1.3: Adsorption using Gibbs, the osmotic, and the grand-canonical ensemble, (a) in the Gibbs ensemble the total volume and the total number of molecules is fixed. The volume move makes one box bigger and the other box smaller which leads to pressure equilibration. The exchange of particles between the boxes leads to equal chemical potential and in both boxes the same temperature is imposed. (b) Adsorption isotherms can be computed in the Gibbs ensemble where the fluid phase is explicitly simulated. (c) The osmotic ensemble replaces the explicit fluid phase by a imaginary reservoir. (d) The grand-canonical ensemble also uses the imaginary reservoir but in addition keeps the volume fixed.

and the acceptance rules are:

particle move
$$P_{\text{acc}}(o \to n) = \min\left(1, \frac{\frac{V^N e^{\beta\mu N}}{\Lambda^{3N} N!} e^{-\beta U_n(\mathbf{s}^N;\mathbf{h})}}{\frac{V^N e^{\beta\mu N}}{\Lambda^{3N} N!} e^{-\beta U_o(\mathbf{s}^N;\mathbf{h})}}\right)$$
$$= \min\left(1, e^{-\beta \left[U_n(\mathbf{s}^N;\mathbf{h}) - U_o(\mathbf{s}^N;\mathbf{h})\right]}\right)$$

insertion
$$P_{\rm acc} \left(o \to n \right) = \min \left(1, \frac{\frac{V^{\left(N+1\right)} e^{\beta\mu\left(N+1\right)}}{\Lambda^{3\left(N+1\right)}\left(N+1\right)!} e^{-\beta U_{n}\left(\mathbf{s}^{N+1};\mathbf{h}\right)}}{\frac{V^{N} e^{\beta\mu N}}{\Lambda^{3N} N!} e^{-\beta U_{o}\left(\mathbf{s}^{N};\mathbf{h}\right)}} \right)$$
$$= \min \left(1, \frac{V e^{\beta\mu}}{\Lambda^{3}\left(N+1\right)} e^{-\beta \left[U_{n}\left(\mathbf{s}^{N+1};\mathbf{h}\right) - U_{o}\left(\mathbf{s}^{N};\mathbf{h}\right) \right]} \right)$$

(1.36)

deletion
$$P_{\text{acc}}(o \to n) = \min\left(1, \frac{\frac{V^{(N-1)}e^{\beta\mu(N-1)}}{\Lambda^{3(N-1)}(N-1)!}e^{-\beta U_n\left(\mathbf{s}^{N-1};\mathbf{h}\right)}}{\frac{V^Ne^{\beta\mu N}}{\Lambda^{3N}N!}e^{-\beta U_o\left(\mathbf{s}^N;\mathbf{h}\right)}}\right)$$

$$= \min\left(1, \frac{\Lambda^3 N}{Ve^{\beta\mu}}e^{-\beta \left[U_n\left(\mathbf{s}^{N-1};\mathbf{h}\right) - U_o\left(\mathbf{s}^N;\mathbf{h}\right)\right]}\right)$$
(1.37)

The pressure p in the reservoir is related to the chemical potential by

$$\beta \mu = \beta \mu_{\rm IG}^0 + \ln \left(\beta f\right) \tag{1.38}$$

where $f = \phi p$ is the fugacity, and μ_{IG}^0 is the chemical potential of the reference state (ideal gas)

$$\mu_{\rm IG}^0 \equiv \frac{\ln\left(\Lambda^3\right)}{\beta} \tag{1.39}$$

The fugacity is not the same as the pressure but it is closely related to it. Fugacity is the activity of a gas and has the same units as pressure. The fugacity coefficient ϕ is the exponential of the difference of the Gibbs free energy g(T, p) and the ideal gas Gibbs free energy $g^{\text{IG}}(T, p)$ at the system (T, p) divided by RT [92]

$$\phi = \frac{f}{p} = \exp\left[\frac{g\left(T,p\right) - g^{\text{IG}}\left(T,p\right)}{RT}\right] = \exp\left[\frac{1}{RT}\int_{0}^{p}\left(\frac{z-1}{p}\right)_{T}dp\right]$$
(1.40)

where z is the compressibility. In simulations, the chemical potential μ is imposed which is closely related to the fugacity (see Eq. 1.38). For an ideal gas f = p and for $p \to 0$ every gas becomes an ideal gas. The conversion between pressure and fugacity can be performed using an appropriate equation of state. Fugacities and fugacity coefficients for components of mixtures can be estimated by the Lewis-Randall rule which states that fugacity coefficient of a component *i* in a mixture of real gases is roughly equal to the fugacity coefficient of the pure gas *i* at the temperature *T* and (total) pressure *p* of the mixture [92]. There are some limitations to this rule. Alternatively one can use an EOS with appropriate mixing rules [93].

The acceptance rules for insertion and deletion in the grand canonical ensemble, taking into account the relationship between the chemical potential and the pressure, are

insertion
$$P_{\rm acc} \left(o \to n \right) = \min \left(1, \frac{\beta V \phi p}{N+1} e^{-\beta \left[U_n \left(\mathbf{s}^{N+1}; \mathbf{h} \right) - U_o \left(\mathbf{s}^N; \mathbf{h} \right) \right]} \right)$$
(1.41)

deletion
$$P_{\rm acc} \left(o \to n \right) = \min \left(1, \frac{N}{\beta V \phi p} e^{-\beta \left[U_n \left(\mathbf{s}^{N-1}; \mathbf{h} \right) - U_o \left(\mathbf{s}^N; \mathbf{h} \right) \right]} \right)$$
 (1.42)

For mixtures, a convenient method is to first randomly choose a component. The acceptance rules (Eqs. 1.41 and 1.42) stay the same, except that N refers to the number of particles of the chosen component and p to the partial pressure.

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To overcome the low insertion rates at low temperature and/or high densities several advanced MC moves were developed, *e.g.* all the Configurational-Bias methods based on the work of Rosenbluth and Rosenbluth [94], energy-cavity biasing [95], Reptation move [96], aggregation-volume-bias [97], as well as MC methods like recoil growth [98, 99], reverse MC [100], phase switch MC [101–103], kinetic MC [104–106], rotational isomeric state MC [107], basin-hopping MC [108], tethered MC [109], smart walking [110], self-referential method [111–113], expanded ensembles [114, 115], Fragement regrowth MC [116], and Waste recycling MC [117, 118].

1.5.3 Configurational-Bias Monte Carlo

Conventional MC is time-consuming for long chain molecules. Moreover, the configurations of long molecules in the framework become increasingly different from the gas phase. The fraction of successful insertions becomes too low. The Configurational-Bias Monte Carlo (CBMC) technique was developed to increase the number of successfully insertions. Figure 1.4 shows the definition of S2-butanol which will be used here to illustrate the method. Instead of generating ideal gas configurations and trying to insert the molecule as a whole, the CBMC method inserts chains part by part biasing the growth process towards energetically favorable configurations, and therefore significantly reduces overlap with the framework and other particles. The CBMC framework is based on the work by Rosenbluth and Rosenbluth [94] and developed by a variety of researchers [119–125]. Later, CBMC was extended to include grow paths for branched molecules [3, 72, 126–129], cyclic molecules [130–134], and reactive CBMC [135].

Growing a chain-molecule Let's first tackle the problem of how to generate a molecule with an appropriate intra-molecular energy (bond, bend, torsion). We can choose any of the atoms as a start point. Let's assume we start our growth process from atom 4 (the labeling is defined in Figure 1.4). The starting atom is connected to atom 0, 5, 6, and 7. One of these can be chosen randomly, for example atom 7. The position of atom 7 lies on a sphere with a radius depending on the bond-length distribution (Figure 1.5a), and is determined by computing a random vector on a unit sphere adjusted in length for the bond-potential. The chosen bond-length can either be generate using an "acceptance-rejection" scheme or using a small MC routine. Having grown atom 4 and 7 one can continue to grow on either side but let's assume we continue along the atom 7 path. Atom 7 is connected to atom 4 (already grown) and atoms 8, 9 and 13. Vlugt et al. noted that atoms 8, 9 and 13 must be grown simultaneously [126, 136]. It would be wrong to first place atom 13, next atom 8, and then atom 9. Because of the bond-bending potentials the branches connected to the same central atom can not be added independently. Vlugt *et al.* developed an MC procedure that can be used to generate the positions of the branch atoms using the following moves:



Figure 1.4: S2-butanol: the OPLS definition has 14 bond-, 25 bend-, and 30 torsion potentials. The chiral center is atom 7.



Figure 1.5: View of (branched) molecule growth: (a) bonds are grown by choosing random positions on a sphere; (b,c,d) bond-lengths and bend-angles between atoms of a branch are changed by a small MC-routine that (b) atoms are displaced along the bond vectors, (c) change of bend-angles, and (d) rotation around axis of the bond that was already grown.

1. Changing the bond-length One of the branch atom is randomly chosen and an attempt to change the bond-length is made (see Figure 1.5b). The probability of generating a branch position **b** with bond-length l is given by

$$P(l) dl = e^{-\beta u^{\text{bond}}(l)} d\mathbf{b}$$
(1.43)

$$= l^2 e^{-\beta u^{\text{bond}}(l)} dl \tag{1.44}$$

and the acceptance rule for a change in bond-length of l(n) to l(o) is

$$P_{\rm acc}\left(o \to n\right) = \min\left(1, \frac{l\left(n\right)}{l\left(o\right)}e^{-\beta\left(u^{\rm bond}\left(l\left(n\right)\right) - u^{\rm bond}\left(l\left(o\right)\right)\right)}\right)$$
(1.45)

2. Changing the bend-angle

One of the branch atom is randomly chosen and an attempt to change the bend-angle is made (see Figure 1.5c). The probability of generating a branch position **b** with bend-angle θ is given by

$$P(\theta) \ d\theta = e^{-\beta u^{\text{bend}}(\theta)} \ d\mathbf{b}$$
(1.46)

$$=\sin\left(\theta\right)e^{-\beta u^{\text{bend}}\left(\theta\right)}d\theta\tag{1.47}$$

and the acceptance rule for a change in bend-angle from $\theta(o)$ to $\theta(n)$ is

$$P_{\rm acc}\left(o \to n\right) = \min\left(1, \frac{\sin\left(\theta\left(n\right)\right)}{\sin\left(\theta\left(o\right)\right)}e^{-\beta\left(u^{\rm bend}\left(\theta\left(n\right)\right) - u^{\rm bend}\left(\theta\left(o\right)\right)\right)}\right)$$
(1.48)

3. Rotation on a cone

One of the branch atom is randomly chosen and rotated randomly on a cone (see Figure 1.5d). This move changes the bend-angle between the branch atoms. The acceptance rule for a rotation on a cone is

$$P_{\rm acc}\left(o \to n\right) = \min\left(1, e^{-\beta\left(u^{\rm bend}(\theta(n)) - u^{\rm bend}(\theta(o))\right)}\right) \tag{1.49}$$

A few hundred of these moves should be sufficient to equilibrate the positions of the branch atoms. The growing scheme of Vlugt *et al.* is able to handle stiff bondand bend-potentials. Another advantage is that it is easy to include chirality. If a wrong chirality is detected during the small MC scheme, then two branch atoms are switched, followed by further equilibration.

The scheme of Vlugt *et al.* handled torsion potentials by including the torsion energy $u^{\text{torsion}}(\phi)$ in Eq. 1.49. Unfortunately, this method still fails to generate the proper distribution when there are multiple torsional angles that share the same two central atoms because the bond bending and torsional angle distributions are no longer independent. Vlugt *et al.* modified the force field for branched alkanes such that only one torsion potential was defined over a central bond. For multiple torsion over a central bond all of the atoms connected to those central atoms must be generated simultaneously in order to get the correct distribution. This implies that the conformation of e.g. the entire 2,3-dimethylbutane molecule must be generated in a single step in order to obtain the correct distribution. One of the methods developed to solve this problem is the coupled-decoupled CBMC algorithm of Martin and Siepmann[127, 129].

The bond angles are selected based solely on the bond angle energies and the phase space terms, and then those angles are used in all subsequent selections (torsion and non-bonded). Thus, the bond angle selection is decoupled from the other selections. In contrast, for each non-bonded trial a full selection is done to generate torsional angles so these two selections are coupled. Before explaining this further, let's see how to actually increase acceptance of insertion using more than one set of "trail-positions".

Trial-positions So far we have shown how to generate a molecule. In order to be able to steer (to "bias") the growth, at each step k sets of branch atoms called "trial positions" are generated of which one is chosen with the appropriate probability. The growth-control is largely based on the "external" environment of the molecule, for example, the framework and/or other molecules that are present in the system. In the CBMC scheme it is therefore convenient to split the total potential energy U of a trial site into two parts:

$$U = U^{\text{int}} + U^{\text{ext}}.$$
(1.50)

The first term U^{int} represents the internal (bonded) potential, and is used for the generation of trial orientations. The second term U^{ext} represents the external (non-bonded) potential, and is used to bias the selection of a set from the other set of trial sites. This bias is exactly removed by adjusting the acceptance rules. In the CBMC technique a molecule is grown segment-by-segment. For each segment a set of k trial orientations is generated according to the internal energy U_i^{int} and the external energy $U_i^{\text{ext}}(j)$ of each set of trial positions j of segment i is computed. The number of trial positions k is usually between 10 and 20. One of these trial positions is selected with a probability

$$P_{i}(j) = \frac{e^{-\beta U_{i}^{\text{ext}}(j)}}{\sum_{l=1}^{k} e^{-\beta U_{i}^{\text{ext}}(l)}} = \frac{e^{-\beta U_{i}^{\text{ext}}(j)}}{w(i)}.$$
(1.51)

and added to the chain. This procedure is repeated until the whole molecule has been grown. Then the new *Rosenbluth factor* W^{new} is computed for the newly grown molecule

$$W^{\text{new}} = \prod_{i} w(i). \tag{1.52}$$

For the computation of the old Rosenbluth factor W^{old} , because there is already an existing chain, only k - 1 trial positions need to be generated. Together with the existing position, these form the set of k trial positions. **Chemical potential reference state** The excess chemical potential μ^{ex} is defined as the difference in chemical potential of the interacting chain and a chain in the ideal gas state. The Rosenbluth weight $\langle W^{\text{IG}} \rangle$ of the reference state of the ideal gas is needed when comparing with real experimental data. When CBMC is used, it is straightforward to show that $e^{-\beta\Delta U}$ has to be replaced by $\frac{W(\text{new chain})}{W(\text{IG})}$ for inserting a particle and by $\frac{W(\text{IG})}{W(\text{old chain})}$ for the deletion of a particle. When W^{IG} is replaced by $\langle W^{\text{IG}} \rangle$, *i.e.* the *average* Rosenbluth weight of a chain in the reservoir, detailed balance is obeyed. This means that for a given temperature and molecule $\langle W^{\text{IG}} \rangle$ has to be computed only *once* [136].

The reference state is important and enters e.g. in the acceptance rules for CBMC insertion and deletion moves:

$$P_{\rm acc}(o \to n) = P_{\rm acc}(N \to N+1) = \min\left(1, \frac{f\beta V}{N+1} \frac{W^{\rm new}}{\langle W^{\rm IG} \rangle}\right)$$
(1.53)

$$P_{\rm acc}(o \to n) = P_{\rm acc}(N \to N-1) = \min\left(1, \frac{N}{f\beta V} \frac{\langle W^{\rm IG} \rangle}{W^{\rm old}}\right)$$
(1.54)

It is best practice to compute $\langle W^{\rm IG} \rangle$ in advance, but for single components the results can also be corrected afterwards for the ideal Rosenbluth weight by "correcting" the fugacity. This is much more cumbersome for mixtures because both partial fugacities are changed and the initial imposed mol-fraction is now different, *i.e.* an equimolar mixture would no longer be equi-molar after correcting. For these reasons it is important to compute $\langle W^{\rm IG} \rangle$ first.

1.5.4 Continuous Fractional Component Monte Carlo

All open-ensembles methods suffer from a major drawback: the insertion probability becomes vanishingly low at high densities. One of the schemes to remedy this problem is the "Continuous Fractional Component Monte Carlo" (CFCMC) method of Shi *et al.* [137–139]. In this method the system is expanded with an additional molecule whose interaction strength with its surroundings is scaled using a parameter λ , here on referred to as a *fractional molecule*. Other methods have been proposed before that make use of "small" molecules to enhance the insertion probability, for example the Inflating-Flea method by de Pablo *et al.* [85], but what makes CFCMC powerful is that the transition from a fractional molecule to a fully interacting molecule is done continuously.

Various choices for the scaling are possible, for example the Lennard-Jones and

charge-charge interactions can be scaled as

$$u_{\rm LJ}(r) = \lambda 4\epsilon \left[\frac{1}{\left[\frac{1}{2} \left(1 - \lambda\right)^2 + \left(\frac{r}{\sigma}\right)^6\right]^2} - \frac{1}{\left[\frac{1}{2} \left(1 - \lambda\right)^2 + \left(\frac{r}{\sigma}\right)^6\right]} \right]$$
(1.55)

$$u_{\rm Coul} = \lambda^5 \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r} \tag{1.56}$$

where ϵ_0 is the dielectric constant in vacuum, r is the interatomic distance, q is the atomic charge, ϵ is the LJ strength parameter and σ is the LJ size parameter.

The modified form forces the potential to remain finite when $r \to 0$ for $\lambda \neq 1$. The scaled potential has the correct behavior at the limits of $\lambda = 0$ and $\lambda = 1$. Note that only the inter-molecular energy is scaled (not the intra-molecular energy). Many variations on the algorithm are possible. For example λ can be changed per molecule or per atom. Both method slowly "inflate" and "deflate" the molecule like a balloon but differently.

CFCMC uses conventional MC for thermalization (such as translation and rotation moves, and/or MC-MD hybrid moves), but in addition attempts to change the scaling parameter λ of the fractional molecule using $\lambda_n = \lambda_o + \Delta \lambda$ are used. The $\Delta \lambda$ is chosen uniformly between $-\Delta \lambda_{\max}$ and $+\Delta \lambda_{\max}$ and scaled to achieve around 50% acceptance. Many systems show behavior where λ -changes are hard. In these cases, an additional bias η on λ can be used, where each λ has an associated biasing factor η . This bias will be removed by the acceptance rules. A careful calibration of η can make the λ -histograms flat and hence can avoid that the system get stuck in certain λ -range. There are three possible outcomes of a change of λ_o to λ_n :

• λ_n remains between 0 and 1.

The change in energy of the particle with the new λ_n compared to the old energy is computed and the move is accepted using

$$P_{\rm acc} = \min\left(1, e^{-\beta \left[U^{\rm ext}(n) - U^{\rm ext}(o)\right] + \eta(\lambda_n) - \eta(\lambda_o)}\right) \tag{1.57}$$

There is no change in the number of particle, nor in the positions, nor in the intra-molecular energies. Only λ and the inter-molecular energy has changed.

• λ_n becomes larger than 1.

When $\lambda_n \geq 1$, the current fractional molecule is made fully present ($\lambda = 1$), and additional particle is randomly inserted with $\lambda = \lambda_n - 1$. Shi *et al.* used a methodology where a rigid conformation is chosen from a "reservoir" of ideal gas molecules generated "on the fly" during the simulation.

• λ_n becomes smaller than 0.

When $\lambda_n \leq 0$, the current fractional molecule is removed from the system $(\lambda = 0)$, and a new fractional molecule is chosen with $\lambda = \lambda_n + 1$.

The acceptance rules for insertion and deletion depend on the ensemble. For use in the grand-canonical ensemble the rules are given by

$$P_{\rm acc}\left(N \to N+1\right) = \min\left(1, \frac{f\beta V}{N+1}e^{\eta(\lambda_n-1)-\eta(\lambda_o)}e^{-\beta\left[U^{\rm ext}(n)-U^{\rm ext}(o)\right]}\right) \quad (1.58)$$

$$P_{\rm acc}\left(N \to N-1\right) = \min\left(1, \frac{N}{f\beta V}e^{\eta(\lambda_n+1)-\eta(\lambda_o)}e^{-\beta\left[U^{\rm ext}(n)-U^{\rm ext}(o)\right]}\right)$$
(1.59)

where N is number of *integer* molecules. Hence, appropriate measured densities and loadings should exclude the fractional molecule.

A downside of CFCMC compared to CBMC is that it takes longer to equilibrate at lower densities. Only at $\lambda = 0$ or $\lambda = 1$ an attempt is made to delete or insert a molecule respectively. Even when the λ moves are made equally likely using biasing, the diffusive nature of λ in the range $0, \ldots, 1$ makes the insertion/deletion rate lower. For this reason, Shi *et al.* used a relatively high percentage of λ -moves in comparison to the other MC moves. A practical way of overcoming this (small) issue is to first use CBMC or restart from a CBMC simulation.

The nature of the CFCMC algorithm can lead to blocking issues. For example, in CFCMC the potentials are scaled such that particle can overlap. Shi *et al.* [137] noted that for water models the lack of Van der Waals interaction for the hydrogens lead to overlap of the negatively charged oxygen with the positively charged hydrogen. The repulsive force that normally prevents this has been reduced by the potential scaling. A simple solution is to reject all MC moves where atoms get closer than 1 Å [137].

Wang-Landau sampling The Wang-Landau sampling method [140–146] has the objective of making all energies equally probable. During a random walk, the weights are iteratively adjusted using importance sampling. The weights that achieve a flat histogram are reciprocal to the density of states $\omega(E)$. The precision by which the weights are adjusted is iteratively increased until the desired precision is reached. The algorithm proceeds as follows:

- 1. Choose a set of energy ranges and set the density of states $\omega(E)$ to unity in each.
- 2. Start random walk in energy space. The acceptance probability is given by:

$$P_{\rm acc}\left(E_1 \to E_2\right) = \min\left[1, \frac{\omega\left(E_1\right)}{\omega\left(E_2\right)}\right] \tag{1.60}$$

The move is initially accepted with unity probability. Each time an energy level is visited, the corresponding density of states is updated by multiplying it's existing value by a modification factor f > 1.

3. Do the random walk until the accumulated histogram of energy is flat.

4. Reset the histogram and reduce the modification factor to continue and converge the $\omega(E)$.

The main drawback of the method is that the statistics to estimate the convergence of the weight update factors are iteratively obtained. If the Wang-Landau technique is employed for systems with an infinite energy range, such as fluids, one often has to choose a finite range of energy (cutting off the high-energy range) either via trial and error or by calculation.

Shi *et al.* found that Wang-Landau sampling is very efficient in obtaining the biasing factors for CFCMC [137–139]. The λ range is for example divided in 10 bins. Initially all biasing factors are zero. During equilibration the bin corresponding to the current λ is modified according to $\eta(\lambda_j) = \eta(\lambda_j) - \nu$ after an MC move attempt, where ν is a scaling parameter initially set to 0.01. Histograms are measured and every 10000 attempts the histograms are checked for flatness. The histogram is considered sufficiently flat when all bins are at least 30% as often visited as the most visited bin. If so, then histograms are set to zero and the scaling factor is modified to $\nu = \frac{1}{2}\nu$. Equilibration of η can be stopped once the value of ν is lower than 1×10^{-6} .

One of the downsides of CFCMC is that molecules are randomly inserted with configurations from the ideal gas distribution. For highly confined systems or systems with strong and directional interactions, this leads to still not high enough insertion probabilities. For example, Shi *et al.* [138], found that for the simulation of water in the Gibbs ensemble (at low temperatures), the exchange trial move is accepted in only around 1% of the attempts. With this in mind, the Configurational Bias Continuous Fractional Component Monte Carlo (CB/CFCMC) method was developed [147]. In this method the strengths of CBMC and CFCMC are combined to enhance the insertion/deletion of molecules.

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CHAPTER 2

Development of CB/CFCMC: a comparison of CBMC and CFCMC methods*

2.1 Introduction

When studying adsorption properties of solid materials, we are interested in the amount of molecules adsorbed (e.q. in units of mol/kg) as a function of the pressure and temperature. At experimental conditions, the pressure and temperature are fixed and for a specific material the loading (e.q. in units of mol/kg) is measured. Computational studies, usually using Monte Carlo (MC) simulations, mimic this situation by attempting to insert and delete particles into and from the system in the grand-canonical ensemble or μ, V, T ensemble [1–3]. In this ensemble, the chemical potential μ , the volume V and the temperature T are fixed. The fixed volume V is determined by the density and extend of the crystal structure of the studied material and the chemical potential μ can be directly related to the fugacity, which is obtained using an equation of state from the pressure. Because the chemical potential is fixed, the number of molecules fluctuates. Therefore, the property that is computed is the average number of molecules per unit of volume. A system where the number of molecules varies is called an *open system*. All openensembles methods so far suffer from a major drawback: the probability that an insertion/deletion is accepted becomes vanishingly low at higher densities due to overlaps with the host structure and/or molecules that are already adsorbed. This makes it e.g. difficult to accurately compute the maximum loading of molecules in a structure (which is required in theoretical models like the Langmuir model).

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To increase the number of successfully inserted molecules, the Configurational-Bias Monte Carlo (CBMC) technique was developed [2, 4, 5]. In CBMC, instead of generating ideal gas configurations and trying to insert the molecule as a whole, chains are inserted segment by segment where the growth process is biased towards energetically favorable configurations. The scheme is therefore able to avoid (or at least reduce the amount of) configurations that overlap with the framework and other particles. This scheme also works for configurations of long molecules which become increasingly different from the gas phase as a function of chain length.

The CBMC method starts to have problems at medium densities and fails at high densities [3]. A new scheme to remedy this problem is the "Continuous Fractional Component Monte Carlo" (CFCMC) method of Shi and Maginn [6-8]. In this method the system is expanded with a single "fractional" molecule per component type that has a scaled interaction with the other molecules and with the framework. The scaling parameter λ ranges from 0 to 1, with $\lambda = 0$ meaning the molecule is not felt by the surroundings (*i.e.* the host structure and the remaining molecules), while $\lambda = 1$ means the molecule is fully present and the interactions with the surrounding are at full strength. In addition to the usual set of MC moves, moves are now also performed on λ , attempting to increase and decrease it. Effectively, increasing λ corresponds to "inflating" the molecule, and decreasing λ corresponds to "deflating" the molecule. A change of λ larger than 1 leads to insertion of a new chain. The fractional molecule is made integer, and a new molecule is randomly inserted into the system with the remainder of λ . This is the new fractional molecule. Similarly, a decrease of λ below zero leads to a deletion of a molecule. Further details will be provided in the methodology section. The crucial point to note here, however, is that the λ moves can be biased, ideally making the λ -histogram flat. The method therefore is able to force molecules in and out of the system, thereby allowing the open ensemble to be efficiently implemented in a simulation.

There are few papers investigating the use of CFCMC for adsorption simulations. In Ref. [3] we previously showed excellent agreement between CFCMC and CBMC for a few simple cases: single component adsorption isotherms of small guest molecules in several zeolites and MOFs. In this work, we compare the CFCMC and CBMC in more complex scenarios: alkanes in Fe₂(BDP)₃, adsorption of small rigid guest molecules in MgMOF-74 and xylenes in MTW-type zeolite. In addition, we show that the methods are easily combined in a CB/CFCMC hybrid method. We evaluate this method with simulations in the grand-canonical and Gibbs ensemble. The algorithms are implemented in our in-house RASPA code [9]. We will show that CFCMC is a very significant improvement over conventional MC and even over CBMC.

2.2 Methodology

2.2.1 Configurational-Bias Monte Carlo (CBMC)

In the CBMC scheme molecule's insertions and deletions are biased towards favourable configurations by growing them segment-by-segment.

The acceptance rules for CBMC insertion and deletion moves in the grandcanonical ensemble are given by [2]

$$P_{\rm acc}(N \to N+1) = \min\left(1, \frac{f\beta V}{N+1} \frac{W^{\rm new}}{\langle W^{\rm IG} \rangle}\right)$$
(2.1)

$$P_{\rm acc}(N \to N-1) = \min\left(1, \frac{N}{f\beta V} \frac{\langle W^{\rm IG} \rangle}{W^{\rm old}}\right)$$
(2.2)

in which W^{new} is the Rosenbluth factor of the new configuration, W^{old} is the Rosenbluth factor of the old configuration, $\langle W^{\text{IG}} \rangle$ is the average Rosenbluth factor of an isolated molecule in the gas phase, f is the fugacity, V the volume and N the number of molecules. The pressures and fugacities are related via the equation of state of the gas phase.

Besides insertions and deletions, translations, rotations and full and partial reinsertions moves are used. For mixtures, especially at higher density, the "identityswitch" move becomes crucial. The identity-change trial move [10–13] is called semi-grand ensemble. In this move one of the components is randomly selected and an attempt to change its identity (to an other species) is performed. The acceptance rule is given by [10, 13]

$$P_{\rm acc} \left(\mathbf{A} \to \mathbf{B} \right) = \min \left(1, \frac{W^{\rm new} f_B \left\langle W_A^{\rm IG} \right\rangle N_A}{W^{\rm old} f_A \left\langle W_B^{\rm IG} \right\rangle (N_B + 1)} \right), \tag{2.3}$$

where f_A and f_B are the fugacities of components A and B, and N_A and N_B are the number of particles.

2.2.2 Continuous Fractional Component Monte Carlo (CFCMC)

CFCMC was developed by Shi and Maginn [6] inspired by a group of schemes known as "expanded ensembles" [14, 15]. In this method the system is expanded with an additional molecule which interactions with the surrounding molecules are scaled using a parameter λ .

Molecules are inserted and deleted by performing a random walk in λ -space using $\lambda_n = \lambda_o + \Delta \lambda$. The value of $\Delta \lambda$ is chosen uniformly between $-\Delta \lambda_{\max}$ and $+\Delta \lambda_{\max}$ and adjusted to achieve approximately 50% acceptance. In many systems λ -changes are difficult [3, 6, 7] because in the Boltzmann ensemble the distribution of λ can go through a deep minimum. An additional bias η on λ can be used, where each state of λ has an associated biasing factor η . There are three possible outcomes of a change from λ_o to λ_n :

- 1. λ_n remains between 0 and 1.
- 2. λ_n becomes larger than 1 (a molecule is fully inserted).
- 3. λ_n become smaller than 0 (a molecule is deleted).

The reader is referred to chapter 1 for details on the moves and acceptance criteria.

The CFCMC method is able to force molecules into and out of the system. If the molecule is too quickly removed after insertion then nothing is gained. The environment should be able to adjust to the new insertion and equilibrate properly. The adjustment is also called thermalization. CFCMC uses conventional MC moves such as translation, rotation, and/or MC-MD hybrid moves for thermalization. In our implementation we also use (partial-)reinsertion moves using configurational biasing (identical to CBMC), for both integer molecules and the fractional molecules. The insertion of an additional molecule is already biased using λ -biasing and as soon as the molecule is present in the system the reinsertion is able to efficiently move the molecules around in the system. For mixtures, we use the identity-switch move but only on integer molecules because each component should always have one and only one fractional molecule.

2.2.3 CB/CFCMC

The insertion and deletion scheme of CFCMC can in certain cases be improved by 'fractionally' growing and retracing a molecule at a fixed λ using CBMC. In this method, new chains are inserted and old chains are removed using configurational biasing at constant λ values. When $\lambda = 1$ or $\lambda = 0$ the algorithm reduces to conventional CBMC for insertion and deletion, respectively. When the number of trials is equal to one, it reduces to CFCMC.

Deriving the Acceptance Rules for CB/CFCMC in the Gibbs ensemble

In the Gibbs ensemble, two simulation boxes are in equilibrium with each other. The two boxes are denoted by '1' and '2' respectively. The equilibrium conditions are $\mu_1 = \mu_2$, $P_1 = P_2$, $\beta_1 = \beta_2$, where μ_i is the chemical potential of molecules in box *i*, P_i is the pressure and $\beta = 1/(k_B T)$. Let N_t denote the total number of molecules in the system, N_1, N_2 the number of molecules in the two phases/boxes, V_1, V_2 the volumes of the boxes 1 and 2 respectively and V_t the total volume ($V_t = V_1 + V_2$). The partition function for the conventional Gibbs ensemble is given by [2],

$$Q(N_t, V_1, V_2, T) = \sum_{N_1=0}^{N_t} \frac{1}{\Lambda^{3N_t} N_1! N_2! V_t} \int_0^{V_t} dV_1 V_1^{N_1} (V_t - V_2)^{N_2} \\ \times \int d\mathbf{s}_2^{N_2} \exp[-\beta U_2(s_2^{N_2})] \int d\mathbf{s}_1^{N_1} \exp[-\beta U_1(\mathbf{s}_1^{N_1})] \qquad (2.4)$$

where $\mathbf{s}_1^{N_1}, \mathbf{s}_2^{N_2}$ are the configurations of all molecules in boxes 1 and 2 respectively and $U_1(\mathbf{s}_1^{N_1}), U_2(\mathbf{s}_2^{N_2})$ are the total potential energies of the molecules in boxes 1 and 2. Before deriving the acceptance rules for CB/CFCMC (which uses configurational-bias on a fractional molecule), we need to derive the acceptance rules after the inclusion of a fractional molecule (CFCMC).

CFCMC: For the Continuous Fractional Component Gibbs ensemble, we introduce one fractional molecule in each of the two boxes. The fractional molecule in each box is denoted by $N_{f,1}, N_{f,2}$. λ is constrained by $\lambda_1 + \lambda_2 = 1$ where λ_1 and λ_2 refer to the λ in the simulation boxes 1 and 2 respectively. Henceforth, the coupling parameter will be denoted by λ only and it will specifically refer to box 1. Therefore the coupling parameter for the fractional molecule inside box 2 is denoted by $1 - \lambda$. The potential energies of the boxes 1 and 2 are now denoted as $U_1(\mathbf{s}_1^{N_1,N_{f,1}},\lambda)$ and $U_2(\mathbf{s}_2^{N_2,N_{f,2}},1-\lambda)$ respectively. The CFCMC scheme now includes trial moves that change λ . The partition function for this system is given by [7]

$$Q_{\rm CFCMC} = Q(N_t, V_1, V_2, T) = \int_0^1 d\lambda \sum_0^{N_t} \frac{1}{V_t} \int_0^{V_t} dV_1 \times Z_{\rm CFCMC}$$
(2.5)

where $Z_{\text{CFCMC}} = Z(N_1, N_2, V_1, V_2, N_{f,1}, N_{f,2}, \lambda, T)$ and is given by

$$Z_{\text{CFCMC}} = \frac{V_1^{N_1+1}V_2^{N_2+1}}{\Lambda^{3N_t}N_1!N_2!} \times \int d\mathbf{s}_2^{N_2,N_{f,2}} \exp[-\beta U_2(\mathbf{s}_2^{N_2,N_{f,2}}, 1-\lambda)] \times \int d\mathbf{s}_1^{N_1,N_{f,1}} \exp[-\beta U_1(\mathbf{s}_1^{N_1,N_{f,1}},\lambda)]$$
(2.6)

It is highly beneficial to have a MC scheme where the changes in λ are governed by a flat probability. Suitable biasing factors $\eta(\lambda)$ can be introduced to improve the probability of transitions in λ . The biasing factors can be calculated on the fly using the Wang-Landau method [16]. The partition function including the biasing factors for box 1, $\eta(\lambda)$, can now be expressed as

$$Q_{\text{CFCMC-biased}} = \int_0^1 d\lambda \sum_{0}^{N_t} \sum_{j=0}^M \frac{1}{V_t} \int_0^{V_t} dV_1 \exp[\eta_j(\lambda)] \times Z_{\text{CFCMC-biased}}$$
(2.7)

where $Z_{\text{CFCMC-biased}} = Z_{CFCMC}$ and M is the number of bins λ -space is divided into to compute the biasing factors. From here on $Q_{\text{CFCMC-biased}}$ will be denoted as Q_{biased} for convenience. The probability of the system to exist in a certain state m is given by

$$p_m = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_1^{N_1+1}V_2^{N_2+1}}{\Lambda^{3N_t}N_1!N_2!V_t} \exp[-\beta(U_1(\mathbf{s}_1^{N_1,N_{f,1}},\lambda) + U_2(\mathbf{s}_2^{N_2,N_{f,2}},1-\lambda)) + \eta(\lambda)]$$
(2.8)

In Gibbs ensemble Monte Carlo simulations, there are three possible Monte Carlo moves:

- 1. Change the position or orientation of a randomly selected molecule in a randomly selected box (either a whole or a fractional molecule)
- 2. Change the volume of the boxes while keeping the total volume constant
- 3. Change the coupling parameter λ The change in λ can be further divided into 3 cases (λ_n being the value of λ in the new configuration and λ_o being the value of λ in the old configuration):

(a)
$$0 < \lambda_n < 1$$

(b) $\lambda_n < 0$
(c) $\lambda_n > 1$.

For the displacement or rotation move, a random molecule (a whole or the fractional molecule) is chosen and a random displacement (or rotation) is performed for the chosen molecule. The old state is denoted by o and the new state is denoted by n. The probabilities to exist in states o and n are given by:

$$p_{o} = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_{1,o}^{N_{1,o}+1}V_{2,o}^{N_{2,o}+1}}{\Lambda^{3N_{t}}N_{1,o}!N_{2,o}!V_{t}} \exp[-\beta(U_{1,o}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{o}) + U_{2,o}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{o})) + \eta(\lambda_{o})]$$

$$(2.9)$$

$$p_n = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_{1,o}^{N_1,o+1} V_{2,o}^{N_2,o+1}}{\Lambda^{3N_t} N_{1,o}! N_{2,o}! V_t} \exp[-\beta (U_{1,n}(\mathbf{s}_1^{N_1,N_{f,1}},\lambda_n) + U_{2,n}(\mathbf{s}_2^{N_2,N_{f,2}},1-\lambda_n)) + \eta(\lambda_n)]$$
(2.10)

Since we are not performing a change in λ , the bias factors are equal: $\lambda_o = \lambda_n$. The acceptance rule is therefore given by

$$P_{\rm acc}(o \to n) = \min(1, \exp[-\beta(U_{1,n}(\mathbf{s}_1^{N_1, N_{f,1}}, \lambda_n) + U_{2,n}(\mathbf{s}_2^{N_2, N_{f,2}}, 1 - \lambda_n) - U_{1,o}(\mathbf{s}_1^{N_1, N_{f,1}}, \lambda_o) - U_{2,o}(\mathbf{s}_2^{N_2, N_{f,2}}, 1 - \lambda_o))])$$
(2.11)

For the volume change move, one of the simulation boxes is chosen randomly and a random walk is performed in $\ln(V_1/V_2)$. This has the advantages that the domain of the random walk coincides with all the possible values of V_1 and the maximum

volume change turns out to be less sensitive to the density [2]. The probabilities to be in the old and new configurations are given by

$$p_{o} = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_{1,o}^{N_{1,o}+2}V_{2,o}^{N_{2,o}+2}}{\Lambda^{3N_{t}}N_{1,o}!N_{2,o}!V_{t}} \exp[-\beta(U_{1,o}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{o}) + U_{2,o}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{o})) + \eta(\lambda_{o})]$$

$$(2.12)$$

$$p_n = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_{1,n}^{1,0} \cdot V_{2,n}^{1,0}}{\Lambda^{3N_t} N_{1,0}! N_{2,0}! V_t} \exp[-\beta (U_{1,n}(\mathbf{s}_1^{N_1,N_{f,1}},\lambda_n) + U_{2,n}(\mathbf{s}_2^{N_2,N_{f,2}},1-\lambda_n)) + \eta(\lambda_n)]$$
(2.13)

As λ does not depend on the volume, we have $\lambda_o = \lambda_n$ and the acceptance rule becomes

$$P_{\rm acc}(o \to n) = \min\left(1, \frac{V_{1,n}^{N_{1,o}+2}V_{2,n}^{N_{2,o}+2}}{V_{1,o}^{N_{1,o}+2}V_{2,o}^{N_{2,o}+2}}\exp[-\beta(U_{1,n}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{n}) + U_{2,n}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{n}) - U_{1,o}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{o}) - U_{2,o}(s_{2}^{N_{2},N_{f,2}},1-\lambda_{o}))]\right)$$

$$(2.14)$$

In the λ change move, the λ is changed by an amount $\Delta\lambda$: if λ_o and λ_n refer to the value of λ in the old and new configurations respectively then $\lambda_n = \lambda_0 + \Delta\lambda$. When $0 < \lambda_n < 1$, the pseudocoupling parameter increases/decreases. The probabilities of existing in the old and new configurations are given by

$$p_{o} = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_{1,o}^{N_{1,o}+1}V_{2,o}^{N_{2,o}+1}}{\Lambda^{3N_{t}}N_{1,o}!N_{2,o}!V_{t}} \exp[-\beta(U_{1,o}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{o}) + U_{2,o}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{o})) + \eta(\lambda_{o})]$$

$$(2.15)$$

$$p_{n} = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_{1,o}^{N_{1,o}+1}V_{2,o}^{N_{2,o}+1}}{\Lambda^{3N_{t}}N_{1,o}!N_{2,o}!V_{t}} \exp[-\beta(U_{1,n}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{n}) + U_{2,n}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{n})) + \eta(\lambda_{n})]$$

As the number of molecules in each box is the same for the old and new configurations, the acceptance criterion becomes

$$P_{\rm acc}(o \to n) = \min(1, \exp[-\beta(U_{1,n}(\mathbf{s}_1^{N_1, N_{f,1}}, \lambda_n) + U_{2,n}(\mathbf{s}_2^{N_2, N_{f,2}}, 1 - \lambda_n) - U_{1,o}(\mathbf{s}_1^{N_1, N_{f,1}}, \lambda_o) - U_{2,o}(\mathbf{s}_2^{N_2, N_{f,2}}, 1 - \lambda_o)) + \eta(\lambda_n) - \eta(\lambda_o)])$$
(2.17)

When $\lambda_n < 0$ or $\lambda_n > 1$, molecules are exchanged between the phases/boxes. First, λ_n is set according to $\lambda_n = \lambda_0 + \Delta \lambda$. If $\lambda_n > 1$, then we set $\lambda_n \to \lambda_n - 1$. If $\lambda_n < 0$, then we set $\lambda_n \to \lambda_n + 1$. We assume the molecule is transferred from box 2 to box 1 (the acceptance rule for the opposite transfer follows from a permutation of the labels of the boxes). In box 1, the existing fractional molecule is converted to a whole molecule and a new fractional molecule with λ_n is randomly inserted in the box. In box 2, the existing fractional molecule is deleted and a random whole molecule is chosen and converted to a new fractional molecule with $1 - \lambda_n$.

The probabilities of existing in a states o and n are given by,

$$p_{o} = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_{1,o}^{N_{1,o}+1}V_{2,o}^{N_{2,o}+1}}{\Lambda^{3N_{t}}N_{1,o}!N_{2,o}!V_{t}} \exp[-\beta(U_{1,o}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{o}) + U_{2,o}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{o})) + \eta(\lambda_{o})]$$

$$(2.18)$$

(2.16)

$$p_n = \frac{1}{Q_{\text{biased}}} \cdot \frac{V_{1,o}^{N_{1,o}+2} V_{2,o}^{N_{2,o}}}{\Lambda^{3N_t} (N_{1,o}+1)! (N_{2,o}-1)! V_t} \exp[-\beta (U_{1,n}(\mathbf{s}_1^{N_1+1,N_{f,1}},\lambda_n) + U_{2,n}(\mathbf{s}_2^{N_2-1,N_{f,2}},1-\lambda_n)) + \eta(\lambda_n)]$$
(2.19)

The acceptance rules for this particle swap move from box 2 to box 1 is therefore given by

$$P_{\rm acc}(o \to n) = \min\left(1, \frac{N_{2,o}}{N_{1,o}+1} \frac{V_{1,o}}{V_{2,o}} \exp\left[-\beta \left(U_{1,n}\left(\mathbf{s}_{1}^{N_{1}+1,N_{f,1}},\lambda_{n}\right) + U_{2,n}\left(\mathbf{s}_{2}^{N_{2}-1,N_{f,2}},1-\lambda_{n}\right)\right.\right.\right.$$
$$\left. - U_{1,o}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{o}) - U_{2,o}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{o})\right) + \eta(\lambda_{n}) - \eta(\lambda_{o})\right]\right)$$

CB/CFCMC: For dense systems, the random insertion/deletion of fractional molecule can be facilitated if we use the Configurational-Bias Monte Carlo scheme [2]. Instead of a random insertion of the fractional molecule, we grow the molecule atom by atom. We denote the intramolecular energies (bond-stretching, bond-bending, torsion) by $U_{\text{atom},i}^{\text{int}}$ and the intermolecular energies of the molecule with the surroundings by $U_{\text{atom},i}^{\text{ext}}(\lambda)$. Here *i* denotes the atom in consideration. We assume the molecule has *l* atoms. We assume that the molecule is transferred from box 2 to box 1. In box 1, the molecule is grown and in box 2 the molecule is retraced. We denote the state *o* for the old configuration of the molecule in box 2 and state *n* for the new configuration of the molecule in box 1. The procedure for the Configurational-Bias Monte Carlo move for inserting a fractional molecule for a new configuration *n* and λ_n is given as follows:

1. For the first atom, we generate k random trial positions. The Boltzmann factor of the first atom in trial position j' is given by $\exp[-\beta U_{\text{atom},1,j'}^{\text{ext}}(\lambda_n)]$. One trial configuration is selected from the k trial configurations with probability

$$p_{\text{atom},1}^{\text{ext}}(b_1) = \frac{\exp[-\beta U_{\text{atom},1,j'}^{\text{ext}}(b_1,\lambda_n)]}{\sum_{j'=1}^k \exp[-\beta U_{\text{atom},1,j'}^{\text{ext}}(b_1,\lambda_n)]}$$
(2.20)

The Rosenbluth factor for the first atom is given by:

$$w_{\text{atom},1}(n) = \frac{\sum_{j'=1}^{k} \exp[-\beta U_{\text{atom},1,j'}^{\text{ext}}(b_1,\lambda_n)]}{k}$$
(2.21)

2. To insert the next atom i, k trial orientations are randomly generated. These k trial orientations are denoted as a set by $\{b\}_k = b_1, b_2, ..., b_k$. The probability of generating a trial orientation b_j is given by,

$$p_{\text{atom},i}^{\text{int}}(b_j) = \frac{\exp[-\beta U_{\text{atom},i}^{\text{int}}(b_j)]}{\int \exp[-\beta U_{\text{atom},i}^{\text{int}}(b_j)] \mathrm{d}b_j} = \frac{\exp[-\beta U_{\text{atom},i}^{\text{int}}(b_j)]}{C_{\text{atom},i}}$$
(2.22)

where $C_{\text{atom},i}$ is the normalization constant.

For all the k trial orientations, we compute the external Boltzmann factors $\exp[-\beta U_i^{\text{ext}}(b_j, \lambda_n)]$ and select one trial conformation/orientation denoted by b_n with a probability given by,

$$p_{\text{atom},i}^{\text{ext}}(b_n) = \frac{\exp[-\beta U_{\text{atom},i}^{\text{ext}}(b_n, \lambda_n)]}{\sum\limits_{j=1}^k \exp[-\beta U_i^{\text{ext}}(b_j, \lambda_n)]} = \frac{\exp[-\beta U_{\text{atom},i}^{\text{ext}}(b_n, \lambda_n)]}{w_{\text{atom},i}(n)}$$
(2.23)

where the Rosenbluth factor for the ith atom is given by,

$$w_{\text{atom},i}(n) = \sum_{j=1}^{k} \exp[-\beta U_{\text{atom},i}^{\text{ext}}(b_j, \lambda_n)].$$
(2.24)

3. Step 2 is repeated for l-1 times until the entire molecule (with l atoms) is grown. The Rosenbluth factor for the entire molecule is given by,

$$W(n) = \prod_{i=1}^{l} w_{\text{atom},i}(n) = \prod_{i=1}^{l} \sum_{j=1}^{k} \exp[-\beta U_{\text{atom},i}^{\text{ext}}(b_j, \lambda_n)]$$
(2.25)

To calculate the Rosenbluth factor of the old configuration o in box 2, we have the following steps. Recall that for box 2, the coupling factor is $1 - \lambda_o$ in the old configuration (and $1 - \lambda_n$ in the new configuration):

- 1. The fractional particle is selected.
- 2. k-1 trial positions are generated. The energy and the Rosenbluth factor of the first atom for the k-1 trial positions and the existing position of the first atom is determined by

$$w_{\text{atom},1}(o) = \frac{\sum_{j'=1}^{k} \exp[-\beta U_{\text{atom},1,j'}^{\text{ext}}(b_1, 1 - \lambda_o)]}{k}$$
(2.26)

3. To determine the Rosenbluth factor for the other l-1 atoms, we generate k-1 trial positions. These k-1 trial positions along with the existing position of the *i*th atom of the fractional molecule will determine the set of k trial positions $\{b'\}_k = b'_1, b'_2, ..., b'_k$. The Rosenbluth factor for the *i*th atom is given by:

$$w_{\text{atom},i}(o) = \sum_{j=1}^{k} \exp\left[-\beta U_{\text{atom},i}^{\text{ext}}(b'_j, 1 - \lambda_o)\right].$$
 (2.27)

4. Repeat the above step for all the l atoms. The Rosenbluth factor for the entire molecule is given by:

$$W(o) = \prod_{i=1}^{l} w_{\text{atom},i}(o).$$
 (2.28)

For the insertion of the fractional molecule using CBMC in box 1, the probability of generating the chain of l atoms with a certain conformation n, $\alpha(o \rightarrow n)$, is the product of generating a trial configuration $(p_{\text{atom},i}^{\text{bond}}(n))$ and the probability of selecting that particular configuration $(p_{\text{atom},i}^{\text{ext}}(n))$ for all the l atoms in the molecule. The probability of generating a new conformation n for a molecule with l atoms is given by,

$$\alpha(o \to n) = \prod_{i=1}^{l} p_{\text{atom},i}(o \to n)$$
(2.29)

$$=\prod_{i=1}^{l} p_{\text{atom},i}^{\text{bond}}(n) p_{\text{atom},i}^{\text{ext}}(n)$$
(2.30)

Similarly, the probability of generating the old conformation o is given by,

$$\alpha(n \to o) = \prod_{i=1}^{l} p_{\text{atom},i}(n \to o)$$
(2.31)

$$=\prod_{i=1}^{l} p_{\text{atom},i}^{\text{bond}}(o) p_{\text{atom},i}^{\text{ext}}(o)$$
(2.32)

A given set of k trial orientations generated for the insertion, which includes the orientation n, is denoted by (b_n, b^*) . The term (b_o, b'^*) is the given set of additionally generated trial orientations around the old orientation o. The probability of generating the combined set of orientations (b^*, b'^*) is given by $P^{\text{bond}}(b^*, b'^*)$. From Eqs. (2.22), (2.23), (2.24) and (2.30), we find that the probability of generating the new conformer n is given by,

$$\alpha(o \to n, b^*, b'^*) = \prod_{i=1}^{l} \left(\frac{\exp[-\beta U_{\text{atom},i}^{\text{int}}(b_j)]}{C_{\text{atom},i}} \frac{\exp[-\beta U_{\text{atom},i}^{\text{ext}}(b_n, \lambda_n)]}{w_{\text{atom},i}(n)} P^{\text{bond}}(b^*, b'^*) \right)$$
(2.33)

We know that $\prod_{i=1}^{l} \exp[-\beta U_{\text{atom},i}^{\text{ext}}(b_n, \lambda_n)] = U_{1,\text{frac}}^{\text{ext}}(\mathbf{s}_1^{N_1+1,N_{f,1}}, \lambda_n)$. Substituting this expression and Eq. (2.25) in Eq. (2.33), we have,

$$\alpha(o \to n, b^*, b'^*) = \frac{\exp[-\beta(U_{1, \text{frac}}^{\text{ext}}(\mathbf{s}_1^{N_1+1, N_{f,1}}, \lambda_n))]}{W(n)} \prod_{i=1}^l \left(\frac{\exp[-\beta U_{\text{atom}, i}^{\text{int}}(b_j)]}{C} P^{\text{bond}}(b^*, b'^*)\right)$$
(2.34)

where C is the total normalization constant for all the beads given by $C = \prod_{i=0}^{l-1} C_{\text{atom},i}$. The probability to generate the old conformer o is given by,

$$\alpha(n \to o, b^{\prime *}, b^{*}) = \prod_{i=1}^{l} \left(\frac{\exp[-\beta U_{\operatorname{atom},i}^{\operatorname{int}}(b_{j}^{*})]}{C_{\operatorname{atom},i}} \frac{\exp[-\beta U_{\operatorname{atom},i}^{\operatorname{ext}}(b_{o}, 1-\lambda_{o})]}{w_{\operatorname{atom},i}(o)} P^{\operatorname{bond}}(b^{*}, b^{\prime *}) \right).$$

$$(2.35)$$

We know that $\prod_{i=1}^{l} \exp[-\beta U_{\text{atom},i}^{\text{ext}}(b_o, 1-\lambda_o)] = \exp[-\beta (U_{2,\text{frac}}^{\text{ext}}(\mathbf{s}_2^{N_2, N_{f,2}}, 1-\lambda_o))].$ Thus we have,

$$\alpha(n \to o, b^{\prime*}, b^*) = \frac{\exp(-\beta(U_{2,\text{frac}}^{\text{ext}}(\mathbf{s}_2^{N_2, N_f, 2}, 1 - \lambda_o)))}{W(o)} \prod_{i=1}^l \left(\frac{\exp[-\beta U_{\text{atom}, i}^{\text{int}}(b_j^*)]}{C} P^{\text{bond}}(b^*, b^{\prime*})\right).$$
(2.36)

Detailed balance states that the probabilities of generating all possible configurations for both states o and n must be the same. We impose super detailed balance, which states that for a particular set of trial orientations (b^*, b'^*) , detailed balance must hold [2]. This is given by,

$$p_o \times \alpha(o \to n, b^*, b'^*) \times \operatorname{acc}(o \to n, b^*, b'^*) = p_n \times \alpha(n \to o, b'^*, b^*) \times \operatorname{acc}(n \to o, b'^*, b^*)$$
(2.37)

Rearranging, we obtain,

$$\frac{\operatorname{acc}(o \to n, b^*, b'^*)}{\operatorname{acc}(n \to o, b'^*, b^*)} = \frac{p_n}{p_o} \frac{\alpha(n \to o, b'^*, b^*)}{\alpha(o \to n, b^*, b'^*)}$$
(2.38)

The probabilities of existing in the old and the new states are given by

$$\frac{p_n}{p_o} = \exp[-\beta(U_{1,n}(\mathbf{s}_1^{N_1+1,N_{f,1}},\lambda_n) + U_{2,n}(\mathbf{s}_2^{N_2-1,N_{f,2}},1-\lambda_n) - U_{1,o}(\mathbf{s}_1^{N_1,N_{f,1}},\lambda_o)$$

$$+U_{2,o}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{o})] \times \frac{N_{2,o}}{N_{1,o}+1} \frac{V_{1,o}}{V_{2,o}} \exp(\eta(\lambda_{n})-\eta(\lambda_{o}))$$
(2.39)

According to the MC move, in box 1 where the molecule is inserted, the new configuration includes the energy for converting the existing fractional molecule into a whole molecule $U_{1,f\to w}(\mathbf{s}_1^{N_1,N_{f,1}},\lambda_o)$ and the energy for inserting a new fractional molecule $U_{1,\text{frac}}(\mathbf{s}_1^{N_1+1,N_{f,1}},\lambda_n)$. We can write

$$U_{1,n}(\mathbf{s}_{1}^{N_{1}+1,N_{f,1}},\lambda_{n}) = U_{1,o}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{o}) + U_{1,f\to\mathbf{w}}(\mathbf{s}_{1}^{N_{1},N_{f,1}},\lambda_{o}) + U_{1,f\mathrm{rac}}(\mathbf{s}_{1}^{N_{1}+1,N_{f,1}},\lambda_{n}).$$
(2.40)

Likewise, in box 2 where the molecule is deleted, the new configuration includes the energy for deleting the existing fractional molecule $U_{2,\text{frac}}^{\text{ext}}(\mathbf{s}_2^{N_2,N_{f,2}}, 1 - \lambda_o)$

and the energy for converting a whole molecule into a fractional molecule $U_{2,w\to f}(\mathbf{s}_2^{N_2-1,N_{f,2}}, 1-\lambda_n).$

$$U_{2,n}(\mathbf{s}_{2}^{N_{2}-1,N_{f,2}},1-\lambda_{n}) = U_{2,o}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{o}) - U_{2,\text{frac}}^{\text{ext}}(\mathbf{s}_{2}^{N_{2},N_{f,2}},1-\lambda_{o}) - U_{2,\text{w}\to\text{f}}(\mathbf{s}_{2}^{N_{2}-1,N_{f,2}},1-\lambda_{n}).$$

$$(2.41)$$

Including these expressions in Eq. (2.42), we obtain,

$$\frac{p_n}{p_o} = \frac{N_{2,o}}{N_{1,o}+1} \frac{V_{1,o}}{V_{2,o}} \exp\left[-\beta (U_{1,f \to w}(\mathbf{s}_1^{N_1,N_{f,1}},\lambda_o) - U_{2,w \to f}(\mathbf{s}_2^{N_2-1,N_{f,2}},1-\lambda_n) + U_{1,\text{frac}}^{\text{ext}}(\mathbf{s}_1^{N_1+1,N_{f,1}},\lambda_n) - U_{2,\text{frac}}^{\text{ext}}(\mathbf{s}_2^{N_2,N_{f,2}},1-\lambda_o))\right] \exp(\eta(\lambda_n) - \eta(\lambda_o))$$

$$(2.42)$$

Substituting Eqs. (2.42), (2.34), (2.36) in Eq. (2.38), gives:

$$\frac{\operatorname{acc}(o \to n, b^*, b'^*)}{\operatorname{acc}(n \to o, b'^*, b^*)} = \frac{N_{2,o}}{N_{1,o} + 1} \frac{V_{1,o}}{V_{2,o}} \exp\left[-\beta \left(U_{1,f \to w}(\mathbf{s}_1^{N_1,N_{f,1}}, \lambda_o) - U_{2,w \to f}(\mathbf{s}_2^{N_2 - 1,N_{f,2}}, 1 - \lambda_n) + +U_{1,\mathrm{frac}}^{\mathrm{ext}}(\mathbf{s}_1^{N_1 + 1,N_{f,1}}, \lambda_n) - U_{2,\mathrm{frac}}^{\mathrm{ext}}(\mathbf{s}_2^{N_2,N_{f,2}}, 1 - \lambda_o)\right)\right] \exp(\eta(\lambda_n) - \eta(\lambda_o))$$

$$(2.43)$$

Therefore, the acceptance rule for the CB/CFCMC for the particle swap from box 2 to box 1 is given by,

$$P_{\rm acc}(o \to n, b^*, b'^*) = \min\left(1, \frac{N_{2,o}}{N_{1,o} + 1} \frac{V_{1,o}}{V_{2,o}} \frac{W(n)}{W(o)} \exp(-\beta (U_{1,f \to w}(\mathbf{s}_1^{N_1, N_{f,1}}, \lambda_o) - U_{2,w \to f}(\mathbf{s}_2^{N_2 - 1, N_{f,2}}, \lambda_n)) + (\eta(\lambda_n) - \eta(\lambda_o)))\right)$$
(2.44)

We can follow the same procedure for a particle swap from box 1 to box 2. From the above, we can see that CB/CFCMC obeys detailed balance and it is possible to carry out such a Monte Carlo move. One can easily see that for k = 1 (only one trial direction) the acceptance rule for particle exchange reduces to CFCMC in the Gibbs ensemble.

Application to the grand-canonical ensemble is straightforward and can be effected by taking one of the simulation boxes as an infinitely large reservoir of non-interacting chain molecules. The procedure for insertion/deletion attempts in the grand-canonical ensemble is
- insertion, $\lambda_n \geq 1$
 - 1. A new fractional molecule with $\lambda = \lambda_n 1$ is grown using CBMC giving W(n).
 - 2. Acceptance rule: $P_{\rm acc} = \min\left(1, \frac{f\beta V}{N+1} \frac{W(n)}{\langle W^{\rm IG} \rangle} \exp[-\beta \Delta U] \exp[\eta \left(\lambda_n - 1\right) - \eta \left(\lambda_o\right)]\right)$
- deletion, $\lambda_n \leq 0$
 - 1. An existing fractional particle is retraced using CBMC with $\lambda = \lambda_o$ giving W(o) and the fractional molecule is subsequently removed.
 - 2. Acceptance rule:

$$P_{\rm acc} = \min\left(1, \frac{N}{f\beta V} \frac{\langle W^{\rm IG} \rangle}{W(o)} \exp[-\beta \Delta U] \exp[\eta \left(\lambda_n + 1\right) - \eta \left(\lambda_o\right)]\right)$$

We tested the CB/CFCMC method by computing the single component and mixture adsorption isotherms of hexane isomers in $Fe_2(BDP)_3$ at 433 K (Figure 2.2). The isotherms computed using CB/CFCMC, CBMC and CFCMC are equivalent within statistical error.

2.3 Results

2.3.1 Alkanes in Fe₂(BDP)₃

The separation of linear, mono-branched, and di-branched isomers of alkanes is of significant importance in the petrochemical industry. This separation can be achieved by selective adsorption in ordered crystalline nanoporous materials such as zeolites, MOFs, COFs, and ZIFs by exploiting subtle differences in molecular configurations [17, 18]. The alkane separation efficiency is generally described by the molecule-wall effective distance [19]. Small pore structures like ZIF-77, MFI, and $Fe_2(BDP)_3$ [20] can show very large selectivities, but have a relatively small pore volume. This class of systems generally favor the adsorption of the linear alkanes. Slightly larger pores show an opposite hierarchy with the dibranched molecules fitting best (e.g. UiO-66), while even larger pores revert back to having the linear alkane adsorb best, albeit with much lower selectivities than the small-pore structures. Figure 2.1, shows CFCMC and CBMC isotherms of hexane isomers at 433 K in $Fe_2(BDP)_3$. $Fe_2(BDP)_3$ is a highly stable framework with 1-dimensional triangular channels made of iron and benzene-1,4-dicarboxylic acid (BDP). The crystal data was taken from Ref. [20] and we used $5 \times 1 \times 1$ unit cells with periodic boundaries. The framework is modeled using the DREIDING force field [21], and atoms not defined in the DREIDING model are taken from the UFF [22]. The alkanes are modeled using the Transferable potentials for Phase Equilibria (TraPPE) force field by Martin and Siepmann [23, 24]. Despite the fact that the model lumps CH₃, CH₂, and CH into single interaction centers, it very accurately



Figure 2.1: Adsorption isotherms of hexane isomers (hexane=n-C6, 2-methylpentane=2-MP, 3-methylpentane=3-MP, 2,2-dimethylbutane= 2,2DMB and 2,3-dimethylbutane=2,3DMB) calculated using CFCMC (closed symbols) and CBMC (open symbols) in Fe₂(BDP)₃ at 433 K. (a) Single component and (b) 5-component equimolar mixture.



Figure 2.2: Adsorption isotherms of hexane isomers in $Fe_2(BDP)_3$ at 433 K calculated using CB/CFCMC. (a) Single component isotherms and (b) 5-component equimolar mixture.

reproduces the experimental phase diagram and critical points. Cross interactions are mixed using Lorentz-Berthelot mixing rule [25, 26].

For both single components as well as the 5-component mixture, we find excellent agreement between the CFCMC and the CBMC method. We also find excellent agreement with the CB/CFCMC method (Figure 2.2). The simulations have been run the same number of cycles (where a cycle consist of N Monte Carlo moves, N the number of molecules present in the system with a minimum of 20 moves), and roughly for the same amount of CPU time. We note that for CFCMC the error bar becomes larger in regions where the isotherms are steeper (however, note the average matches very well with CBMC). This is an indication that



Figure 2.3: Adsorption isotherms calculated using CFCMC (closed symbols) and CBMC (open symbols). (a) Single component isotherms of CO_2 , CH_4 , H_2 in Mg-MOF-74 at 313 K and (b) 3-component mixture with a ratio 1:4:20 CH_4 : CO_2 : H_2 in Mg-MOF-74 at 313 K.

CFCMC is able to explore more phase-space than CBMC. Also note that CFCMC matches CBMC even at very low loadings. It is the integer number of molecules that is the relevant property and the fractional molecule should be excluded in the analysis. Our simulations agree both qualitatively and quantitatively with the CBMC simulations of Ref. [20] further supporting the correctness of the simulation results. From our simulations we observe that, for these flexible molecules with internal degrees of freedom, the CFCMC is just as efficient as CBMC.

2.3.2 Small gas molecules in MgMOF-74

The separation of light gases is becoming increasingly important from an energetic and environmental point of view. Separation of CO_2 from CH_4 in natural gas helps reducing CO_2 emission into the atmosphere and increases the energetic value of the gas, while separation of CO_2 , CH_4 and H_2 is important in hydrogen flow purifications [27, 28]. The separation of these gases can be achieved by adsorption processes using porous materials with high selectivity (such as zeolites, silicas and MOFs) which exploit the differences in kinetic diameter, polarizability, dipole and quadrupole moments of the molecules. It has already been reported that materials with open metal sites enhance the binding strength of H_2 and CH_4 [28] making them suitable candidates for separation of small gases. Screening studies by *e.g.* Yazaydin *et al.* [29] also showed that MgMOF-74 has a very high CO_2 capacity.

In Figure 2.3, we show the CFCMC and CBMC adsorption isotherms for CO_2 , CH_4 and H_2 at 313 K in MgMOF-74, a metal organic framework with 1dimensional channels and a high concentration of Mg^{2+} . The crystallographic data was taken from Ref. [28] and a $2 \times 2 \times 5$ unit cell with periodic boundaries was used. The Lennard-Jones parameters for the framework were taken from DREIDING force field. Charges were obtained from quantum

calculations (using the REPEAT method [30]). The interaction parameters for the gas molecules were taken from TraPPE force field [23, 31] in which H₂ is modeled as a rigid molecule with one dispersive center in the center of mass (COM) and partial charges in both hydrogens and the COM, CO₂ as a rigid molecule with three interaction centers with partial charges and CH₄ as one interaction center. For the mixture isotherms 1:4:20 CH₄:CO₂:H₂ ratios were used in order to compare with previous results [32] which model a realistic hydrogen purification process composition. In both cases we can see excellent agreement between CBMC and CFCMC. There is also good agreement between our results for single components and previously published data [28].

2.3.3 Xylenes in MTW

Xylenes is a term that refers to dimethylbenzenes obtained from petroleum and generally produced as a mixture of all three isomers: ortho-, meta- and paraxylene. The industrial applications of the isomers differ, *p*-xylene is the main precursor of polyethylene terephtalate (PET) for polyester industry, o-xylene is used to obtain phtahalic anhydride and *m*-xylene to produce isophthalic acid used in PET resin blend, and therefore their separation is of great interest. However, the similarities in the physicochemical properties of xylenes make this process challenging [33]. The current preferred technology is based on adsorption in nanoporous structures [34], in which energetic and entropic effects are responsible for the selectivity of the different isomers. In Figure 2.4, we show the CFCMC and CBMC isotherms of xylenes at 433 K in MTW, a zeolite with 1-dimensional channels and 12-rings openings. The crystallographic data was taken from Ref. [35] and modeled with the DREIDING force field. Interactions with both oxygen and silicon are taken into account. A $1 \times 6 \times 3$ unit cell was used. Xylenes were modeled using OPLS-UA force field [36]. There is good agreement between CBMC and CFCMC for the single components isotherms at low pressures, however, at high pressures CBMC has difficulties with inserting more molecules in the system. This behavior is particularly clear in the case of o-xylene. CBMC simulations will lead to an incorrect maximum loading. We have noticed something similar for small guest molecules at saturation in our previous work [3]. In Figure 2.5, we show a snapshot of the mixture adsorption. In the top and bottom channel of MTW, only *p*-xylenes are present, we can observe how the molecules are able to efficiently pack. In the middle channel also an o-xylene and a m-xylene are present. We can observe that these isomers are not able to stack in the same mode. In Figure 2.5. we can observe how the different isomers interact with the framework. This specific fitting between the xylenes makes the system extremely difficult to sample.



Figure 2.4: Pure component adsorption isotherms of xylenes isomers in MTW zeolite at 433 K calculated with (a) CFCMC and (b) CBMC.



Figure 2.5: (a) YZ view of MTW channels with an equimolar mixture of xylenes isomers at 10^8 Pa and 433 K. The channels are cut open and volume-rendered based on an energy-grid probed with methane. (b) View into one channel of MTW with an equimolar mixture of xylenes isomers at 10^8 Pa and 433 K. The channel shape is a transparent isocontour of a high energy from an energy-grid probed with methane. Channel runs from left to right. Color code: carbon (cyan), hydrogen (white), oxygen (red), and silicon (yellow).

2.4 Lennard-Jones chains in Gibbs ensemble

To test the Continuous Fractional Monte Carlo with Configurational-Bias, we computed the coexistence densities for Lennard-Jones chains of length m = 8 and octane using three different algorithms: CBMC, CFCMC, and CB/CFCMC in the Gibbs Ensemble. For the algorithms with CBMC, simulations were performed with 10 trial positions. The results for the coexistence densities $(\langle \rho_1 \rangle$ and $\langle \rho_2 \rangle)$ are shown in Table 2.1 and Table 2.2. For the Lennard-Jones 8-mers, the results are presented in reduced units to compare with the literature. They are in good agreement with each other and with the results reported by Ref. [37] For the octanes, our results are in good agreement with each other and equivalent within

Lennard-Jones chain length $m = 8$				
Method	T^*	$\langle \rho_1^* \rangle$	$\langle \rho_2^* \rangle$	
Literature [37]	1.887	0.033 ± 0.005	$0.521 {\pm} 0.006$	
	1.923	$0.031 {\pm} 0.005$	$0.506 {\pm} 0.005$	
	1.980	$0.058{\pm}0.004$	$0.453 {\pm} 0.005$	
CBMC	1.887	$0.034{\pm}0.005$	$0.519 {\pm} 0.009$	
	1.923	$0.043 {\pm} 0.005$	$0.494{\pm}0.009$	
	1.980	$0.060 {\pm} 0.006$	$0.430{\pm}0.021$	
CFCMC	1.887	$0.034{\pm}0.005$	$0.514{\pm}0.009$	
	1.923	$0.038 {\pm} 0.005$	$0.484{\pm}0.009$	
	1.980	$0.063 {\pm} 0.024$	$0.43 {\pm} 0.034$	
CB/CFCMC	1.887	$0.029 {\pm} 0.003$	$0.510 {\pm} 0.007$	
	1.923	$0.038 {\pm} 0.008$	$0.478 {\pm} 0.012$	
	1.980	$0.073 {\pm} 0.019$	$0.433 {\pm} 0.020$	

Table 2.1: The vapor-liquid coexistence densities for Lennard-Jones chains of length m=8 computed using CBMC, CFCMC, CB/CFCMC algorithms. The simulations were done with 500.000 cycles and 100.000 initialization/equilibration cycles. The number of Monte Carlo moves per Monte Carlo cycle is equal to the total number of particles with a minimum of 20. The errors are calculated as standard deviations of the block averages. Reduced units were used to compare with literature.

Octane, TraPPE force field.			
Method	Temperature[K]	$\langle \rho_1 \rangle [kg/m^3]$	$\langle \rho_2 \rangle [kg/m^3]$
Literature [23]	390	3.9 ± 0.5	624 ± 2
	440	$12.9 {\pm} 0.6$	574 ± 1
	490	28.0 ± 4.0	505 ± 4
	515	54.0 ± 6.0	473 ± 5
	540	78 ± 17	425 ± 14
CBMC	390	4.2 ± 0.3	629.1 ± 1.7
	440	13.2 ± 0.45	578.5 ± 1.4
	490	36.3 ± 1.7	521.5 ± 2.2
	515	59.9 ± 2.0	485.9 ± 0.7
	540	102.1 ± 20.0	$420.9 {\pm} 20.60$
CFCMC	390	4.2 ± 0.6	625.0 ± 1.6
	440	$13.9 {\pm} 1.0$	575.0 ± 3.8
	490	37.7 ± 4.4	512.2 ± 4.2
	515	63.2 ± 7.3	477.0 ± 3.5
	540	78.6 ± 7.7	426.6 ± 14.7
CB/CFCMC	390	3.6 ± 0.5	626.5 ± 2.2
	440	12.2 ± 1.0	575.0 ± 1.0
	490	31.1 ± 4.6	512.6 ± 2.9
	515	48.9 ± 1.8	471.8 ± 5.5
	540	$83.7{\pm}14.1$	$424.0{\pm}14.3$

Table 2.2: The vapor-liquid coexistence densities for octane using TraPPE model computed with CBMC, CFCMC, CB/CFCMC algorithms. The simulations were run with 50000 initialization cycles and 500000 cycles. The errors are calculated as standard deviations of the ensemble averages. The results are equivalent within the error bar to the results of Martin and Siepmann.

the error bar to the results reported by Ref. [23]. We can observe that, as expected, that amount of accepted exchanges per MC cycle for both CBMC and CB/CFCMC increases with the number of trial positions.

The gas phase density value at $T^*=1.923$ of Mooij *et. al.* [37] differs from our value. However this density is lower than the density at $T^*=1.887$ which seems



Figure 2.6: (a) Acceptance percentage of particle transfers and (b) efficiency (accepted particle transfers/cpu time) for CBMC, CFCMC and CB/CFCMC algorithms for Lennard-Jones chains with 8 beads. Total number of chain molecules N = 200, temperature $T^* = 1.887$, total volume $V_t^* = 3456$. The number of MC production cycles = 50000.

inconsistent. Our data points have been run 10 times longer. Considering this difference, the data agree well. However, this raises a discussion on the magnitude of error bars. Our error bars are computed by dividing the simulation in five blocks and computing the error from the standard deviation of the averages of these five blocks. We report a 95% confidence interval. In Gibbs simulations the density fluctuates as the volume and the number of particles fluctuate individually. The magnitude of the fluctuations are the most sensitive to the frequency and magnitude of the volume move. Longer simulations times give a better estimate of the "true" average but also an increased contribution to the error from exploring a larger region of phase space. In order to evaluate this "hidden" error it is advisable to plot the full VLW curve and check that the graph is smooth and continuous. This would also reveal that the T*=1.923 data point of Mooij *et. al.* can be considered an outlier.

The gas and liquid branch are well separated by a free energy barrier at low temperatures. At high temperature the barrier becomes low, which makes Gibbs difficult to apply at these temperatures. This manifests itself as swapping between the liquid and gas boxes. This must be avoided to accurately compute the gas and liquid densities separately. However, sometimes the better you sample (*i.e.* CFCMC and CB/CFCMC) the more probable the swapping becomes.

The performance and efficiency of the CB/CFCMC algorithm in the Gibbs Ensemble can be assessed by computing the number of accepted particle exchanges between the boxes per Monte Carlo cycles performed and also the number of accepted particle exchanges between the boxes per total CPU time for the different algorithms. Moves are chosen with the following probabilities: Gibbs-volume 0.2%, translation 19.96 %, rotation 19.96 %, reinsertion 19.96 %, partial reinsertion 19.96 % and Gibbs swap 19.96 %. For the CFCMC and CB/CFCMC, the number of

accepted particle exchanges are defined as the total number of accepted moves in λ that result in particle exchanges between the boxes. The measured time is the time of just the Gibbs insertion/deletion move for an insertion. The clock-routine was used which measured only CPU time. We ran on a 12-core machine using 10 jobs simultaneously (and with 2 cores free for system tasks) to make sure none of them can make use of the cache (or at least all used the same cache). The results for the number of accepted particle exchanges per MC cycle and per CPU-time for the different algorithms are presented in Figure 2.6.

CB/CFCMC increases significantly the amount of acceptance percentage with respect to CBMC. In CBMC the efficiency as a function of the number of trial directions has not a pronounced maximum but rather a broad plateau while for CB/CFCMC there is a pronounced maximum at only a few trial directions. The acceptance probability cannot exceed 50% because of the choice of $\Delta\lambda$, so that having more trial directions (than the optimum) results in a decrease in acceptance. Note that we fixed $\lambda_{\text{max}} = 0.332$ and fixed the biasing factors for all runs.

2.5 Efficiency of CFCMC

To assess the efficiency of CFCMC we considered the system of xylenes in MTW because sampling this system for mixtures turned out to be very difficult. An interesting property of the single component isotherms is that p-xylene has an inflection point in its loading at approximately 10 Pa (see Figure 2.4), which causes it to have a lower loading than m- and o-xylene within a small fugacity range. This sampling difficulty is reflected in Figure 2.7 where the mixture comparison between CFCMC and CBMC is plotted.

In Figure 2.7(a) for the simulation time of 500,000 initialization and 500,000 production cycles we observe that CFCMC and CBMC give very different answers. The question is: "which one is more correct than the other, and/or are both methods giving wrong answers here?". We have run the simulation using both methods longer and in Figure 2.7(b) we observe that CFCMC provide the same qualitative answer and a slightly improved quantitative result. Figures 2.7(b) and 2.7(c) show that when running CBMC (much) longer, CBMC converges to the CFCMC result. This means that CFCMC is able to provide qualitative correct results in short simulation times, while CBMC is easily stuck/trapped in metastable states. Hence, CFCMC is not only more efficient, it is for all but the shortest simulation almost guaranteed to find the proper solution (if biasing is used with appropriate biasing factors).

Since biasing is so essential, we analyze this in some more detail. In Figure 2.8, we plot the λ -histograms for 2000000 and 3000000 equilibration cycles. During equilibration of λ the histograms are measured and used to calibrate the biasing factors using Wang-Landau method. Ideally, the final histograms should be flat. In Figure 2.8(a), we observe that the histograms are reasonably flat but in Figure 2.8(b) the histograms become increasingly flat with longer calibration times. The latter histograms are sufficiently flat to appropriately analyze the bi-



Figure 2.7: Adsorption isotherms calculated with CFCMC (closed symbols) *vs.* CBMC (open symbols) for a 3-component equimolar mixture of xylenes isomers in MTW at 433 K a) CFCMC and CBMC 500000 cycles, b) CFCMC and CBMC 2000000 cycles, and c) CFCMC 2000000 and CBMC 3000000 cycle. The circled points are discussed further in the text.



Figure 2.8: Probability distributions of λ at different fugacities for *p*-xylene in MTW at 433 K measured in production time after using Wang-Landau a) 2000000 cycles and b) 3000000 cycles.

asing factors. If the histograms would be completely flat then the difference of the biasing factor at $\lambda = 0$ and $\lambda = 1$ is the free energy difference of inserting a molecule [6], and therefore it increases with increasing molecule size. Moreover, a flat histogram indicates that most free energy barriers in λ space have been eliminated. This leads to an order of magnitude better insertion efficiency. Not only is the insertion "forced" but also the adjustment of the surrounding molecules. It is this adjustment that is so difficult to sample with CBMC, especially with "packing-effects" like we showed in Figure 2.5. For the 3-component xylenes mixture the individual loadings are determined by the relative differences between the components. Seen from the viewpoint of a particular molecule, there is a preferred packing of molecules around it. This preference changes as a function of loading. Because one always starts from either the zero-loading or a previously stored nonequilibrated snapshot (for example at a lower pressure) the system needs to adjust to the new pressure and there is a change in free energy between this and the state



Figure 2.9: Biasing factors in units of k_BT at different fugacities for single component a) *o*-xylene, b) *m*-xylene and c) *p*-xylene in MTW at 433 K.



Figure 2.10: Biasing factors in units of k_BT at different fugacities for a) *o*-xylene, b) *m*-xylene and c) *p*-xylene in MTW at 433 K in a equimolar ternary mixture.

that one would like to compute. Using CFCMC, the free energy barrier is largely removed while it is very difficult for CBMC to overcome this barrier. As we will see these barriers are very large.

In Figures 2.9 and 2.10 the biasing factors for the single component o_{-} , m_{-} , and *p*-xylene and the mixture are plotted as a function of λ and fugacity. It is important to note that for each fugacity the biasing factor is taken as zero for $\lambda = 0$ and the non-zero λ biasing factors are relative to this value. At low fugacities, increasing λ leads to lower biasing values. This corresponds to the regime where increasing the molecule gains energy, *i.e.* the interaction of the framework (and other molecules in general) with the fractional molecule is very favorable and increasing λ leads to lower free energies. If we increase the fugacity we start to feel the effect of loading. At a certain point the surrounding molecules start to become a repulsive influence. Increasing the loading even further we observe that there appears a λ -bottleneck somewhere at an intermediate λ value, *i.e.* a minimum in λ space. This free energy barrier is also related to the barrier for an orientational re-arrangement of the molecules. One pushes the fractional molecule in but half-way the other molecules need to adapt to the new situation. In CBMC simulations, the molecule would have been removed immediately (because it is energetically very unfavorable) but by forcing it to remain one forces the environment to respond. This process is not very different for the mixtures as can be seen in Figure 2.10. When compared to the



Figure 2.11: Biasing factors in units of k_BT for some of the alkanes in $\rm Fe_2(BDP)_3$ at 433 K, 500000 equilibration cycles.



Figure 2.12: Biasing factors in units of k_BT for small gases in $\rm MgMOF\text{-}74$ at 313 K, 500000 equilibration cycles.

biasing plots for alkanes in $Fe_2(BDP)_3$ and small gases in MgMOF-74 (Figures 2.11 and 2.12), we note that the magnitude of the biasing for these two cases is much lower, which indicates these systems are feasible to sample with both CFCMC and CBMC. The magnitude of the required biasing factors is directly proportional to the difficulty of sampling the system.

In Table 2.3, we show the average number of molecules in the zeolite for some simulations (circled points in Figure 2.7) in different stages. The simulation is divided into 5 blocks, and if all 5 averages show a systematic increase in loading then the loading values are not yet converged. In Table 2.3 we show that for short simulations of CBMC the average number of molecules has small fluctuations. This however does not mean the simulations are equilibrated, as mentioned before this is only a consequence of the system being trapped in a meta-stable state. For longer simulations of CBMC, the average number of molecules has large changes (which is reflected by the error bars in Figure 2.7(b)) but we can notice the loading is drifting upwards, so the simulations are clearly not converged. For CFCMC, the average loading has large fluctuations with no obvious direction. This together with a flat enough λ -histogram indicates that the system is exploring large regions in phase space around the correct average loadings.

Simulation	Fugacity1	Fugacity2	Fugacity3
CBMC Figure 2.7(a)	$10^{4}(Pa)$	$10^{5}(Pa)$	$10^{6}(Pa)$
Block1	10.3	9.3	10.1
Block2	10.0	9.1	10.4
Block3	9.7	9.6	10.5
Block4	10.0	9.0	9.9
Block5	10.2	9.1	9.8
CFCMC Figure 2.7(a)	$10^{3}(Pa)$	$10^{4}(Pa)$	$10^{6}(Pa)$
Block1	21.2	24.5	29.4
Block2	21.1	23.7	32.4
Block3	14.5	22.2	31.6
Block4	16.8	24.9	30.0
Block5	16.1	26.8	31.2
CBMC Figure 2.7(b)	$10^{6}(Pa)$	$10^{7}(Pa)$	$10^{8}(Pa)$
Block1	12.5	11.0	16.4
Block2	13.7	12.6	18.1
Block3	14.4	15.6	20.3
Block4	15.6	16.1	23.8
Block5	17.8	20.3	23.6

Table 2.3: Average loading of molecules per simulation in blocks of cycles.

2.6 Conclusions

The efficiency of insertion, depends on the density of the system. At low densities and for a fixed number of Monte Carlo cycles, CBMC is more efficient, since the attempts of insertion are more frequent, no diffusion in λ -space is needed. At medium densities, the efficiency of insertion can be summarized by CB/CFCMC \gg CFCMC \gg CBMC \gg MC. Methods using CFCMC really shine, since they are rather insensitive to meta-stable states because of the λ biasing. A molecular structure or packing can be broken down if the λ -histogram is relatively flat. This requires an equilibration period during which the λ -biasing is iteratively setup using *e.g.* Wang-Landau sampling but in our experience this does not require *longer* equilibration. After a simulation the λ -histogram can be examined. If it is relatively flat, then block-averages are an indication of equilibration. In contrast, CBMC can show an apparent small, but erroneous, error bar. Where there is no drift in block averages, but the simulations are unconverged.

In addition, CB/CFCMC has a clear advantage for long chain molecules, since it avoids having to generate ideal gas configurations for the CFCMC insertions. Although this generation might be cheap, for increasing chain lengths the molecular configurations inside the host framework increasingly deviate from their ideal gas configuration. The CFCMC would fail here, while the CB/CFCMC could still work by growing the molecule atom by atom.

However, also the CB/CFCMC and CFCMC are not applicable around saturation conditions. For relatively large pores systems the fluid inside the pores can be compressed further and further with no bounds (in practice, the bound is the maximum pressure that the experimental equipment can handle and/or the nanoporous material remains stable), but for small pores and relatively bulky molecules (using hard potentials) the saturation can be an *integer* number of molecules. A typical example is a xylene in UiO-66 or an heptane molecule in ERI-type zeolite. There fits only one heptane molecule in an ERI-type cage at reasonable pressures. For these cases it is impossible to insert an additional molecule at saturation conditions, and similarly, at saturation it is energetically highly unfavorable to delete a molecule. In this case however, for single components the loading is known, and for mixtures it is the ratio of components that is of interest. This ratio is better sampled using MC moves like identity-switches, or methods like replica exchange in temperature or mol-fraction [38]. Alternatively, especially when simulating flexible hosts, sampling efficiency can be gained by combing the insertion/deletion schemes with the MD methodology.

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CHAPTER 3

Optimization of Particle Transfers in the Gibbs Ensemble Using CB/CFCMC *

3.1 Introduction

Many open ensemble simulation methods, such as the Gibbs Ensemble [1-3] or the grand-canonical ensemble Monte Carlo methods, suffer from a major problem: if the system's density is too high or the molecules are too large or complex, the acceptance probability of insertions and deletions of molecules in the system, necessary to achieve equilibrium, becomes very low. This results in very inefficient simulations. For the insertion move, the low probability arises from the energy penalty due to overlaps with molecules already present in the system, and for the deletion move, the low probability arises from the high energy penalty of breaking strongly favorable interactions when removing molecules.

Many biasing techniques have been proposed to overcome this difficulty, among them the various configurational bias Monte Carlo methods (CBMC) [4–7] based on the work by Rosenbluth and Rosenbluth [8, 9]. In these methods, the molecular growth is biased towards energetically favorable configurations by using the internal bonded potential energy to generate a set of trial positions and the external potential energy to bias the selection of a site from the set of trial positions. Although these methods enhance the insertion and deletion of molecules, especially for long chains [10], they still possess a weakness: they all rely on the existence of cavities in the accepting phase large enough to accommodate the molecule being

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inserted, and they do not solve the problem of the energy penalty from "breaking interactions" when removing molecules. To overcome this problem, several methods have been developed, such as Cavity Bias [11], the Excluded-Volume Map-Sampling scheme (EVMS) [12], Rotational Insertion Bias Monte Carlo (RIB) [13], Inflating Flea Method [14], Replica-exchange [15], and Parallel Tempering in both the chemical potential and the potential strength [16]. An alternative scheme, inspired by expanded-ensembles, is Continuous Fractional Component Monte Carlo (CFCMC) developed by Shi et al. [17]. In this method, the insertion and deletion of molecules is facilitated by expanding the system with an additional molecule (fractional molecule). The interactions of the fractional molecule with the surroundings (inter-molecular Lennard-Jones and Coulombic interactions) are scaled using a parameter λ . When the $\lambda = 0$ the molecule has no interactions, when $\lambda = 1$ the fractional molecule has full interactions. For thermalization of the system, the scheme employs conventional Monte Carlo moves such as translations, rotations, and/or MC-MD hybrid moves, but in addition to these, attempts to change the scaling factor λ of the fractional molecule using $\lambda_n = \lambda_o + \Delta \lambda$ are performed. When the scaling parameter of the fractional molecule is greater than or equal to one $(\lambda \geq 1)$, the fractional molecule is 'fully' inserted and a new position is selected at random to start inserting a new fractional molecule. When the scaling parameter is less than or equal to zero ($\lambda \leq 0$), the fractional molecule is 'fully' deleted and an existing molecule in the system is randomly selected to be the fractional molecule. Because λ is changed gradually, no spontaneous or explicitly forced cavity formation is necessary and also the energy penalty for breaking interactions is much smaller. The latter can even be eliminated by adding an additional free energy bias on λ , which avoids that the λ -move becomes "stuck" at certain values [17]. Torres-Knoop et al. introduced the Configurational Bias Continuous Fractional Component Monte Carlo method (CB/CFCMC) [18], a combination of CBMC and CFCMC. This method combines the strengths of both CBMC and CFCMC to enhance the acceptance probability of the insertion/deletion moves (1) by biasing the insertion of molecules in the system towards favorable configurations and, (2) by gradually inserting/deleting the molecules using a coupling parameter λ . The CB/CFCMC method dramatically improves the insertion/deletion acceptance probability in the grand-canonical and Gibbs ensemble.[18]

Calculations of Vapor-Liquid Equilibrium (VLE) curves are often used to develop/fit force field parameters of molecules due to the sensitivity of the parameters to the VLE curves (as a function of temperature) [19]. This is largely because the resulting parameters are fitted over a wide range of densities, and because the simulated intensive variables (e.g. T and P or chemical potential of species) need to be the same to high precision in the dense liquid phase as in the coexisting low-density vapor phase. The latter also makes VLE calculations computationally demanding. Adjusting the force field parameters to VLE data is currently a cumbersome and computationally expensive task, leading to the development of methods to improve this procedure [20–22]. Systems with directional and/or strong interactions, like water and dimethylformamide (DMF), are especially difficult. In this work, we explore the CB/CFCMC method (compared to CFMC and CBMC) in the Gibbs ensemble for water and DMF, and study the adsorption of water in metal-organic frameworks. Shi and Maginn [23] showed that CFCMC gives the same correct results as CBMC when computing the VLE curve of water with Gibbs ensemble simulations, but enhances the acceptance percentage from around 0.03% to above 1.0%. Here, we show that using CB/CFCMC the probability of insertions/deletions increases to almost 10% and we analyze the insertion/deletion probabilities and dependencies in detail. The increase in efficiency and accuracy makes the CB/CFCMC one of the most suitable methods to study water, solvents like DMF and DEF (diethylformamide), and ionic liquids [24, 25] at low temperatures.

3.2 Methodology

CB/CFCMC

In general, if insertions and deletions are not a bottleneck in the simulations, histogram reweightening in temperature space [26, 27] is a very efficient algorithm to calculate vapor-liquid equilibrium curves [28]. However, for multiple components, storing the histograms becomes computationally expensive, and the use of histogram-bins introduces an additional (systematic) error. In practice, accurate estimations of chemical potentials and partition functions turn out to be nontrivial and often involve statistical uncertainties [29].

Here, we explore an alternative approach, Gibbs ensemble Monte Carlo (GEMC), which relies on the efficient insertion/deletion of molecules [1, 2]. In this method, a macroscopic system with two phases coexisting at equilibrium is represented by two microscopic systems in different phases (simulated concurrently in two separate boxes) coupled by the exchange of volume and matter. The thermodynamic requirements for phase coexistence are that each region should be in internal equilibrium, and that temperature, pressure and the chemical potentials of all components should be the same in the two regions [30]. The temperature is specified in advance and equilibrium is achieved by performing three types of Monte Carlo moves:

- 1. Moves to satisfy internal equilibrium in each of the boxes: displacements or orientation rotations of a randomly selected molecule in a randomly selected box.
- 2. Moves to satisfy equality of pressures: changes in the volume of the boxes while keeping the total volume constant.
- 3. Moves to satisfy equality of chemical potentials: exchanges of molecules between boxes.

In CB/CFCMC (as in CFCMC) the system is expanded with a fractional molecule which interacts with the surroundings via Lennard-Jones (LJ) interactions $u_{\rm LJ}(r)$ and charge-charge interactions $u_{\rm Coul}(r)$ that are scaled using a parameter λ [17, 18, 23]. Instead of random insertions and deletions of the fractional molecule (as in CFCMC), in CB/CFCMC the fractional molecule is inserted or removed using configurational biasing at constant λ values: the internal bonded potential $U^{\rm int}$, is used to generate trial positions and the external non-bonded potential $U^{\rm ext}$, at a given λ , is used to bias the selection of a site from the set of trial positions [4, 5].

In the displacement or rotation move, a random molecule (a whole or the fractional molecule) is chosen and a random displacement (or rotation) is performed. In the volume change move, one of the simulation boxes is chosen randomly and a random walk is performed in $\ln(V_1/V_2)$. The exchange of molecules between the boxes is achieved by changing the coupling parameter λ of the fractional molecule by an amount $\Delta\lambda$ such that if λ_o and λ_n refer to the value of λ in the old and new configurations, respectively, then $\lambda_n = \lambda_o + \Delta\lambda$. The value of $\Delta\lambda$ is chosen uniformly between $-\Delta\lambda_{\text{max}}$ and $+\Delta\lambda_{\text{max}}$ and adjusted to achieve approximately 50% acceptance [17].

For the Gibbs ensemble simulations, in each simulation box (box 1 and box 2) there is a fractional molecule $N_{f,1}$ and $N_{f,2}$ with coupling parameters λ_1 and λ_2 respectively. These parameters are coupled with each other to ensure a constant number of molecules in the simulation ($\lambda_1 + \lambda_2 = 1$). In the following we refer to λ as the coupling parameter of box 1 (the coupling parameter of box 2 is $1 - \lambda$). There are two possible outcomes of a change from λ_o to λ_n :

• When $0 < \lambda_n < 1$, the coupling parameter increases/decreases.

If $\lambda_n > \lambda_o$ the fractional molecule in box 1 increases its interactions with the surrounding molecules and the fractional molecule in box 2 decreases its interactions by an equal amount. If $\lambda_n < \lambda_o$ then the fractional molecule in box 1 decreases its interactions with the surroundings by a factor $\Delta \lambda$ and the fractional molecule in box 2 increases its interactions by the same amount.

• When $\lambda_n \leq 0$ or $\lambda_n \geq 1$, molecules are exchanged between the phases/boxes. If $\lambda_n \leq 0$ then in box 1, the existing fractional molecule is retraced with $\lambda = \lambda_o$ and a "full" molecule is chosen randomly and converted into the fractional molecule with coupling parameter $\lambda_n + 1$. In box 2, the existing fractional molecule becomes a "full" molecule and a new fractional molecule is grown with coupling parameter $\lambda = \lambda_n - 1$.

If $\lambda_n \geq 1$ then the fractional molecule in box 1 becomes full and a new one is grown with coupling parameter $\lambda = \lambda_n - 1$ and the fractional molecule in box 2 is retraced with $\lambda = \lambda_o$ and a new molecule is chosen randomly and converted into the fractional molecule with coupling parameter $\lambda_n + 1$.

Many systems show behavior where λ -changes are difficult because in the Boltzmann ensemble the distribution of λ can go through a deep minimum. For these cases, an additional bias η on λ can be used, where each state of λ has an associated biasing factor η which will be removed in the acceptance rules.

The acceptance rule using CB/CFCMC for the particle swap from box 2 to box 1 with additional bias is given by [18],

$$P_{\rm acc}(o \to n) = \min\left(1, \frac{N_{2,o}}{N_{1,o}+1} \frac{V_{1,o}}{V_{2,o}} \frac{W(n)}{W(o)} \exp(-\beta (U_{1,f \to w}(\mathbf{s}_1^{N_1,N_{f,1}}, \lambda_o) - U_{2,w \to f}(\mathbf{s}_2^{N_2-1,N_{f,2}}, \lambda_n)) + (\eta(\lambda_n - 1) - \eta(\lambda_o)))\right)$$
(3.1)

where $V_{1,o}$ is the volume of box 1 in the old configuration, $V_{2,o}$ is the volume of box 2 in the old configuration, $N_{1,o}$ is the amount of integer molecules in box 1 in the old configuration, $N_{2,o}$ is the amount of integer molecules in box 2 in the old configuration, $\beta = 1/k_BT$, $U_{1,f\rightarrow w}$ the energy of converting the existing fractional molecule into a whole in box 1, $U_{2,w\rightarrow f}$ the energy of converting a whole molecule into a fractional in box 2, W(o) is the Rosenbluth weight associated with the removal of the fractional molecule in box 2 (with coupling parameter λ_o), W(n)is the Rosenbluth weight associated with the growth of a new fractional molecule in box 1 with coupling parameter $\lambda = \lambda_n - 1$ and $\eta(\lambda)$ is a self adapting biasing potential to ensure the λ space is uniformly visited. More details on the method and the derivation of the acceptance rules can be found in Torres-Knoop *et al.* [18].

For computing the adsorption isotherms, simulations in the grand-canonical ensemble are performed. In this ensemble, the chemical potential (μ) , the volume (V) and temperature (T) are kept fixed, and the number of molecules is allowed to fluctuate. As in the Gibbs ensemble, the insertion and deletion of molecules is performed by changing the coupling parameter λ . More details can be found in chapter 1.

Force fields

For the water simulations, three well-known force fields were selected: SPC [31], SPCFw [32] and Tip5p-Ew [33, 34]. SPC is a rigid three point model, SPCFw is a flexible three point model and Tip5p-Ew is a rigid five point model. The water force field parameters are listed in Table 3.1. The van der Waals interactions are truncated and smoothed with a third order polynomial using a cut off of 10 Å. For the long-range charge interactions, the Ewald summation method with a relative precision of 10^{-6} was used. The hydrogen atoms and lone-pair pseudo atoms (L) are charge-sites but do not have VDW potentials. In the methods using continuous fraction (CF), a blocking radius of 1 Å was used on these non-VDW atoms to avoid the charge-sites from overlapping and causing numerical instability [17].

N,N- dimethylformamide (DMF) was modeled using the re-parametrized OPLS-UA-CS2 force field by Vahid and Maginn [35] based on the model proposed by Chalaris and Samios [36]. In the re-parametrization, the bonds, bend and dihedral are the same as original, but the Lennard-Jones parameters have been modified for a better fit to the experimental VLE curve. In this force field, the carbon and

		(
SPC	SPCFw	Tip	o5p-Ew
atom	ϵ/k_B (K)	σ (Å)	q (e)
H _{SPC}	-	-	0.41
O_{SPC}	78.2	3.166	-0.82
$H_{\rm SPCFw}$	-	-	0.41
O_{SPCFw}	78.2	3.166	-0.82
$H_{Tip5p-Ew}$	-	-	0.241
$O_{Tip5p-Ew}$	80.51	3.12	0.0
$L_{Tip5p-Ew}$	-	-	-0.241

Table 3.1: Force field models and parameters used for the water molecule. The parameters were taken as follow: for SPC from [31], for SPCFw from [32] and for Tip5p-Ew from [34]. For SPCFw the bond-stretching and bond-bending are described with an harmonic potential. For the bond-stretching a force constant of 533000 K/Å² and an equilibrium value of 1.012 Å were used and for the bond-bending a force constant of 38195 K/rad² and an equilibrium value of 113.24° were used.

DMF	ϵ/k_B (K)	σ (Å)	q (e)	
$C_{\rm DMF}$	47.3	3.7	0.45	
$\mathrm{H}_{\mathrm{DMF}}$	7.18	2.20	0.06	
$O_{\rm DMF}$	226.0	2.96	-0.5	
$N_{\rm DMF}$	144.0	3.2	-0.57	
CH_3	69	3.8	0.28	

Table 3.2: Force field parameters of DMF [35]. The molecule is considered rigid.

hydrogen atoms of the methyl groups are merged together in a united atom CH_3 group and the bonds and bends are considered rigid. In the original paper by Vahind and Maginn [35], the dihedral angle is flexible. We kept it rigid for simplicity. Force field parameters of DMF are listed in Table 3.2. A cut-off of 12 Å was used for both the van der Waals and the charge interactions. The Ewald summation method was used for the long-range electrostatics with a relative precision of 10^{-6} .

Finally, Zn-DMOF-TM, the metal-organic framework used for the adsorption of water in the grand-canonical ensemble, was modeled as rigid, with charges computed using the REPEAT method [37] and force field parameters were based on the work of Burtch *et al.* [38]. The force field parameters are listed in Table 3.3.

Zn-DMOF-TM	ϵ/k_B (K)	σ (Å)
Zn	6.29	2.49
О	105.67	2.95
\mathbf{C}	35.22	3.55
Η	15.09	2.42
Ν	85.54	3.25

Table 3.3: VDW parameters used for the Zn-DMOF-TM metal organic framework. Based on [38].

All the simulations were done using the RASPA molecular simulation software for adsorption and diffusion in flexible nanoporous materials [39].

3.3 Results and discussion

3.3.1 Vapor-Liquid Equilibrium

To test the efficiency of Configurational Bias Continuous Fractional Component Monte Carlo (CB/CFCMC) in systems with strong directional interactions, we computed the VLE curve for the three different water models, SPC, SP-CFw and Tip5p-Ew, using the three different algorithms: CBMC, CFCMC and CB/CFCMC, in the Gibbs Ensemble. For CFCMC and CB/CFCMC, the number of accepted particle exchanges is defined as the total number of accepted trial moves in λ that result in particle exchanges between the boxes. For each temperature, the systems started from the same initial configuration, previously equilibrated for 500000 cycles, and were run for 20000 production cycles. Each Monte Carlo cycle consists of N Monte Carlo moves, N being the number of molecules present in the system with a minimum of 20.

In Figure 3.1a, the acceptance percentage of the exchange move (accepted particle exchanges between the boxes divided by the amount of attempts) as a function of trial moves for the SPC model using CBMC, CFCMC and CB/CFCMC algorithms is presented. Each color corresponds to a different temperature. The filled circles are the results obtained using the CBMC algorithm, the crosses using the CB/CFCMC and the filled squared are labeled CFCMC. The latter are actually CB/CFCMC simulations with one trial direction (to compare fairly). For chains there are conceptual differences between CBMC and CFCMC, which are also implementation dependent. For example, for CBMC the growing process can be terminated prematurely once all trial-direction are deemed as overlapping (with other molecules, or in adsorption simulations, with the framework). For CFCMC, however, the fractional molecule is allowed to overlap with other molecules, and also all atoms need to have been inserted before any biasing can be applied (after which the acceptance rule can be applied).

For all temperatures, the acceptance percentage of CFCMC and CB/CFCMC methods is greatly increased compared to CBMC. The continuous fraction (CF)



Figure 3.1: (a) Acceptance percentage of the exchange move, and (b) efficiency for the Gibbs ensemble simulations using CBMC and CB/CFCMC algorithms and for the SPC water model. The simulations using CB/CFCMC with one trial orientation are denoted as the CFCMC algorithm. Each color corresponds to a different temperature. The filled circles are the results obtained using CBMC, the crosses the results obtain with CB/CFCMC, and the filled squares the results from CFCMC. Using a fractional molecule greatly improves the acceptance percentage and efficiency.

methods do not rely on the presence of spontaneously formed cavities to insert molecules, but rather it dynamically creates one by slowly inflating and deflating the molecules like a balloon. As expected, the acceptance percentages for all the algorithms increase with temperature. For the simulations using the configurationalbias algorithm, the acceptance probability increases with increasing number of trial positions and reaches a plateau value. That is, the acceptance can be increased by using more trial orientations, but at the expense of a higher cpu-time cost.

In Figure 3.1b, the efficiency (number of accepted exchanges per cpu-time in units of seconds) for the different algorithms and temperatures as a function of the number of trial positions is shown. The measured time is the time of just the Gibbs insertion/deletion move for an insertion. The clock-routine was used to measured the user CPU time. In the simulations using CBMC and CB/CFCMC the efficiency as a function of the number of trial directions has a maximum at around 2-3 trial positions. It is well known that for CBMC [40] there is an optimal number of trial positions, after which the cpu-time time increases and the acceptance stays flat, leading to a decrease in the overall efficiency. The biasing used for water is orientational biasing. For water that forms a hydrogen bonded network, this biasing is highly advantageous, but in continuous fraction methods the "average" can be biased away. Moreover, in Gibbs simulations the effect is reduced by the coupling of the vapor and the liquid box. Also note that, despite the fact that CBMC has very low acceptance ratios, the performance of CBMC in terms of efficiency is relatively fair at high temperatures. In CBMC many more insertion/deletion attempts are performed per cpu-time in contrast to CF-methods which have to diffuse in λ -space to reach $\lambda < 0$ or $\lambda > 1$. However, at low temperature the insertion/deletions are almost absent in CBMC, rendering the CBMC method very inefficient at low temperatures.

It is important to note that the acceptance percentage and efficiency of CFCMC and CB/CFCMC strongly depend on (1) the size of the $\Delta \lambda_{\rm max}$ and (2) the quality of the biasing. Shi and Maginn scaled the $\Delta \lambda_{\rm max}$ to 50% acceptance for the λ change move [17]. A larger value leads to less cpu-time for the random walk in λ -space, a smaller value leads to a higher acceptance ratio. In all the simulations presented above, we kept $\Delta \lambda_{\rm max} = 0.5$. This means that $\Delta \lambda$ is randomly chose between [-0.5, 0.5]. In Figure 3.2a the acceptance percentage of the exchange move as a function of $\Delta \lambda_{\rm max}$ for 280 K with 3 trial positions is presented. We can see that the acceptance percentage exponentially decays with an increase in the maximum $\Delta\lambda$ change. If the histograms were perfectly flat, the acceptance percentage would go to 50% for the exchange move in the Gibbs ensemble (the exchange is 50% from box 1 to box 2 and 50% from box 2 to box 1) and to 100%for the insertion move in grand-canonical ensemble as $\Delta \lambda_{\rm max}$ approaches zero. In Figure 3.2a, also the efficiency as a function of $\Delta \lambda_{\rm max}$ is presented. We find that there is an optimal size of $\Delta \lambda_{\rm max}$ of around 0.2, corresponding to about 25% acceptance. This is significantly lower than the usual values of 40-50% acceptance recommended for MC-moves like translation and rotation. Woods and Jacobson



Figure 3.2: (a) Acceptance percentage and efficiency of the exchange move as a function of the maximum $\Delta\lambda$ displacement in Gibbs ensemble simulation using CB/CFCMC of SPC water at 280 K. For all simulations, 3 trial positions were used. The smaller the maximum change in λ (the more gradual the insertion and deletion) the higher the acceptance percentage. A smaller maximum $\Delta\lambda$ change, also leads to more cpu-time. In this system the efficiency is optimal around a maximum $\Delta\lambda$ change of 0.2. (b) Acceptance percentage of the exchange move as a function of the slope of the added bias in the Gibbs ensemble simulation of SPC water at 280 K (3 trial positions). By adding an extra bias equal to $a^*\eta$, we modified the original biasing factors needed to avoid λ from getting trapped in the minimum close to $\lambda = 1$. The larger the change in the biasing factors (the bigger the slope of the added bias), the smaller the acceptance percentage.



Figure 3.3: (a) Final biasing factors (in units of k_BT) after adding $a^*\eta$ extra biasing with a varying from 0 to 1 to the biasing factors obtained during the equilibration (using the Wang-Landau method) to ensure all λ values are visited uniformly. As we increase the slope, this biasing factors are modified more and more, specially around $\lambda = 1$. (b) Obtained histograms in λ -space when using modified biasing factors. With an increasing slope (modification of the original biasing factors), the coupling parameter gets 'more stuck' in values close to $\lambda = 1$ (more number of occurrences of $\lambda = 1$).

already suggested that even for these moves in their system (hard spheres) the most cost effective is a rather low acceptance ratio of 10% [41, 42].

The next results will illustrate the crucial importance of the biasing. Ideally, there should be no "diffusion-limitation" of the random walk in λ . If all λ values are equally likely, then the histogram of λ would be "flat" and the random walk can not get "stuck" at certain λ -values. In Figure 3.2b, the acceptance percentage for simulations with different levels of "flatness" in λ -space is presented. The different levels of flatness were created by modifying the biasing factors from the original run (which was flat; $\Delta \lambda_{\rm max} = 0.5$). In order to do this in a systematic way, we added an extra biasing to the biasing-factors equal to $a^*\eta$ with a varying from 0 to 0.8. In Figure 3.3, we show the modified biasing factors and the corresponding obtained histograms. We can see that by removing the bias necessary to overcome the minimum in λ -space close to $\lambda = 1$ (Figure 3.3a), the acceptance ipercentage drops from 9% to almost zero. We note that we find higher acceptance rates than Shi and Maginn in their work. These authors used a sufficient, but non-optimal biasing (see Figure 8 from ref. [23]), which significantly diminishes the potential acceptance ratios because the coupling parameter λ still gets stuck in certain λ ranges.

In Figure 3.4a, the results for the vapor-liquid equilibrium curve using the different algorithms and the SPC water model are presented. The results of the various methods are in good agreement with each other. The results show that the SPC water model underestimates the density of liquid water at high temperatures as compared to the experimental results reported by NIST [43]. It is known that



Figure 3.4: (a) VLE curve of water using SPC model and three different algorithms: CBMC, CFCMC and CB/CFCMC. (b) VLE curve of water using three different models and the CB/CFCMC algorithm.

the SPC water model accurately reproduces the properties of liquid water at ambient temperatures but fails to reproduce the liquid-vapor equilibrium curve [44–48]. In Figure 3.4b, the vapor-liquid equilibrium curves for the different water models using the CB/CFCMC algorithm are presented. For the Tip5p-Ew model, again only the liquid density data around ambient temperature is in good agreement. As for the SPC model, this problem has been reported before [49]. A fundamental problem in the water models using a fixed geometry is that the dipole is fixed, which in reality strongly differs in the vapor and liquid phase [50] due to the effect of polarizability at high densities. A possible remedy is to use flexible models. For adsorption, electric-field dependent water models have also been developed [51].

Since biasing is so essential, we analyzed this in some more detail. In Figure 3.5, the λ -histograms for 500000 equilibration cycles as a function of temperature for the different models using CB/CFCMC are presented. During equilibration of λ the histograms are measured and used to calibrate the biasing factors using the



Figure 3.5: Histograms (number of occurrences of a given λ value) as a function of temperature for the different water models using CB/CFCMC. A uniform color (flat histogram) indicates that the λ -space is uniformly sampled.



Figure 3.6: Biasing factors difference between $\lambda = 0$ and $\lambda = 1$ as a function of temperature for the different water models. The top lines correspond to the gas phase and bottom lines to the liquid phase.

Wang-Landau method [52]. Ideally, the final histograms should be flat to ensure the system can visit all λ -states uniformly. If the histograms are completely flat then the difference of the biasing factor at $\lambda = 0$ and $\lambda = 1$ is the related to the difficulty of inserting a molecule. As can be observed, all of the histograms are reasonably flat.

In Figure 3.6, the difference in biasing factors between $\lambda = 0$ and $\lambda = 1$ as a function of temperature is presented for the three different models. The total biasing needed to swap a molecule from the liquid to the gas phase and vice versa increases with decreasing temperature, and is of around 12 k_BT at 280 K. Without biasing, single-step insertion/deletions would be rare events at this temperature, leading to acceptance ratios close to zero.

We further tested the CB/CFCMC method by computing the vapor-liquid coexistence curve of an other strong and directional self-interacting system: N,Ndimethylformamide (DMF). DMF is broadly used as a solvent (for example in metal-organic framework synthesis) and its strong interactions are mostly a consequence of its dipole moment (μ =3.8 D).

In Figure 3.7, the VLE curve of DMF is presented. The simulations were equilibrated for 50000 cycles and 100000 production cycles were performed, both of them using 10 trial positions. The experimental values for low temperatures from reference [53] are well reproduced. Also the results by Vahid *et al.* [35] are reasonably well reproduced. They obtained these results by performing Monte Carlo simulations in the NPT ensemble at 1 atm with fragment-based configurational bias, thus not relying on insertions and deletions like the Gibbs ensemble.

In the Gibbs ensemble simulations of DMF, $\Delta \lambda_{\text{max}}$ was scaled to achieve 50% acceptance in the λ -moves. This lead in most of the temperatures to very small maximum $\Delta \lambda$ changes, which means that even small changes in λ have a large energy penalty. As we already showed in Figure 3.2a, as $\Delta \lambda_{\text{max}}$ approaches zero, the particle exchange probability becomes close to 50%. For all temperatures we



Figure 3.7: Vapor-liquid equilibrium curve for N,N- dimethylformamide (DMF). The blue dots were obtain in this work using CB/CFCMC. The red crosses were taken from the work of Vahind *et al.* [35] and were obtained using MC simulations in the NPT ensemble at 1 atm with fragmented-based configurational-bias and the black triangles are experimental values from Nikam *et al.* [53].



Figure 3.8: (a) Biasing factors (in units of k_BT) used and (b) obtained histogram (number of occurrences of a given λ value) for Gibbs ensemble simulation of N,N-dimethylformamide (DMF) at different temperatures. There appears to be a minimum around $\lambda = 0.4$.

obtained an acceptance percentage of the exchange move of around 40%, even though the histograms are not completely flat (Figure 3.8b). Interestingly there appears to be a minimum around $\lambda = 0.4$ at low temperatures (Figure 3.8a). The minimum in λ space is related with the density, shape, and packing of the molecules. We also computed the vapor-liquid equilibrium using the CBMC method for 280 K and 303 K. For both temperatures we obtained densities that are in good agreement with the experimental results and with our CB/CFCMC simulations, however, the acceptance percentage of the exchange move is close to zero. The equilibration of the system is further achieved via fluctuations in the volume.

For both, DMF and water, CBMC and CB/CFCMC reproduce the VLE curves

equally well. However, CB/CFCMC is an order of magnitude more efficient than CBMC. We also see an improvement when using CB/CFCMC as compared to CFMC, but we expect this to be more substantial for longer and more flexible molecules, like alkanes. If we would be interested in the VLE curves of more complicated solvents like DMSO (dimethylsulfoxide), tetrahydrofuran, teramethylamine or mixtures of solvents, using CBMC or CFCMC would require a great amount of computational time. These simulations would be more feasible using CB/CFCMC. The efficiency of the method also highlights its applicability for the optimization of force field parameters.

3.3.2 Adsorption of water in metal-organic frameworks

In the field of metal-organic frameworks (MOFs), one of the concerns for practical applications is the water stability of the materials [54, 55]. Understanding water adsorption is important to understand MOF water-(in)stability and therefore help in the design of next generation porous materials. Water adsorption in nanoporous materials is also interesting for the purification of water waste [56, 57], catalysis [58] or heat-pumps [59]. Adsorption isotherms are obtained by performing Monte Carlo simulations in the grand-canonical ensemble. Water adsorption is very sensitive to the water model and the chemical composition of the pores [60, 61]. Especially for hydrophobic zeolites, there is hardly any water adsorption at low pressures, but once adsorption starts the increase in loading is very steep. Water adsorption at low pressures is usually related to adsorption at defects. The steepness of the inflection in the isotherm brings forth a computational problem. The slope of the isotherm is related to the amount of fluctuations in the number of molecules which means a large phase-space needs to be sampled [62, 63]. Two problem areas are: (1) accuracy and (2) efficiency. The former means that the sampling method needs to be ergodic, and the latter implies that a scheme should be used with efficient insertions and deletions.

To analyze the performance of CB/CFCMC in the simulation of water adsorption isotherms, we studied the adsorption of SPC water at 298 K in the Zn-DMOF-TM metal-organic framework. Zn-DMOF-TM is a well known metalorganic framework that is stable in the presence of humidity [64, 65] and is synthesized using terephthalic acid functionalized with four methyl groups on the aromatic forming 2D sheets connected to each other in the third dimension using 4-diazabicyclo[2.2.2]-octane (DABCO). In Figure 3.9a, the isotherms for the SPC water model using CBMC and CB/CFCMC algorithms are presented. The system was simulated for 500000 equilibration cycles followed by 500000 production cycles. The saturation loading obtained in the simulations agrees very well with the experimental results from Jasuja et al. [65]. The simulations, however, show an onset of the isotherm step that is shifted to the right. This will be addressed later. Although both CBMC and CFCMC give the same results within the error bar and the trends are qualitatively the same, there are quantitative differences in how the isotherm step occurs in the two approaches. The slope of an isotherm is proportional to the fluctuations in the number of absorbed particles in the sys-



Figure 3.9: (a) Adsorption isotherms of SPC water in Zn-DMOF-TM at 298 K using CBMC and CB/CFCMC algorithms. (b) Adsorption isotherms of SPC water in Zn-DMOF-TM at 298 K using CB/CFCMC for an evacuated structure, a structure with one preloaded water molecule per unit cell and a structure with two preloaded water molecules per unit cell.



Figure 3.10: (a) Biasing factors (in units of k_BT) used and (b) obtained histograms (number of occurrences of a given λ value) in the simulation of water adsorption in Zn-DMOF-TM at 298 K.

tem [62]. For the adsorption of water in Zn-DMOF-TM, the fluctuations are very large. CB/CFCMC inserts and deletes molecules gradually, thus sampling large fluctuations (even with a flat histogram) takes more production cycles than normal CBMC.

In addition to the slow sampling of the large fluctuations in the number of adsorbed molecules, when analyzing the λ -histogram for the CB/CFCMC method (Figure 3.10b), we see that the histogram is not entirely flat. As pointed out before, this means that the values of λ are not uniformly sampled, thus insertion and deletion of molecules is not performed in an optimal way.

We ran longer simulations (10000 more equilibration cycles and 100000 more

Table 3.4: Water loading in Zn-DMOF-TM after running the CB/CFCMC simulations for 10000 more equilibration cycles and 100000 more production cycles.



Figure 3.11: (a) Insertion acceptance percentage as a function of vapor pressure for water adsorption in Zn-DMOF-TM using the CBMC and the CB/CFCMC methods. (b) Biasing factors for different vapor pressure points. In the step of the isotherms the biasing factors are either similar to the zero loading biasing factors or to the saturation biasing factors.

production cycles) for two pressure points in the isotherm step: 4.75 kPa and 5.7 kPa. In both cases, the water loading increased (Table 3.4) and the biasing changed. This suggests that (1) equilibration is slow, and (2) no proper biasing profile had been obtained. In Figure 3.11a, the acceptance percentage of insertion as a function of vapor pressure for both methods is presented. For CBMC after around 4.75 kPa, where the simulations reach saturation, the acceptance percentage is close to zero. This, together with the fact that in Figure 3.9a, the error bars for CBMC after 4.75 kPa are negligible, suggests that the system is trapped in a metastable state. CB/CFCMC on the other hand has very good acceptance percentage for all pressure points. The difficulty of sampling the large fluctuations in the isotherm step for CB/CFCMC is reflected in the decrease of the acceptance percentage in this pressure range from around 20% to 5%.

Note that adsorption is usually started from a lower pressure point, while desorption is started from an equilibrated system at higher pressures. Many systems do not show hysteresis and in the absence of hysteresis it is convenient to run all pressure points independently starting from zero loading (using an "embarrassing parallelization" scheme). However, this can lead to slower convergence as the Wang-Landau biasing is obtained while the loading is still increasing. The correct biasing should have been the biasing factors from the final equilibrated system, but instead we sometimes obtain biasing values that can actually hamper reaching equilibration. This can for example be seen in Figure 3.11b. For pressure points with zero loading (2.6 kPa), at the beginning of the isotherm step (4.75 kPa), and in the middle of the isotherm step (5.7 kPa), all the biasing factors are basically the same and correspond to the biasing factors from zero loading. In principle, they should continuously change between the zero loading biasing factors and the saturation biasing factors, but this is only the case for the pressure point 6.8 kPa. For the rest of the pressure points, the biasing factors are still unconverged. A possible remedy is to fix the biasing values by hand, setting them in the inflection region to values in between low and high loading.

We conclude that it is an advantage to combine CB/CFCMC with regular CBMC. That is, we have a fractional molecule and do λ trial moves, but we also do conventional insertion attempts to insert integer molecules as a whole. In the isotherm's region of large fluctuations the insertion probability of CBMC is sufficiently high, and a quicker change in the overall number of molecules can be achieved.

Even with better sampling there is still disagreement between the experimental results and the simulations. This can be due to the water/framework model, as it has been highlighted before [61], or it could be due to the presence of defects or initial moisture in the structure in the experiments, which act as nucleation centers [66].

For example, it has been observed that solvent molecules like DMF can act as adsorption sites [67]. In Figure 3.9b we present the simulated adsorption isotherms assuming one and two water molecules per unit cell are already present in the structure. These structures were created by taking the evacuated Zn-DMOF-TM and inserting one and two water molecules close to the metal sites (where they would naturally adsorb first) respectively. The extra molecules were kept fixed during the simulations, since we were only interested in analyzing how much would the presence of a nucleation center shift the shooting pressure of the isotherm. Qualitatively, pre-loaded water molecules shift the water isotherm to the left and



Figure 3.12: Effect of adding one and two preloaded water molecules in Zn-DMOF-TM structure on the adsorption isotherm of water at 298 K using the CBMC method.

closer to experiments for both the CBMC and CB/CFCMC methods. CBMC results are presented in Figure 3.12. These results suggest that a possible source of disagreement between simulations and experiments for the onset of the water isotherms comes from the presence of water (or left-over solvents) that can not be removed easily.

3.4 Conclusions

Computing VLE curves is important to understand fluid phase properties, but also because VLE curves are often used for force field development. The CFCMC and CB/CFCMC methods are well-adapted to compute VLE properties for strongly interacting solvents, like water and DMF, even at low temperatures. These methods would therefore also be the method of choice for studying adsorption in ionic liquids. However, in these cases it is crucial to use λ -biasing which makes the histograms in λ -space sufficiently flat. A non-optimal biasing of even 4 or 5 k_BT severely reduces acceptance ratios. Optimal biasing leads to acceptance ratios roughly between 20-30%, depending on the system and $\Delta\lambda_{\max}$. For adsorption simulations of systems where the isotherms steeply increase the CFCMC and CB/CFCMC are relatively slow to change the number of molecules. The methods have to diffuse, effectively performing a random walk in λ -space. Under these steep-isotherm conditions the sampling of large fluctuations in the number of molecules becomes a problem. This problem can be remedied by enhancing CFCMC and CB/CFCMC methods with regular CBMC moves on integer molecules.

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CHAPTER 4

Computing the Heat of Adsorption in Nanoporous Materials close to Saturation Conditions*

4.1 Introduction

In the last decades, there has been a large growth of adsorption separation technologies, such as Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA), in the chemical and petrochemical industries [1]. In PSA and TSA processes, separation relies (mostly) on the difference in the adsorption equilibrium (determined by macroscopic state variables, such as T and P) of the mixture components [2]. Ideally, PSA and TSA are isothermal processes, but in reality they operate under almost adiabatic conditions [2]. PSA and TSA operate by passing the mixture through a large column packed with adsorbent material and heat is produced as the mixture components are adsorbed (adsorption is generally an exothermic process). The heat of adsorption or enthalpy of adsorption (ΔH_{ads}) is a quantitative measure of the strength of the adsorbates binding to the adsorbent, and it determines the extent of the adsorbent temperature changes during adsorption (exothermic process) and desorption (endothermic process). It is therefore a critical design variable to improve the performance of adsorption-based separation processes.

Many industrial separations work at saturation conditions to operate cost efficiently. In this regime, separations are driven by entropic mechanisms [3–5]. The variation in the enthalpy of adsorption with loading provides information on the changes in the entropy of the system as adsorption occurs [6]. Close to saturation, the enthalpy of adsorption provides important insight in the separation process.

^{*}Based on: A. Torres-Knoop, A. Poursaeidesfahani, T. J. H. Vlugt, D. Dubbeldam, submitted

However, little is known about the enthalpy of adsorption close to saturation conditions. Most of the experimental and simulation studies focus on the low loadings regime [7–10]. The main reason behind this is the complexity associated with studying saturation conditions. In experiments, the pressure range that can be explored for adsorption (before the adsorbates turn into a liquid) is limited by the vapor pressure and in molecular simulations its restricted by the current simulation methodologies. In this chapter, we further develop the current computational methods to study the heat of adsorption close to saturation conditions.

4.2 Theory

The enthalpy of adsorption is defined as the change in the total enthalpy of the system (gas phase, host and guest molecules) as a molecule is transferred from the gas phase to the adsorbed phase at constant temperature [11]:

$$\Delta H_{\rm ads} = \left(\frac{\partial(\Delta H)}{\partial N}\right)_{V,T} = \left(\frac{\partial(H_{hg} - H_g)}{\partial N}\right)_{V,T} \tag{4.1}$$

where H_{hg} refers to the enthalpy of the host with guest molecules and H_g to the enthalpy of a reference gas phase, N is the number of molecules, V is the volume, and T is the absolute temperature.

If we assume that the gas phase behaves as an ideal gas and the adsorbent is rigid such that the molecular volume of the adsorbed phase can be neglected, it can be shown that the enthalpy of adsorption is given by [11, 12]

$$\Delta H_{\rm ads} = \left(\frac{\partial U}{\partial N}\right)_{V,T} - \langle U_g \rangle - k_B T \tag{4.2}$$

where U refers to the total energy of the host and adsorbed molecules, $\langle U_g \rangle$ is the average energy of a molecule in the gas phase, and k_B is the Boltzmann constant.

In experiments, the enthalpy of adsorption can be determined from the heat released in calorimetric experiments [13, 14] or using the isosteric method, where a series of isotherms are measured at different temperature. The Clausius-Clapeyron equation [12, 15] at constant loading (Θ) is used to compute the change in enthalpy. The later is called *isosteric heat* and is the negative of the enthalpy of adsorption:

$$q_{st} = -\Delta H_{ads} = k_B \left(\frac{\partial \ln(P/P_0)}{\partial T^{-1}}\right)_{\Theta}$$
(4.3)

where P is the pressure and P_0 an arbitrary reference pressure.

In molecular simulations, the enthalpy of adsorption can be obtained by several methods:

1. *Isosteric method*: computing adsorption isotherms at different temperatures and using the Clausius-Clapeyron equation (Eq. 4.3) 2. Isosteric method with Widom insertion [16, 17]: at low loadings (where the adsorption isotherm becomes a linear function of pressure, $\Theta = K_H P$), it can be calculated using a modified Clausius-Clapeyron equation [18]

$$\Delta H_{\rm ads} = -\left(\frac{\partial \ln(K_H)}{\partial \beta}\right) \tag{4.4}$$

where $\beta = 1/(k_B T)$ is the inverse temperature. In Eq. 4.4, K_H is known as the Henry coefficient and can be obtained using Widom's test particle insertion method [19]

$$K_H = \beta \times e^{-\beta\mu_{ex}} = \beta \times \frac{\left\langle e^{-\beta u^+} \right\rangle_H}{\left\langle e^{-\beta u^+_{IG}} \right\rangle_{IG}}$$
(4.5)

where μ_{ex} is the excess chemical potential of the guest molecules in the host system, u^+ the energy of the test (guest) molecule in the host, u_{IG}^+ the energy of the test (guest) molecule in the ideal gas phase and $\langle \cdots \rangle_H$ and $\langle \cdots \rangle_{IG}$ refer to the *NVT*-ensemble average over the host-test molecule configurations and to the *NVT*-ensemble average over the test molecule configurations in the ideal gas phase, respectively. Alternatively, the Rosenbluth method can be used for Widom's test particle insertions [16].

3. *NVT-Method* [20]: at zero coverage, the partial derivative in Eq. 4.2 can be estimated by the energy difference in the *NVT*-ensemble:

$$\left(\frac{\partial U}{\partial N}\right)_{V,T} \approx \langle U \rangle_{N+1} - \langle U \rangle_N \tag{4.6}$$

$$\Rightarrow \Delta H_{\rm ads} = \langle U \rangle_{N+1} - \langle U \rangle_N - \langle U_g \rangle - k_B T \tag{4.7}$$

in which U is the total energy of a host with the adsorbed (guest) molecules, $\langle \cdots \rangle_{N+1}$ refers to the ensemble average at constant T, V and N+1 guest molecules and $\langle \cdots \rangle_N$ refers to the ensemble average at constant T, V and Nguest molecules. In principle, the two first averages in Eq. 4.7 can also be computed in a single simulation in the canonical ensemble. [16, 17].

4. Slope method [6]: if we can approximate (locally) the variation of the total energy U with the number of guest molecules N by a function f(N), then the partial derivative in Eq. 4.2 can be estimated from the slope of f

$$\left(\frac{\partial U}{\partial N}\right)_{V,T} \approx \left(\frac{df(N)}{dN}\right)_{V,T} \tag{4.8}$$

5. Energy/particle fluctuation method: [12, 21, 22] the partial derivative in Eq. 4.2 can be estimated using the energy/particle fluctuation method in the

grand-canonical ensemble

$$\left(\frac{\partial U}{\partial N}\right)_{V,T} = \frac{\left(\frac{\partial U}{\partial \mu}\right)_{V,T}}{\left(\frac{\partial N}{\partial \mu}\right)_{V,T}} = \frac{\langle U \times N \rangle_{\mu} - \langle U \rangle_{\mu} \langle N \rangle_{\mu}}{\langle N^{2} \rangle_{\mu} - \langle N \rangle_{\mu} \langle N \rangle_{\mu}}$$
(4.9)

$$\Rightarrow \Delta H_{\rm ads} = \frac{\langle U \times N \rangle_{\mu} - \langle U \rangle_{\mu} \langle N \rangle_{\mu}}{\langle N^2 \rangle_{\mu} - \langle N \rangle_{\mu} \langle N \rangle_{\mu}} - \langle U_g \rangle - 1/\beta \tag{4.10}$$

where $\langle \cdots \rangle_{\mu}$ refers to averages in the grand-canonical ensemble.

Most of these methods are not well suited to determine the enthalpy of adsorption as a function of loading (especially at saturation loadings). With the isosteric method, several simulations or adsorption experiments are required at different temperatures and the accuracy of the obtained enthalpy of adsorption strongly depends on the accuracy of the individual simulations [7, 23]. Using the NVT method, as the loading increases, the difference in $|\langle U \rangle_{N+1} - \langle U \rangle_N|$ becomes very small compared with $\langle U \rangle_{N+1}$ or $\langle U \rangle_N$ and the direct computation of these quantities can lead to a very inaccurate estimate of $\Delta H_{\rm ads}$ [17]. The slope method can be used to determine the heat of adsorption as a function of loading (including isotherms inflections), but becomes difficult to use as the system approaches saturation. Close to saturation, the energy of the system as a function of loading has very sharp changes and is not always straight forward to approximate with a polynomial function. The most appropriate method to compute the enthalpy of adsorption as a function of loading (including saturation) is the fluctuation method. The main problem with the fluctuation method is that it relies on the insertion and deletions of molecules to sample the fluctuations. Therefore, it breaks at saturation conditions, where most Monte Carlo techniques have a very low probability of inserting or deleting molecules.

The recently proposed method by Shi *et al.*, Continuous Fractional Component Monte Carlo (CFCMC) [24], facilitates the insertion and deletion of molecules by expanding the system with an additional molecule, from now on refer to as *fractional molecule*. The interactions of the fractional molecule with the surroundings (Lennard-Jones and charge interactions) are scaled using a parameter λ :

$$u_{\rm LJ}(r) = \lambda 4\epsilon \left[\frac{1}{\left[\frac{1}{2} \left(1 - \lambda\right)^2 + \left(\frac{r}{\sigma}\right)^6\right]^2} - \frac{1}{\left[\frac{1}{2} \left(1 - \lambda\right)^2 + \left(\frac{r}{\sigma}\right)^6\right]} \right]$$
(4.11)

$$u_{\text{Coul}}(r) = \lambda^5 \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r}.$$
(4.12)

where ϵ_0 is the dielectric constant in vacuum, r is the interatomic distance, q is the atomic charge, ϵ is the LJ strength parameter and σ is the LJ size parameter. When $\lambda = 1$, the fractional molecule has full interactions with the surroundings and when $\lambda = 0$ it has no interactions with the surroundings. Molecules are inserted and deleted by performing a random walk in λ -space using $\lambda_n = \lambda_o + \Delta \lambda$, where $\Delta \lambda$ is chosen between $-\Delta \lambda_{\max}$ and $\Delta \lambda_{\max}$. $\Delta \lambda_{\max}$ is adjusted to achieve roughly 50% acceptance. When $\lambda_n \geq 1$ molecules are inserted and when $\lambda_n \leq 0$ molecules are deleted.

The procedures for insertion/deletion attempts are

- insertion, $\lambda_n \geq 1$
 - 1. A new fractional molecule with $\lambda = \lambda_n 1$ is randomly inserted
 - 2. Acceptance rule: $P_{\text{acc}} = \min\left(1, \frac{f\beta V}{N+1} \exp[-\beta \Delta U] \exp[\eta \left(\lambda_n - 1\right)\right) - \eta \left(\lambda_o\right)]\right)$
- deletion, $\lambda_n \leq 0$
 - 1. The existing fractional particle is deleted and an existing molecule is randomly selected and converted into the fractional molecules with $\lambda = 1 + \lambda_n$
 - 2. Acceptance rule: $P_{\text{acc}} = \min\left(1, \frac{N}{f\beta V} \exp[-\beta \Delta U] \exp[\eta \left(\lambda_n + 1\right) - \eta \left(\lambda_o\right)]\right)$

where $\beta = 1/(k_B T)$, f is the fugacity of the system, N the current number of adsorbed molecules, ΔU the difference in the energy between the old and the new configuration and $\eta(\lambda)$ is a biasing potential to avoid λ from getting trapped in a certain range [24].

The method introduced by Torres-Knoop *et al.* [25], the Configurational Bias Continuous Fractional Component Monte Carlo method (CB/CFCMC), further improves the probability of insertions and deletions by biasing the insertion of molecules in the system towards favorable configurations using the Configurational-Bias Monte Carlo (CBMC) [26–28] technique at a constant λ value [25]. The procedures for insertions and deletions in this case are

- insertion, $\lambda_n \geq 1$
 - 1. A new fractional molecule with $\lambda = \lambda_n 1$ is grown using CBMC resulting in W(n).
 - 2. Acceptance rule: $P_{\text{acc}} = \min\left(1, \frac{f\beta V}{N+1} \frac{W(n)}{\langle W^{\text{IG}} \rangle} \exp[-\beta \Delta U] \exp[\eta \left(\lambda_n - 1\right) - \eta \left(\lambda_o\right)]\right)$
- deletion, $\lambda_n \leq 0$
 - 1. The existing fractional particle is retraced using CBMC with $\lambda = \lambda_o$ resulting in W(o) and the fractional molecule is subsequently removed.
 - 2. Acceptance rule: $P_{\rm acc} = \min\left(1, \frac{N}{f\beta V} \frac{\langle W^{\rm IG} \rangle}{W(o)} \exp[-\beta \Delta U] \exp[\eta \left(\lambda_n + 1\right) - \eta \left(\lambda_o\right)]\right)$

where N is the number of adsorbed molecules, f the fugacity, ΔU the energy change due to insertions/deletions, $\langle W_{IG} \rangle$ the average Rosenbluth weight of an isolated molecule in the gas phase, and W(n) and W(o) the Rosenbluth weights of the old an new configuration respectively. CFCMC and CB/CFCMC significantly improve insertions and deletions at saturation conditions, where most Monte Carlo methods, such as standard CBMC, fail. However it is not clear how the heat of adsorption should be computed using the fluctuation method with these algorithms.

In this work, we derive an expression for the heat of adsorption using CFCMC (an extension to the CB/CFCMC algorithm can be done following similar steps), we validate it and we use it to study the enthalpy of adsorption at saturation conditions. We show that the heat of adsorption strongly increases near the maximum loading and that CBMC in the GC ensemble fails to capture this behaviour while CFCMC and CB/CFCMC correctly compute it.

4.3 Results

Derivation of the heat of adsorption in CFCMC

As pointed out in Eq. 4.10, in the energy/particle fluctuation method, the change in the potential energy upon adsorption can be approximated by

$$\left(\frac{\partial \langle U \rangle_{\mu}}{\partial \langle N \rangle_{\mu}}\right)_{V,T} = \frac{\langle U \times N \rangle_{\mu} - \langle U \rangle_{\mu} \langle N \rangle_{\mu}}{\langle N^{2} \rangle_{\mu} - \langle N \rangle_{\mu} \langle N \rangle_{\mu}}.$$
(4.13)

Therefore, the enthalpy of adsorption (or isosteric heat of adsorption) is given by:

$$-q = \Delta H_{\text{ads}} = \frac{\langle U \times N \rangle_{\mu} - \langle U \rangle_{\mu} \langle N \rangle_{\mu}}{\langle N^2 \rangle_{\mu} - \langle N \rangle_{\mu} \langle N \rangle_{\mu}} - \langle U_g \rangle - 1/\beta$$
(4.14)

where $\langle \cdots \rangle$ refers to the ensemble average in the conventional GC ensemble and $\langle U_g \rangle$ is the average energy of a gas molecule. For CFCMC, the partition function in the grand canonical ensemble is given by [25]:

$$Q_{\rm CFCMC} = \sum_{N=0}^{\infty} \sum_{j=0}^{M} \frac{V^{N+1} e^{\beta \mu N} e^{\eta_j}}{\Lambda^{3N+3} N!} \int ds^{N+1} e^{-\beta U_{\rm total}(s^{N+1})}$$
(4.15)

where the total energy of the system is the sum of the energy of the integer molecules plus the energy of the fractional molecule $(U_{\text{total}} = U_{\text{int}} + U_{\text{frac}})$, the total number of molecules is the integer number of molecules in the system $(N = N_{\text{int}})$ and the factor e^{η_j} accounts for the biasing in λ -space (M equals the number of bins λ space is divided in). Therefore, using CFCMC, the change in the potential energy upon adsorption (Eq. 4.9) can be approximated by:

$$\frac{\partial \langle U_{\rm CFCMC} \rangle_{\rm CFCMC}}{\partial \langle N_{\rm CFCMC} \rangle_{\rm CFCMC}} = \frac{\frac{\partial \langle U_{\rm CFCMC} \rangle_{\rm CFCMC}}{\partial \mu}}{\frac{\partial \langle N_{\rm CFCMC} \rangle_{\rm CFCMC}}{\partial \mu}}.$$
(4.16)

where $U_{\rm CFCMC}$ and $N_{\rm CFCMC}$ refer to the total energy and number of molecules obtained using the CFCMC algorithm and $\langle \cdots \rangle_{\rm CFCMC}$ refers to the ensemble average in the GC ensemble using CFCMC.

In CFCMC the total average loading and total average energy are not uniquely defined. In the most general case, $U_{\rm CFCMC}$ and $N_{\rm CFCMC}$ have the form:

$$U_{\text{CFCMC}} = U_{\text{int}} + f(\lambda, s^{N+1}) ; \ N_{\text{CFCMC}} = N_{\text{int}} + g(\lambda)$$

where $f(\lambda, s^{N+1})$ is the interaction energy of the fractional molecule with the surroundings and $g(\lambda)$ is the 'size' or degree of presence of the fractional molecule. Thus,

$$\frac{\partial \left\langle U_{\rm CFCMC} \right\rangle_{\rm CFCMC}}{\partial \mu} = \frac{\partial}{\partial \mu} \left[\frac{\sum\limits_{N=0}^{\infty} \sum\limits_{j=1}^{M} \frac{V^{N+1} e^{\beta \mu N} e^{\eta_j}}{\Lambda^{3N+3} N!} U_{\rm CFCMC} \int ds^{N+1} e^{-\beta U_{\rm total}(s^{N+1})}}{\sum\limits_{N=0}^{\infty} \sum\limits_{j=1}^{M} \frac{V^{N+1} e^{\beta \mu N} e^{\eta_j}}{\Lambda^{3N+3} N!} \int ds^{N+1} e^{-\beta U_{\rm total}(s^{N+1})}} \right]$$

$$= \left[\frac{\sum\limits_{N=0}^{\infty} \sum\limits_{j=1}^{M} \frac{v^{N+1} e^{\beta \mu N} e^{\eta j}}{\Lambda^{3N+3} N!} \beta N U_{\text{CFCMC}} \int ds^{N+1} e^{-\beta U_{\text{total}}(s^{N+1})} \times \sum\limits_{N=0}^{\infty} \sum\limits_{j=1}^{M} \frac{v^{N+1} e^{\beta \mu N} e^{\eta j}}{\Lambda^{3N+3} N!} \int ds^{N+1} e^{-\beta U_{\text{total}}(s^{N+1})}}{\left(\sum\limits_{N=0}^{\infty} \sum\limits_{j=1}^{M} \frac{v^{N+1} e^{\beta \mu N} e^{\eta j}}{\Lambda^{3N+3} N!} \int ds^{N+1} e^{-\beta U_{\text{total}}(s^{N+1})} \right)^2} \right]$$

$$-\left[\frac{\sum\limits_{N=0}^{\infty}\sum\limits_{j=1}^{M}\frac{V^{N+1}e^{\beta\mu N}e^{\eta j}}{\Lambda^{3N+3}N!}\beta_{N}\int ds^{N+1}e^{-\beta U_{\text{total}}(s^{N+1})}\times\sum\limits_{N=0}^{\infty}\sum\limits_{j=1}^{M}\frac{V^{N+1}e^{\beta\mu N}e^{\eta j}}{\Lambda^{3N+3}N!}U_{\text{CFCMC}}\int ds^{N+1}e^{-\beta U_{\text{total}}(s^{N+1})}}{\left(\sum\limits_{N=0}^{\infty}\sum\limits_{j=1}^{M}\frac{V^{N+1}e^{\beta\mu N}e^{\eta j}}{\Lambda^{3N+3}N!}\int ds^{N+1}e^{-\beta U_{\text{total}}(s^{N+1})}\right)^{2}}\right]$$
$$=\beta\left[\langle U_{\text{CFCMC}}N\rangle_{\text{CFCMC}}-\langle U_{\text{CFCMC}}\rangle_{\text{CFCMC}}\langle N\rangle_{\text{CFCMC}}\right] \qquad (4.17)$$

In the same way, one can show that:

$$\frac{\partial \langle N_{\rm CFCMC} \rangle_{\rm CFCMC}}{\partial \mu} = \beta \left[\langle N_{\rm CFCMC} N \rangle_{\rm CFCMC} - \langle N_{\rm CFCMC} \rangle_{\rm CFCMC} \langle N \rangle_{\rm CFCMC} \right]$$
(4.18)

Therefore,

$$\frac{\partial \langle U_{\rm CFCMC} \rangle_{\rm CFCMC}}{\partial \langle N_{\rm CFCMC} \rangle_{\rm CFCMC}} = \frac{\langle NU_{\rm CFCMC} \rangle_{\rm CFCMC} - \langle N \rangle_{\rm CFCMC} \langle U_{\rm CFCMC} \rangle_{\rm CFCMC}}{\langle NN_{\rm CFCMC} \rangle_{\rm CFCMC} - \langle N \rangle_{\rm CFCMC} \langle N_{\rm CFCMC} \rangle_{\rm CFCMC}}$$
(4.19)

For large systems, ensemble averages in the CFCMC and the conventional GC ensemble are identical:

$$\frac{\langle NU \rangle_{\mu} - \langle N \rangle_{\mu} \langle U \rangle_{\mu}}{\langle N^{2} \rangle_{\mu} - \langle N \rangle_{\mu}^{2}} = \frac{\langle NU_{\rm CFCMC} \rangle_{\rm CFCMC} - \langle N \rangle_{\rm CFCMC} \langle U_{\rm CFCMC} \rangle_{\rm CFCMC}}{\langle NN_{\rm CFCMC} \rangle_{\rm CFCMC} - \langle N \rangle_{\rm CFCMC} \langle N_{\rm CFCMC} \rangle_{\rm CFCMC}}$$
(4.20)

The most trivial choice to guarantee that

$$\frac{\partial \langle U \rangle_{\mu}}{\partial \langle N \rangle_{\mu}} = \frac{\partial \langle U_{\rm CFCMC} \rangle_{\rm CFCMC}}{\partial \langle N_{\rm CFCMC} \rangle_{\rm CFCMC}}$$
(4.21)

i.e ΔH is equal in both ensembles, is to set

$$U_{\text{CFCMC}} = U_{\text{int}} \to f(\lambda, s^{N+1}) = 0 \; ; \; N_{\text{CFCMC}} = N_{\text{int}} \to g(\lambda) = 0 \tag{4.22}$$

Therefore, when using the fluctuation method with the CFCMC algorithm, the energy of the fractional molecule should not be considered and the total number of molecules should not count the fractional molecule.

This formulation can be generalized to mixtures by using that the energy upon adsorption is given by [29]:

$$\left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \sum_k \left(\frac{\partial U}{\partial \mu_k}\right)_{T,V,N_{j\neq i}} \left(\frac{\partial \mu_k}{\partial N_i}\right) \tag{4.23}$$

To validate the obtained expressions, we computed and compared the enthalpy of adsorption of mixtures of CO_2 and CH_4 at three different pressures and with different molarities using the CBMC and CFCMC methods in MFI zeolite at 300 K (Figure 4.1). MFI zeolite was modeled as rigid with crystallographic positions taken from ref. [30] and force field parameters taken from ref. [31]. The adsorbates were modeled using the TraPPE [32, 33] force field.



Figure 4.1: (a) Mixture adsorption isotherm of an equimolar CH_4 and CO_2 mixture in MFI zeolite at 300 K obtained using CB/CFCMC. (b) Heat of adsorption of mixtures of CO_2 and CH_4 with different molarities at three different pressures in MFI zeolite at 300 K. The open symbols correspond to the results obtained using CBMC and the close symbols to the results obtained using CB/CFCMC. For all molarities and pressures the results obtained with both methods are identical.

Figure 4.1a corresponds to an equimolar mixture. In this Figure, we can see that for all the mixture molarities used in Figure 4.1b the system is not saturated at the simulated pressures (dashed lines in Figure 4.1a). Becasue of this, we expect CBMC to still be able to perform without problems. In Figure 4.1b, we show that there is excellent agreement between the methods in the obtained enthalpies of adsorption for the three pressures and all the mixture molarities.



Figure 4.2: Single component adsorption isotherms of (a) CH_4 and (b) CO_2 in MFI zeolite at 300 K. The two methods are in excellent agreement with each other.



Figure 4.3: Enthalpy of adsorption as a function of adsorbed amount of (a) CH_4 in MFI and (b) CO_2 in MFI at 300 K.

4.3.1 Case Studies

CH_4 and CO_2 in MFI zeolite

As a first case study, we computed the enthalpy of adsorption as a function of loading of CO_2 and CH_4 in MFI zeolite at 300 K. In Figure 4.2, the adsorption isotherms obtained with CBMC and CFCMC are presented. We can see that for both, CO_2 and CH_4 , CBMC and CFCMC simulations are in excellent agreement. They are also in agreement with the results of Garcia-Perez *et al.* [34] and experimental references therein.

In Figure 4.3, the enthalpies of adsorption as a function of loading using CBMC and CFCMC are presented. For CH_4 , the results are in good agreement up to roughly twelve molecules per unit cell. For CO_2 the results are in good agreement up to roughly fifteen molecules per unit cell. These loadings correspond to the (first) inflection in the isotherms of CH_4 and CO_2 , respectively (Figure 4.2). In-

flections in the isotherms reflect a local upper bound (either per site or per system) in the adsorption and occur due to a change in the adsorption energy. In Monte Carlo simulations, a less favorable adsorption energy is reflected in a decrease in the probability of insertions.

In Figure 4.4, the acceptance percentage of inserting CH_4 molecules as a function of loading for both methods is presented. For CBMC, the acceptance percentage decreases with increasing loading and is lower than 5% after fifteen molecules per unit cell. CFCMC is able to overcome the energy penalty of insertions and this leads to an acceptance percentage above 40% for all loadings.

A comparison with the enthalpy of adsorption obtained using the isosteric method (Clausius-Clapeyron equation) shows that the results of the enthalpy of adsorption obtained using CFCMC are more accurate (Figure 4.5). This is most likely because CFCMC efficiently samples the system's configurations at *high* loadings.

For the adsorption of CO_2 and CH_4 in MFI, even though CBMC is not able to sample the system's configurations as efficiently as CFCMC, the systems are still far enough from saturation (the isotherms in Figure 4.2 are still going up) for CBMC to capture the changes in the enthalpy of adsorption in the loading range considered.



Figure 4.4: Acceptance percentage of insertion of CH_4 molecules in MFI as a function of loading.



Figure 4.5: Enthalpy of adsorption obtained using the CBMC method, the CFCMC method and the isosteric method for (a) CH_4 and (b) CO_2 in MFI at 300 K.

CH₄ in CHA zeolite

As a second case study, we simulated the adsorption of methane in CHA zeolite at 300 K. CHA zeolite is a structure with cages separated by narrow channels. In Figure 4.6a the adsorption isotherm is presented. An interesting feature of this structure is that adsorption reaches a saturation plateau at six molecules per unit cell that remains constant for a large range of pressures. In principle, it is always possible to push more molecules inside the structure (as the Lennard-Jones potential is soft), but in this case, the necessary energy (related with the pressure range in which the saturation plateau stays constant) is very large. The values for the enthalpy of adsorption obtained using CBMC and CFCMC are in good agreement up to around five molecules per unit cell (Figure 4.6b), where the inflection in the isotherm occurs. After this point, the enthalpy of adsorption obtained with CFCMC sharply increases and has an asymptotic behavior towards the saturation loading, while the CBMC results remain constant, albeit higher fluctuations.

The Clausius-Clapeyron equation (Eq. 4.3) also points to the fact that the enthalpy of adsorption diverges as we approach saturation loading. Lets assume for example that the isotherms of a system at different temperatures can be described with the Langmuir-Freundlich model:

$$\theta = \frac{q_{\rm sat} b P^{1/n}}{1 + b P^{1/n}},\tag{4.24}$$

where θ is the loading, P the pressure, and b and n the Langmuir-Freundlich parameters for a given adsorbent-adsorbate and temperature. Then the slope of $\ln P$ as a function of 1/T as we approach the saturation loading is given by:

$$\lim_{\theta \to q_{\text{sat}}} \left. \frac{\partial \ln P}{\partial (\frac{1}{T})} \right|_{\theta} = \lim_{\theta \to q_{\text{sat}}} \left. \frac{\partial \ln \left(\frac{\theta}{b(\theta - q_{\text{sat}})} \right)^n}{\partial (\frac{1}{T})} \right|_{\theta}$$
(4.25)

In its simplest form, the temperature-dependence of the Langmuir-Freundlich isotherm parameter b is $b = b_0 e^{-kT}$, where k is related with adsorption strength [35]. If we assume n is an arbitrary function which depends on temperature denoted f(T) then:

$$\begin{split} \lim_{\theta \to q_{\text{sat}}} \frac{\partial \ln P}{\partial(\frac{1}{T})} \bigg|_{\theta} &= \lim_{\theta \to q_{\text{sat}}} \frac{\partial \ln \left(\frac{\theta}{b_0 e^{-kT(\theta - q_{\text{sat}})}}\right)^{f(T)}}{\partial(\frac{1}{T})} \bigg|_{\theta} \\ &= \lim_{\theta \to q_{\text{sat}}} -T^2 \frac{\partial \left(f(T) \ln(\frac{\theta}{b_0 e^{-kT(\theta - q_{\text{sat}})}}\right)}{\partial T} \bigg|_{\theta} \\ &= \lim_{\theta \to q_{\text{sat}}} -T^2 \left(\frac{df(T)}{dT} \bigg|_{\theta} \ln \left(\frac{\theta}{b_0 e^{-kT(\theta - q_{\text{sat}})}}\right) + f(T) \frac{\partial \ln \left(\frac{\theta}{b_0 e^{-kT(\theta - q_{\text{sat}})}}\right)}{\partial T} \bigg|_{\theta} \right) \\ &= \lim_{\theta \to q_{\text{sat}}} -T^2 \left(f'(T) \ln \left(\frac{\theta}{b_0 e^{-kT(\theta - q_{\text{sat}})}}\right) + f(T) \frac{1}{\left(\frac{1}{b_0 e^{-kT(\theta - q_{\text{sat}})}\right)} - \frac{\theta(\theta - q_{\text{sat}})(-k)b_0 e^{-kT}}{(b_0 e^{-kT(\theta - q_{\text{sat}})})^2} \right) \\ &= \lim_{\theta \to q_{\text{sat}}} -T^2 \left(f'(T) \ln \left(\frac{\theta}{b_0}\right) + f'(T)kT - f'(T) \ln(\theta - q_{\text{sat}}) + f(T)k\right) \end{split}$$

Therefore

$$\lim_{\theta \to q_{\text{sat}}} \left. \frac{\partial \ln P}{\partial(\frac{1}{T})} \right|_{\theta} = \infty$$
(4.26)

A sharp increase in the enthalpy of adsorption has experimentally already been reported for the adsorption of n-heptane on silicalite [36]. It was found an almost constant heat of adsorption up to the point where the first saturation plateau was reached. At this point, the enthalpy of adsorption increased sharply.

CBMC is not able to capture the sudden increase in the enthalpy of adsorption caused by a saturation plateau (Figure 4.6b). Again, this is because the fluctuation formula breaks down at saturation conditions using CBMC (low insertion probability). Figure 4.6c shows that after five molecules per unit cell, the acceptance percentage of insertions using CBMC is practically zero. For CFCMC, the acceptance is above 20% for all loadings. The behavior of the acceptance percentage in CFCMC is because the maximum change in $\Delta\lambda$ adapts to achieve (in each pressure/loading point) roughly 50% of acceptance in the lambda moves. As the loading increases, $\Delta\lambda_{\rm max}$ becomes smaller. If $\Delta\lambda_{\rm max}$ decreases, the acceptance percentage of insertions and deletions increases [37]. However this also leads to an increase in the cpu-time, as diffusion through λ -space becomes slower.

Interestingly for this system, at around three molecules per unit cell there is also a slight inflection in the isotherm. A careful look into the energy contributions of the system shows that this inflection is caused by the adsorbate-adsorbate interactions (Figure 4.6d). This is also the reflected in the bump of the enthalpy of adsorption as a function of loading.



Figure 4.6: Adsorption of methane in CHA zeolite at 300 K. (a) Adsorption isotherm.(b) Enthalpy of adsorption as a function of loading. (c) Acceptance percentage of the insertion move as a function of loading. (d) Energy contributionsi as a funciton of loading.

2,4-dimethylpentane in MFI zeolite

As a third case study, we simulated the adsorption of 2,4-dimethylpentane in MFI and MEL zeolites at 400 K. For these simulations we used CB/CFCMC, as this method is especially powerful when simulating chain molecules. The results are presented in Figure 4.7. MFI and MEL are structures with intersecting channels and 2,4-dimethylpentane adsorbs in the intersections. There are four intersection per unit cell. In MEL zeolite, the enthalpy of adsorption (Figure 4.7a) has two regimes before sharply increasing, which reflects the two types of intersections in the structure. In MFI the enthalpy of adsorption has only one regime before shooting up. In both cases, the distance between the intersections is large enough to make the adsorbate-adsorbate interactions negligible (Figure 4.7b and 4.7e).

As in the case of CH_4 in CHA zeolite, CBMC is not able to capture the sharp increase expected in the enthalpy of adsorption as saturation is approached. Because of the tight fit between the intersections and the 2,4-dimethylpentane mo-





Figure 4.7: Top: Adsorption of 2,4-dimethylpentane in MEL zeolite. (a) Enthalpy adsorption as a function of loading, (b) energy contributions as a function of loading (the black line is just a guide to the eye to see the difference in slopes) and (c) adsorption isotherm. Bottom: Adsorption for 2,4-dimethylpentane in MFI zeolite. (d) Enthalpy of adsorption as a function of loading, (e) energy contributions as a function so for a function of loading and (f) adsorption isotherm.

lecules, insertions and deletions in these cases are even more difficult. In both, MEL and MFI, using CB/CFCMC the insertion percentage is of around 25% and using CBMC is less than 1% for all loadings.

In all the case studies presented above, the enthalpy of adsorption obtained with CFCMC and CB/CFCMC sharply increases as the system approaches saturation. From a physical point of view, this means that adsorbing molecules becomes very unfavorable and even an endothermic process. Although the Clausius-Clapeyron suggests the enthalpy of adsorption increases indefinitely, in reality this does not occur. Is important to mention, that the Clausius-Clapeyron equation is in principle invalid at higher pressures, as it assumes an ideal gas phase and that the adsorbed phase volume is negligible. However, in ref. [38] the effect of these assumptions was studied by predicting the adsorbed phase molar volume by nonlocal density functional theory (NDFT), and describing the bulk gas by the Carnahan-Starling equation of state plus a mean-field attraction. They showed that the effect of relaxing these assumptions increases the enthalpy of adsorption as a function of loading even more sharply (see Figure 1a and 2a in ref. [38]).

The enthalpy of adsorption can not indefinitely increase because saturation never *truly* occurs (except for lattice models) as in simulation, but also in ex-



Figure 4.8: Enthalpy of adsorption as a function of loading of 2,4-dimethylpentane in (a) MEL and (b) MFI zeolites. At sufficiently high pressures, a new adsorption lattice is created in the structures. This increases the entropy and lowers the enthalpy.

periments, more molecules can always be adsorbed if we increase the chemical potential [39]. However, a sharp increase in the enthalpy of adsorption should be observed anytime the isotherm can be extrapolated to a plateau value.

For lattice models, the adsorption of molecules can *create* more adsorption sites or change the adsorption lattice [40, 41], inducing an increase in the entropy of the system. This has already been reported for the adsorption of alkanes in MFI.

In the case of 2,4-dimethylpentane, if we increase the pressure enough, the adsorption lattice changes [41]. At this point, the rapidly increasing enthalpy of adsorption is counteracted by an increase in the entropy of the system. The enthalpy of adsorption jumps back to lower values (Figure 4.8). These pressures are unrealistic as in experiments the structures would collapse before this occurs, but from a theoretical point of view it shows the interplay between entropy and enthalpy during adsorption.

4.4 Conclusions

Computing the heat of adsorption at saturation conditions is important for industrial applications and to get insight on the adsorbate-adsorbent interactions and adsorbate-adsorbate interactions. Most of the methodologies to obtain the enthalpy of adsorption are not suited for saturation conditions. The most appropriate method to obtain the enthalpy of adsorption from molecular simulations is using the energy/particle fluctuation formula. With conventional Monte Carlo methods, the fluctuation formula breaks down because of the difficulty of inserting and deleting molecules at saturation conditions. Here, we have shown that by using the CFCMC and CB/CFCMC algorithms the fluctuation formula in the grand-canonical ensemble can be used to compute the heat of adsorption close to saturation. Both methods enhance the probability of molecules insertions and deletions close to saturation. The enthalpy of adsorption rapidly increases any time it approaches a saturation plateau and diverges to infinity if real saturation is attain. For lattice systems, the rapidly increasing enthalpy close to a saturation plateau is caused by tighter and tighter confinement (an increase in entropy). The same happens close to an inflection point, but after applying a sufficiently high pressure a new lattice is formed along with a new favorable drop in entropy. At the inflection itself, reliable experimental results would therefore be difficult to obtain reliably.

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CHAPTER 5

Separating Xylene Isomers by Commensurate Stacking of *p*-xylene within Channels of MAF-X8 *

The separation of C8 aromatic hydrocarbons is of great importance in the petrochemical industries. Some mixed xylenes are used for blending in gasoline, as solvents, and in the printing, rubber and leather industries [1]. Most mixed xylenes are separated and the individual isomers consumed in specific end-uses. *Para*-xylene, the most valuable of the isomers, is primarily used as a feedstock with purity requirements of 99%+, for terephthalic acid or dimethyl terephthalate, whose end uses include polyester fibers and polyethylene terephthalate (PET) resins for beverage bottles [2]. The separation of C8 aromatic hydrocarbons is difficult because of the small differences in the boiling points. There are, however, significant differences in the freezing points that allow fractional crystallization to be used for separations [3]. The differences in the freezing points arise because of differences in the stacking efficiency of molecules. *Para*-xylene has the highest freezing point because the molecules stack most efficiently; pure p-xylene crystals are the first to emerge from the solution. However, the energy requirements for fractional crystallization are high because of the need to cool to temperatures of about 220 K. Selective adsorption of xylene isomers within the pores of ordered crystalline micro-porous materials is an energy efficient alternative to fractional crystallization [4]. In industrial processing, the feed to the xylenes separation unit are most commonly in the liquid phase, and the operation is under conditions of pore saturation. At these conditions, differences in saturation capacities are of great importance in determining separations (as explained in detail in Section S5

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of ref. [5]). Because of the low p-xylene content of the feed it is often easier to reach a high productivity with p-xylene-selective adsorbents [6]. Thanks to early simulation work on xylenes in zeolites by e.g. Snurr et al. [7], molecular simulations have now evolved sufficiently in speed and accuracy that large-scale screening studies have become feasible. Moghadam and Düren [8] found that small pore structures are para-selective and slightly larger pores are *ortho*-selective. However, this paraselectivity mechanism is based on sieving: the channel-dimensions are selected such that p-xylene is adsorbed and the larger o- and m-xylene are excluded from the channels. Sieving is therefore usually associated with small pore systems with low p-xylene loadings. Moreover, such sieving is unable to separate p-xylene from ethylbenzene because of the diffusional limitations in such systems.

To search for systems that are superior to current technology (Ba-X zeolite adsorbent used in UOP Parex and IFP Eluxyl which employ simulated moving beds [4, 9, 10]) we require (1) a high para-selective structure, (2) with a high pore volume, and (3) a structure that is able to operate near or at saturation conditions. In this work, we show that these goals can be achieved by exploiting "commensurate stacking".

5.1 Methodology

The adsorption isotherms were obtained using the Configurational-Bias Monte Carlo (CBMC), Continuous Fractional Component Monte Carlo (CFCMC) [11] and Configurational-Bias Continuous Fractional Component Monte Carlo (CB/CFCMC) [12] algorithms in the grand-canonical ensemble. The adsorbates are described as multisite rigid molecules with properties and configurations shown in Fig. 5.1. Force field parameters are listed in Table 5.1. Cross-interactions with other molecules and the framework are computed using Lorentz-Berthelot mixing rules.

Table 5.2 shows typical lengths, widths, and heights of the modeled adsorbates. Distances are "molecular shadow lengths" [14] from Materials Studio [15] calculated by projecting the molecular surface on three mutually perpendicular planes. The molecules are first rotated to align the principal moments of inertia with the X, Y and Z axes (*i.e.* the distances depend on the conformation, but also on the orientation of the molecule).

type	ϵ/k_B [K]	σ [Å]	q [e]
C, benzene	35.2254	3.55	-0.115
H, benzene	15.0966	2.42	0.115
C, CH_3 of toluene	33.2125	3.50	-0.065
C, CH_2 of ethylbenzene	33.2125	3.50	-0.005
C, RCH_3	33.2125	3.50	-0.180
H, RH, alkanes	15.0966	2.50	0.060

Table 5.1: Force field VDW parameters for the adsorbates [13].



Figure 5.1: Xylenes are a family of C8 aromatic hydrocarbons obtained from petroleum and generally produced as a mixture of all three isomers: *ortho-, meta-* and *para-,* with methyl groups attached to the aromatic ring in positions 1-2, 1-3, 1-4 respectively, and ethylbenzene. The differences in boiling points are small. There are, however, significant differences in the freezing points that allow fractional crystallization to be used for separations. The differences in the freezing points arise because of differences in the stacking efficiencies of molecules. In this work we have included benzene and toluene in the simulations to verify that their presence in the fluid mixture does not alter the sequence of breakthroughs. The mixture of all these components is often refered to as BTEX.

The frameworks are modeled as rigid with atom positions taken from crystallographic experimental data. The structure of most MOFs were further optimized using VASP [16, 17] (PBE, precision=high) with the cell fixed to the experimentally determined unit cell size and shape. Periodic boundary conditions where applied to overcome the problems of surface effects. The DREIDING force field [18] was used to model the framework atoms. DREIDING is a well-known force field developed to handle a wide range of small organic molecules, including organometallic systems. The small number of adjustable parameters in this force field makes it easy to extend the force field to more complex systems. Van der Waals parameters not found in DREIDING were taken from the universal force field (UFF) [19]. DREIDING and UFF force fields were designed to be generic with the aim of covering a broad range of atoms (this includes inorganic compounds, metals, and transition metals). For the zeolites the TraPPE [20] force field was used. All van der Waals parameters used for the frameworks are listed in Table 5.3.

The charge-charge interactions were computed using the Ewald summation

molecule	$\mid L_x \ [\text{\AA}]$	L_y [Å]	L_z [Å]
o-xylene	7.95	7.36	4.18
m-xylene	8.85	7.40	4.16
p-xylene	9.25	6.70	4.16
ethylbenzene	9.51	6.71	4.86
benzene	6.87	7.34	3.40
toluene	8.31	6.70	4.16

Table 5.2: Molecular shadow distances [14].

Table 5.3: Framework force field VDW parameters. Charges for the frameworks are computed using the REPEAT [21] methodology on primitive unit cells for each structure. Values denoted with a * correspond to the TraPPE zeolite force field.

type	ϵ/k_B [K]	σ [Å]	type	ϵ/k_B [K]	σ [Å]	type	ϵ/k_B [K]	σ [Å]
0	48.1581	3.03315	Ν	38.9492	3.26256	С	47.8562	3.47299
F	36.4834	3.0932	В	47.8058	3.58141	P	161.03	3.69723
S	173.107	3.59032	Cl	142.562	3.51932	Br	186.191	3.51905
Н	7.64893	2.84642	Zn	62.3992	2.46155	Be	42.7736	2.44552
Cr	7.54829	2.69319	Fe	6.54185	2.5943	Mn	6.54185	2.63795
Cu	2.5161	3.11369	Co	7.04507	2.55866	Ga	208.836	3.90481
Ti	8.55473	2.8286	Sc	9.56117	2.93551	V	8.05151	2.80099
Ni	7.54829	2.52481	Zr	34.7221	2.78317	Mg	55.8574	2.69141
Ne	21.1352	2.88918	Ag	18.1159	2.80455	Te	200.281	3.98232
Cd	114.734	2.53728	\mathbf{Sb}	225.946	3.93777	Si*	22	2.3
Al	155.998	3.91105	Si	155.998	3.80414	0*	53	3.30

(relative precision 10^{-6}). Charges for the frameworks were computed by minimizing the difference of the classical electrostatic potential and a quantum mechanics electrostatic potential over many grid points using the REPEAT method [21, 22].

Computing adsorption isotherms

In experimental adsorption studies one measures the amount of materials adsorbed as a function of pressure and temperature. To mimic this, in simulations, it is natural to use the grand-canonical ensemble (or μ, V, T ensemble). In this ensemble, the temperature T, the volume V, and the chemical potential μ are fixed. The partition function is given by:

$$Z_{\mu \text{VT}} \equiv \sum_{N=0}^{\infty} \frac{e^{\beta \mu N} V^N}{\Lambda^{3N} N!} \int e^{-\beta U(\mathbf{s}^N)} \, \mathrm{d}\mathbf{s}^N$$
(5.1)

with a corresponding probability density

$$\mathcal{N}_{\mu \mathrm{VT}} \propto \frac{e^{\beta \mu N} V^N}{\Lambda^{3N} N!} e^{-\beta U(\mathbf{s}^N)}$$
(5.2)

The Metropolis algorithm in the grand-canonical ensemble is similar to the NVT ensemble, but with two extra moves: insertion and deletion of particles.

The insertion of a particle is accepted with a probability

$$\operatorname{acc}(N \to N+1) = \min\left(1, \frac{V\beta f}{(N+1)}e^{-\beta(U(N+1)-U(N))}\right)$$
 (5.3)

and the removal of a particle is accepted with a probability

$$\operatorname{acc}(N \to N - 1) = \min\left(1, \frac{N}{V\beta f} e^{-\beta(U(N-1) - U(N))}\right)$$
(5.4)

where f is the fugacity coefficient and is related to the pressure by $f = \phi p$ (ϕ is the fugacity coefficient computed directly from the equation of state of the vapor in the reservoir). In our study we have plotted absolute loading versus the fugacity as this is not affected by gas-liquid transitions of the reservoir.

IAST

The Ideal Adsorbed Solution Theory (IAST) [23] is a model to predict the multicomponent adsorption data using only pure-component adsorption isotherms. The main assumption of the theory is that the adsorbed phase is an ideal solution in which interactions between molecules are equivalent in strength [24, 25]. IAST provides good predictions of mixture adsorption and selectivities for mixtures that are close to ideal and mixtures in which the components are adsorbed at similar levels. However, it often fails to capture the proper behavior for mixtures of polar species or for mixtures in which one component is adsorbed strongly and the other component is weakly adsorbed [26].

In this work, for the IAST calculations of component loadings in a 4-component (o/m/p/e) and 6-component (o/m/p/e/b/t) mixture of C8 hydrocarbons, the single component isotherms data (absolute loading) were fitted with the dual-site Langmuir-Freundlich model:

$$q_{i} = q_{i,A,\text{sat}} \frac{b_{i,A} f_{i}^{\nu_{i},A}}{1 + b_{i,A} f_{i}^{\nu_{i},A}} + q_{i,B,\text{sat}} \frac{b_{i,B} f_{i}^{\nu_{i},B}}{1 + b_{i,B} f_{i}^{\nu_{i},B}}$$
(5.5)

The saturation capacities $q_{i,\text{sat}}$, Langmuir constants b_i , for the two sites, A, and B for various MOFs discussed in this article are provided in Tables S4-S11 in the Supporting Information.

Breakthroughs

Fixed bed, packed with crystals of nanoporous materials, are commonly used for separation of mixtures (see schematic in Figure 5.2); such adsorbers are commonly operated in a transient mode, and the compositions of the gas phase, and within the crystals, vary with position and time. Experimental data on the transient



Figure 5.2: Schematic of packed bed adsorber.

breakthrough of mixtures across fixed beds are commonly used to evaluate and compare the separation performance of zeolites and MOFs [27–30]. For a given separation task, transient breakthroughs provide a more realistic evaluation of the efficacy of a material, as they reflect the combined influence of adsorption selectivity, and adsorption capacity [30, 31].

Furthermore, transient breakthroughs are influenced by both mixture adsorption equilibrium, and intra-crystalline diffusion. In order to determine the extent of the relative importance of adsorption and diffusion in the separation performance, we perform transient breakthrough simulations, and compare these with experimental data. We describe below the simulation methodology used to perform transient breakthrough calculations.

Assuming plug flow of an *n*-component gas mixture through a fixed bed maintained under isothermal conditions, the partial pressures in the gas phase at any position and instant of time are obtained by solving the following set of partial differential equations for each of the species i in the gas mixture [32]

$$\frac{1}{RT}\frac{\partial p_i\left(t,z\right)}{\partial t} = -\frac{1}{RT}\frac{\partial\left(v\left(t,z\right)p_i\left(t,z\right)\right)}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}\rho\frac{\partial \overline{q}_i\left(t,z\right)}{\partial t}; \qquad i = 1, 2, \dots, n$$
(5.6)

In equation 5.6, t is the time, z is the distance along the adsorber, ρ is the framework density, ε is the bed voidage, v is the interstitial gas velocity, and $\overline{q}_i(t, z)$ is the spatially averaged molar loading within the crystallites of radius r_c , monitored at position z, and at time t.

At any time t, during the transient approach to thermodynamic equilibrium, the spatially averaged molar loading within the crystallite r_c is obtained by integration of the radial loading profile:

$$\bar{q}_{i}(t) = \frac{3}{r_{c}^{3}} \int_{0}^{r_{c}} \bar{q}_{i}(r,t) r^{2} dr$$
(5.7)

For transient unary uptake within a crystal at any position and time with the fixed bed, the radial distribution of molar loadings, q_i , within a spherical crystallite, of radius r_c , is obtained from a solution of a set of differential equations describing the uptake

$$\frac{\partial q_i\left(r,t\right)}{\partial t} = -\frac{1}{\rho} \frac{1}{r^2} \frac{\partial\left(r^2 N_i\right)}{\partial r} \tag{5.8}$$

in which both correlation effects and thermodynamic coupling effects are considered to be of negligible importance

$$N_i = -\rho \,\mathcal{D}_i \frac{\partial q_i}{\partial r} \tag{5.9}$$

 \mathcal{D}_i the Maxwell-Stefan diffusivity coefficient of component *i* in the crystallite.

Summing equation 5.7 over all n species in the mixture allows calculation of the *total average* molar loading of the mixture within the crystallite

$$\overline{q}_{t}\left(t,z\right) = \sum_{i=1}^{n} \overline{q}_{i}\left(t,z\right)$$
(5.10)

The *interstitial* gas velocity is related to the *superficial* gas velocity by

$$v = \frac{u}{\varepsilon} \tag{5.11}$$

In industrial practice, the most common operation is to use a step-wise input of mixtures to be separated into an adsorber bed that is initially free of adsorbates, *i.e.* we have the initial condition

$$t = 0;$$
 $q_i(0, z) = 0$ (5.12)

At time, t = 0, the inlet to the adsorber, z = 0, is subjected to a step input of the *n*-component gas mixture and this step input is maintained till the end of the adsorption cycle when steady-state conditions are reached

$$t \ge 0;$$
 $p_i(0,t) = p_{i0};$ $u(0,t) = u_0$ (5.13)

where u_0 is the superficial gas velocity at the inlet to the adsorber.

Besides, the breakthrough simulations with a step-input (equation 5.13), we also carried out simulations for a packed bed adsorber with injection of a short duration pulse of the mixture to be separated. This type of simulation is particularly useful to demonstrate the fractionating capability of adsorbents. For simulation of pulse chromatographic separations, we use the corresponding set of inlet conditions

$$0 \le t \le t_0; \qquad p_i(0,t) = p_{i0}; \qquad u(0,t) = u_0 \tag{5.14}$$

where the time for duration of the pulse is t_0 .

- 1. The characteristic contact time $\frac{L}{v} = \frac{L\varepsilon}{u}$ between the crystallites and the surrounding fluid phase, and
- 2. $\frac{\mathcal{D}_i}{r_c^2}$ that reflect the importance of intra-crystalline diffusion limitations.

It is common to use the dimensionless time, $\tau = \frac{tu}{L\varepsilon}$, obtained by dividing the actual time, t, by the characteristic time, $\frac{L\varepsilon}{u}$ when plotting simulated breakthrough curves [31].

For all breakthrough simulations reported here we use the parameter values: L = 0.3 m; voidage of bed, $\varepsilon = 0.4$; interstitial gas velocity, v = 0.1 m/s; superficial gas velocity, u = 0.04 m/s. In pulse chromatographic simulations we take the pulse duration $t_0 = 10$ s. When matching experimental data on breakthroughs, the parameter values used correspond to those relevant to the experiments being simulated. Further details of the numerical procedures used in this work are provided by Krishna and co-workers [32–35].

There are essentially two different scenarios to quantify the influence of intracrystalline diffusion effects on breakthroughs. If the value of $\frac{\mathcal{D}_i}{r_c^2}$ is large enough to ensure that intra-crystalline gradients are absent then the entire crystallite particle can be considered to be in thermodynamic equilibrium with the surrounding bulk gas phase at that time t and position z of the adsorber

$$\overline{q}_{i}\left(t,z\right) = q_{i}\left(t,z\right) \tag{5.15}$$

The molar loadings at the outer surface of the crystallites, *i.e.* at $r = r_c$, are calculated on the basis of adsorption equilibrium with the bulk gas phase partial pressures p_i at that position z and time t. The adsorption equilibrium can be calculated on the basis of the IAST. This scenario is the one that is commonly adopted for screening different nanoporous materials for a given separation task [31, 35–37].

5.2 Results and Discussion

Commensurate stacking is much like stacking books on a bookshelf. In Figure 5.3 we show a prototypical stacking of o- and p-xylene in a carefully chosen rectangular channel system. A MOF with channels of 0.85 nm allows the most efficient stacking of o-xylene. Channels of 1 nm are desirable for stacking p-xylene. In a 1 nm system, p-xylene is able to make full use of all the available pore volume and has a strong interaction, adsorbing flat on a wall while both methyl-groups interact with a sidewall. For molecules with different dimensions four effects occur: (1) "wider" molecules (like o- and m-xylene) will be able to stack less molecules per channel-length, (2)"longer" molecules (ethylbenzene) have to align obliquely and therefore also stack less molecules per channel-length, (3) "shorter" molecules (o- and m-xylene) will have a less optimal interaction with the pore structure; (4) more bulky molecules (ethylbenzene) are unable to form commensurate layers and



Figure 5.3: Schematic of "commensurate stacking" of xylenes in rectangular channels. The yellow arrows denote the characteristic lengths of the molecules, which have to be commensurate with the channel dimensions. Channels of about 0.85 nm in size allow an efficient stacking of *o*-xylene molecules. The same channel size forces *p*-xylene molecule to align obliquely, reducing the adsorption of *p*-xylene compared to *o*-xylene. A *p*-xylene stacking would require channel dimensions of about 1.0 nm.

there will have a lower saturation loading. The strategy we adopt in this work is to exploit differences in the stacking efficiencies of C8 aromatic hydrocarbons within the MOF channels. In the Supporting Information of ref. [5], we have compiled the adsorption and breakthrough simulation results. In the following discussions, Figure numbers starting with S refer to those in this Supporting Information

5.2.1 Ortho-selective structures

Consider adsorption of ethylbenzene, and o-, m-, p- xylenes within the onedimensional, lozenge-shaped rhombohedric channels of MIL-47(V) of approximately 0.85 nm. Adsorption within the channels of MIL-47(V) favors o-xylene because the molecules can most effectively stack along the channel length [30, 38]. Essentially, MIL-47(V) offers the appropriate "bookshelf" structure that is required to optimally stack o-xylene molecules (see Figure 5.4). The channel dimensions of MIL-47(V) are not large enough to allow p-xylene to stack vertically; these molecules align obliquely along the channel length (Figure S9a). Breakthroughs curves are the combined effect of selectivity and capacity in a



Figure 5.4: Snapshot of *o*-xylene in MIL-47 at 433 K. MIL-47 offers a 0.85 nm "book-shelf" which optimally stacks molecules that are commensurate with this dimension (*i.e. o*-xylene).



Figure 5.5: Step breakthrough simulations at 25 Pa of an equimolar mixture of *o*-xylene/*m*-xylene/*p*-xylene/ethylbenzene in (a) MIL-47 and (b) MIL-53. Both, MIL-47 and MIL-53, are *o*-xylene selective structure.

single quantity. For MIL-47, the breakthrough simulations for 4-component o-xylene/m-xylene/p-xylene/ethylbenzene (Figure 5.5a) show that the sequence of breakthroughs in a fixed bed adsorber is ethylbenzene, p-xylene, m-xylene, and o-xylene. This is in agreement with the experimental breakthroughs reported by Finsy *et al.*[39]. The computed 6-component breakthroughs of o-xylene/m-xylene/p-xylene/ethylbenzene

/benzene/toluene in MIL-47 (Figure S11b) show that the presence of benzene and toluene in the fluid mixture does not alter the sequence of breakthroughs.

MIL-53(Al) metal-organic framework has slightly larger (0.85 nm) lozengeshaped rhombohedric than MIL-47. The size of the channels is still not large for an other molecule (other than *o*-xylene) to "effectively" stack. Therefore, the adsorption and breakthrough order in the MIL-53(Al) are similar to that of MIL-47(V) (Figure 5.5b). The sequence of breakthroughs is in qualitative agreement with experiments of Remy *et al.* [40]. The work of Remy *et al.* [40] appears to indicate that guest-induced structural changes of MIL-53(Al) are also to be considered in quantitative modeling of the breakthrough characteristics.



Figure 5.6: (a) Experimental pulse breakthrough at 309 K and (b) simulated pulse breakthrough at 433 K of an *o*-xylene/*m*-xylene/*p*-xylene/ethylbenzene mixture in MOF-CJ3.

Fang et al. [41] report pulse breakthrough simulations for 4-component oxylene/m-xylene/p-xylene/ethylbenzene in MOF-CJ3 that clearly indicate adsorption selectivity towards o-xylene. MOF-CJ3 has square channels of approximately 0.8 nm size. The rationalization of o-xylene selective adsorption is expected to be similar to that of MIL-47. CBMC simulations of pure component isotherms confirm that the adsorption is selective to the ortho isomer. Breakthrough simulations for 4-component o-xylene/m-xylene/p-xylene/ethylbenzene in MOF-CJ3 show the hierarchy of breakthroughs to be ethylbenzene, p-xylene, m-xylene, and o-xylene (Figure S19). This hierarchy is not influenced by the presence of benzene and toluene in the feed mixture. For comparison with the pulse chromatographic experiments of Fang et al. 13, we also conducted pulse breakthrough simulations. The pulse chromatographic simulations (Figure 5.6) indicate that ethylbenzene and p-xylene peak at nearly the same time, in precise agreement with the experiments. The subsequent breakthroughs of m-xylene and o-xylene are in good agreement with the experimental data, albeit on a different time scale.

Nicolau *et al.* [42] report experimental breakthrough data for C8 hydrocarbons in beds packed with Zn(bdc)dabco, a framework that has two types of intersecting channels of about 0.75 nm 0.75 nm along the x-axis. The sequence of breakthroughs of xylene isomers is *p*-xylene, *m*-xylene, *o*-xylene. Barcia *et al.* [43] and Moreira *et al.* [44] report breakthrough data for C8 aromatic hydrocarbons in UiO-66(Zr) a zirconium based metal-organic framework (MOF). Its cubic rigid 3D pores structure consists of an array of octahedral cavities of diameter 1.1 nm, and tetrahedral cavities of diameter 0.8 nm. The two types of cages are connected through narrow triangular windows of approximately 0.6 nm. The sequence of experimental breakthroughs of xylene isomers is *p*-xylene, *m*-xylene, *o*-xylene. The adsorption selectivity is in favor of *o*-xylene; this is mostly likely due to the more compact configuration of *o*-xylene that allows preferential location in the smaller tetrahedral cages of UiO-66. The separation performance is strongly influenced



Figure 5.7: Xylene separation at 433 K using MAF-X8 (a) equimolar mixture isotherms and IAST prediction based on pure component isotherms, (b) simulated step breakthrough at 25 kPa partial pressure. The IAST prediction is in excellent agreement with the mixture simulations and its validation is important because IAST is the basis for the breakthrough computations. The mixture and breakthrough simulations show high *p*-xylene selectivity combined with a high *p*-xylene loading in the mixture (about 2.2 mol/kg at 1 bar). At 433 K the bulk fluid is in the liquid phase if the total mixture fugacity is higher than about 1 MPa. Our breakthrough simulations operate at 100 kPa, and therefore are somewhat conservative as regards to the separation.

by intra-crystalline diffusion considerations because of the small windows at the entrance to the cages.

All the MOFs (MIL-47(V), MIL-53(Al), MOF-CJ3, UiO-66 and Zn(bdc)dabco) discussed in the foregoing paragraph are selective to the adsorption of o-xylene, and less suitable for use in industrial practice. Let us turn our attention to MOFs that have the desired selectivity towards p-xylene.

5.2.2 Para-selective structures

MIL-125(Ti) comprises of two different types of cages: large 1.2 nm octahedral cages, and small tetrahedral 0.6 nm cages. The two types of cages are connected through narrow triangular windows of 0.5 nm. Amino-functionalisation of the benzene linker yields MIL-125(Ti)-NH₂. Due to the protrusion of the amino groups in the pore space the pore space of MIL-125(Ti)-NH₂ are slightly smaller than in MIL-125(Ti). The CBMC pure component isotherm for both MIL-125(Ti) and MIL-125(Ti)-NH₂, together with breakthrough simulations (Figure S23 and S27, respectively), show that these materials have selectivity towards the *para* isomer. The experimental data of Vermoortele *et al.* [45] and Moreira *et al.* [46, 47] on breakthroughs of xylene isomers in MIL-125(Ti) and MIL-125(Ti)-NH₂, appear to confirm that these materials have the desirable selectivity towards *p*-xylene. However, the breakthrough experiments also show that the selectivity towards *p*-



Figure 5.8: Stacking of *p*-xylene in the MAF-X8 structure. Note that *p*-xylene is commensurate in three directions: it fits perfectly lengthwise, it forms two layers that fit snugly, and along the channel *p*-xylene stacks in an alternating fashion.

xylene appears to depend on the concentration of ethylbenzene in the feed stream. Indeed, for a range of feed compositions *p*-xylene and ethylbenzene breakthrough at the same time. This indicates that both MIL-125(Ti) and $MIL-125(Ti)-NH_2$ are unlikely to be considered as suitable adsorbents because industrial feed mixtures invariably contain a sizable proportion of ethylbenzene. CBMC simulation data for adsorption C8 hydrocarbons with 1.0 nm square-shaped 1D channels of Co(BDP) show separation characteristics that are desirable from an industrial perspective. The channel dimension is large enough to allow the p-xylene molecules to align vertically. This leads to a good packing of the *para* isomer within the 1D channels. The simulations of the pure component isotherms clearly demonstrate a higher adsorption loading of *p*-xylene than any of the other C8 hydrocarbons. Breakthrough simulations confirm that *p*-xylene is the last component to emerge from the fixed bed (Figure S31). Jin et al. [48] have presented isotherm data for xylene isomers in JUC-77 which is a MOF that has rhombus-shaped channels running in two perpendicular directions. The size of the channels is such as to favor only p-xylene that has the smallest width; this results in para-selectivity in separation. The simulations of pure component isotherms and breakthrough simulations (Figure S34 and S35) confirm the para selectivity observed in the experiments. Diffusional limitations are expected to be of paramount importance for JUC-77.

MAF-X8 possesses the right channel dimensions for stacking of *para*-xylene to occur. MAF-X8 is a Zn(II) pyrazolate-carboxylate framework whose synthesis has been reported by He *et al.* [49]. We observe a high adsorption selectivity of



Figure 5.9: Comparison of *p*-xylene selective MOFs, (a) adsorption selectivity vs. *p*-xylene capacity, (b) comparison of adsorption selectivity vs. *p*-xylene cycle time for various MOFs. The adsorption selectivity is defined as q3/(q1+q2+q4) where 1=o-xylene, 2=m-xylene, 3=p-xylene, and 4=ethylbenzene. We define the cycle time for *p*-xylene as the dimensionless time, τ cycle, at which the concentration of the gas at the outlet is 99% of the value at the inlet.

p-xylene with respect to o- and *m*-xylene and ethylbenzene; see mixture isotherm data in Figure 5.7(a). The IAST prediction of the mixture based on the pure components is of excellent accuracy as verified by molecular simulations of mixture adsorption. The breakthrough simulations presented in Figure 5.7(b) confirm the strong *para* selectivity. The presence of benzene and toluene in the feed mixture does not seem to influence the sharp separations that are achievable with MAF-X8 (Figure S43b). In contrast to CoBDP, MAF-X8 is commensurate with the structure in all three dimensions. Snapshots shown in Figure 5.8 highlight that the high selectivity is due to stacking. This raises the question: "How good is molecular stacking compared to other separation mechanisms?"

Figure 5.9 compares the separation characteristics of materials that are selective to p-xylene adsorption. We note that MAF-X8 has nearly the same adsorption selectivity as Ba-X, but has a significantly higher capacity to adsorb p-xylene. This higher capacity of MAF-X8 results in a significantly longer cycle time; this implies that less frequent regeneration will be required. All other MOFs appear to be significantly poorer in selectivity as compared to Ba-X and MAF-X8. The other MOFs are also lower in p-xylene adsorption capacity. This shows that molecular stacking is able to make (near-) optimal use of the available pore-volume.

5.3 Conclusions

Using state-of-the-art molecular simulation methodologies, we have conducted a systematic screening of a wide variety of zeolites and metal-organic frameworks (MOFs) to investigate the possibilities of achieving separation performances that are superior to Ba-X. Our investigations have highlighted the crucial importance of

channel dimensions on separations. MOFs such as MIL-47(V), MIL-53(Al), MOF-CJ3, UiO-66 and Zn(bdc)dabco exhibit selectivity towards o-xylene, a feature that is not desirable in industrial practice. On the other hand, MAF-X8, Co(BDP), MIL-125(Ti), MIL-125(Ti)-NH₂, MFI, and JUC-77 have the desirable selectivity towards p-xylene isomers. Of these MOFs, MAF-X8 is particularly noteworthy because the channel dimensions and geometry allow efficient and commensurate stacking of p-xylene molecules. Such efficient stacking results in adsorption selectivities that are comparable to that of Ba-X. More importantly, the p-xylene adsorption capacity of MAF-X8 is significantly higher than that of Ba-X. Consequently, the cycle times for p-xylene are found to be about a factor 4.5 longer with MAF-X8 and this is expected to result in significant process improvements.

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CHAPTER 6

Entropic Separations of Mixtures of Aromatics by Selective Face-to-Face Molecular Stacking in One-Dimensional Channels*

6.1 Introduction

Nanoporous materials such as zeolites, metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs) offer considerable potential as energy-efficient alternatives to conventional separation processes like distillation, absorption, and extraction. Separation in nanoporous materials relies on adsorption and/or diffusion properties and can be achieved by size/shape exclusion (steric separation), by differences in the adsorbate-adsorbent interactions and/or adsorbate packing interactions (thermodynamic equilibrium effect) or by differences in the diffusion rate of the adsorbates within the adsorbent channels.

At low loadings (*i.e.* the Henry regime) adsorbate-adsorbate interactions are of little importance. The selectivity is mainly driven by enthalpic effects, and is in favor of the molecule that has the strongest interaction with the framework. This is the principle behind most separations of mixtures of light gaseous compounds, where a common feature is that saturation conditions are often not reached. For example, the selective adsorption of CO_2 from mixtures containing N₂, H₂, CO, and CH₄ by selective binding of CO₂ with either the metal atoms (M) of CuBTC [1], Cu-TDPAT [2], M-MOF-74 [3], or the extra-framework cations

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of NaX zeolite [4] and the selective adsorption of N_2 from O_2 based on the larger quadrupole moment of N_2 in both LTA-4A and LTA-5A [5].

However, many industrially used setups operate close to saturation conditions, e.q. liquid-phase adsorption. At these conditions, adsorption is dominated by entropic effects and therefore highly influenced by adsorbate-adsorbate interactions and packing efficiency. Upto date several entropy effects have been discovered and exploited for mixture separations: (1) size-entropy, (2) configurational-entropy, (3) commensurate stacking, and (4) length-entropy [6]. "Size entropy" effects arises from the fact that smaller molecules can fit easier in the "gaps" between adsorption sites, leading to higher saturation capacities with decreasing molecules size. An example is the separation of alkanes in MFI [7]. "Configurational-entropy" effects favor molecules with better packing within the pores structure. The length and topology of one of the mixture components is comparable with the channels leading to "commensurate freezing" [8]. This is the case in the separation of linear from branched alkanes in silicalite-1, where the linear n-hexane (nC6) is favour over the di-branched isomers 2,2-dimethylbutane (22DMB) and 2,3-dimethylbutane (23DMB) [9, 10]. "Commensurate-stacking" occurs when the packing arrangement of one of the components is commensurate with the channel size, which allows this component to stack like books on a bookshelf. This is observed in the adsorption of o-xylene in MIL-47 and p-xylene in MAF-X8 [11]. "Length-entropy" effects favor molecules with the shortest length (footprint) in one-dimensional channels, since they can be pack more efficiently within the channels. A good example is the separation of hexane isomers in AFI channels, where selectivity relies on the smaller footprints of the branched isomers 22DMB and 23DMB [12–15]. In this article, we describe a new entropy-based separation mechanism in one-dimensional channels at saturation capacity. In this mechanism, the selectivity relies on a loading driven reorientation of one of the mixture components into a "pile" configuration where all the molecules are in a "face-to-face" orientation. We demonstrate this effect in two systems: (i) o-xylene and benzene in AFI and MAZ zeolite channels (which can be efficiently separated from m-, p-xylene and ethylbenzene), (ii) and 1,3,5-trichlorobenzene in a triangular MOF (which can be efficiently separated from 1, 2, 4 - /1, 2, 3-trichlorobenzene).

6.2 Methodology

The force fields and methodology used in this chapter are the same as the ones used in chapter 5.

6.3 Results and discussion

AFI zeolite posses one dimensional channels with corrugated pore topology; the channel diameter at the narrow constrictions is 7.3 Å and at the protracted segments is 8.4 Å. MAZ zeolite is slightly smaller than AFI; the channel diameter at the narrow and protracted segments are 6.7 Å and 7.4 Å, respectively. Figure



Figure 6.1: Snapshots of benzene, o-, p- and m-xylene and ethylbenzene in AFI (left) and MAZ (right) channels at saturation conditions. Benzene and o-xylene are able to change their orientation from parallel to perpendicular (relative to the channel axis). At high loadings this leads to a "face-to-face arrangement that reduces their "footprint" compared to p-, and m-xylene and ethylbenzene.

6.1 shows snapshots of benzene, o-, p-, m-xylene and ethylbenzene at saturation loading. The height and width of o-xylene and benzene are both smaller than 8.4 Å and 7.4 Å, allowing a perpendicular alignment (with respect to the channel axis) within the protracted channel segments in both AFI and MAZ. For m-, p-xylene and ethylbenzene, either the height or width is too large to allow vertical alignment; consequently their orientations within the channels are aligned obliquely.

Because of the perpendicular alignment, o-xylene and benzene reduce their effective footprint and achieve much higher saturation capacities as shown in Figure 6.2a where Configurational-Bias Continuous Fractional Component Monte Carlo (CB/CFCMC) simulations [16] of pure component isotherms for hydrocarbons in AFI at 433 K are presented. The simulations are in very good qualitative agreement with the experimental data (at 303 K) of Chiang *et al.* [17] and provide the means to understand why. For MAZ zeolite, the simulation results show the same difference in saturation capacity between adsorbates that can change their orient-ation compared to those that cannot (Figure 6.2b). In MAZ however, a difference between benzene and o-xylene shows up that is not present in AFI. This is because MAZ is slightly smaller than AFI and although o-xylene is able to align perpendic-



Figure 6.2: Single component isotherms in (a) AFI and (b) MAZ zeolite at 433 K. At saturation conditions, benzene and *o*-xylene can reach higher loadings because of molecular reorientation. This can be exploited as a separation mechanism in liquid conditions. The smaller channel of MAZ compared to AFI allows for a better reorientation of benzene.

ular, the tighter confinement does not allow for a complete "face-to-face" stacking at this range of pressures. This suggests that a 1D channel slightly smaller than that observed in MAZ would be perfect to separate benzene from other aromatics. Benzene is the main precusor for ethylbenzene, cumene and cyclohexane, used for the production of styrene/polystyrene, resins and Nylon.

In Figure 6.3 we show the CB/CFCMC simulation isotherms (inset) and the simulated breakthroughs at 100 kPa for an equimolar mixture of o-xylene/p-xylene/m-xylene/ethylbenzene in AFI at 433 K. The CB/CFCMC mixture simulations for the 4-component mixture are in excellent agreement with the IAST calculations based on pure component isotherms fits (fit parameters are provided in the SI of ref. [18]). The isotherms clearly show AFI selectivity for o-xylene at saturation conditions. The sequence of breakthroughs show that the breakthrough of o-xylene occurs significantly later than that of ethylbenzene and p- and m-xylene. This ensures highly selective separation of a 4-component o-xylene/m-xylene/p-xylene/ethylbenzene mixture on the basis of molecules reorientation provided pore saturation conditions are attained. Our results are in good agreement with Hu *et al.* [19, 20] transient breakthrough experiments.

The experimental results of Chiang *et al.* [17] already suggest that benzene and o-xylene arrange in a "face-to-face" configuration in AFI. By dividing the loading per channel by the channel-length it is clear that the footprint of the molecules is small, but the experimental data is insufficient to elucidate how and why. Chiang *et al.* purported that even at low loading benzene molecules would prefer to be orientated perpendicular in AFI. But this is not the case. It is not an energetic, but an entropic effect. We note that perpendicular alignments of aromatics has been observed before by Lucena *et al.* [21, 22] in AEL and AFI zeolite and by



Figure 6.3: Breakthroughs simulation at 100 kPa and mixture isotherms (inset) for an equimolar mixture of *o*-xylene/*p*-xylene/*m*-xylene/ethylbenzene in AFI zeolite at 433 K. The breakthrough simulation methodology is the same as that used in chapter 5. The reorientation of *o*-xylene allows higher saturation capacity and drives the other mixture components out of AFI zeolite. This makes AFI an *o*-xylene selective structure. Diffusion considerations do not change this.

Rungsirisakun et al. [23] in MFI (ZSM-5 type).

In order to investigate and elucidate the molecular mechanism, we measured the distribution of the angle between the aromatic ring plane of o-xylene and the channel axis of AFI at different loadings. In Figure 6.4, the data is presented in a form where a horizontal line corresponds to no preferred orientation (as occurs in an ideal gas). We observe that at low loadings the preferred orientation of the molecules is parallel to the channel axis (0,180°). This orientation was further confirmed by energy minimizations. As the loading increases adsorbate-adsorbate interactions come into play and the distribution of the orientation of the molecules changes. Adsorbates start to confine each other and if the loading is increased the o-xylene adsorbates are more and more often found in the perpendicular orientation (90°) leading to a pile of molecules. The reorientation of o-xylene into a pile reduces its footprint within the AFI channels and therefore higher saturation capacities are obtained. The mechanism could be viewed as a footprint-entropy effect where the footprint-entropy is now strongly loading dependent and changed by a favorable reorientation of the molecule.

We found that the effect is not caused by the corrugation of the wall. Even without walls (in simulations we achieve this by omitting the framework and in-



Figure 6.4: Distribution of the angle between the aromatic ring of *o*-xylene and the channel axis of AFI at 433 K for different loadings. As loading increases, molecules orient with the aromatic ring perpendicular to the channel axis (90°). The flat black line represents the distribution of an ideal gas.



Figure 6.5: Infinite dilution heat of adsorption of benzene, *o*-, *m*-, *p*-xylene and ethylbenzene in (a) AFI and (b) MAZ zeolites at different temperatures. For AFI zeolite, our results agree qualitatively with the experimental results of Chiang *et al.* [17]. In the Henry regime, benzene is the least strongly adsorbed species in both zeolites.

stead restrict the molecules to a volume and shape corresponding to a channel) the effect can be observed. Also, the effect is largely independent of the molecular properties at the Henry regime. A weaker adsorbing molecule that is able to reorient wins at saturation from a stronger adsorbate that is unable to reorient. This is the case of benzene in AFI and MAZ zeolite. In both cases, benzene has a higher saturation capacity than p-xylene, m-xylene or ethylbenzene, but a lower heat of adsorption (Figure 6.5).



Figure 6.6: Fe₂(BDP)₃ variant with a 4, 4' - bis(1H - pyrazol - 4 - yl)biphenyl instead of a BDP linker. The topology of the metal organic framework is the same as the Fe₂(BDP)₃, triangular 1D channels running in the z-direction, but the size of the channels is larger due to the extra aromatic molecule in the linker. Color code: organic linker (cyan), iron (brown), nitrogen (blue).

A class of molecules that have a reduced footprint by reorientation are aromatics, but the effect should be applicable to any adsorbate with one dimension significantly smaller than the other two. The effect is also not limited to the smallest molecules in a mixture. If the larger molecule is (when reoriented) close to the dimensions and shape of the channel and able to change its orientation, but the smallest is not, then the largest molecule will be both entropically and energetically favored at saturation conditions.

As an example on how to exploit the reorientation, we predicted the separa-



Figure 6.7: (a) Snapshots of trichlorobenzene isomers in $Fe_2(BDP)_3$ variant. Only 1,3,5-trichlorobenzene is able to reorient into a pile configuration. This reorientation reduces the footprint of the molecule and permits a higher saturation capacity. Color code: carbon (cyan), chlorine (brown), hydrogen (white). (b) Mixture isotherms for a 1,3,5-/1,2,4-/1,2,3-trichlorobenzene equimolar mixture in the modified Fe2(BDP)3 structure at 433 K. Molecules that are able to reorient into a "face-to-face" configuration have higher saturation capacities. Differences in the saturation capacities have a strong influence on the separation performance.

tion of 1,3,5-trichlorobenzene from its isomers based on the reorientation into a pile configuration of this isomer in a modified $Fe_2(BDP)_3$ metal organic framework. In the modify structure the BDP linkers (BDP=1,4-benzenedipyrazolate) were substituted by 4,4- bis(1H-pyrazol-4-yl) biphenyl linkers [24] to increase the channel size (Figure 6.6). Figure 6.7a shows that the small differences in the isomers shape are enough to only permit the 1,3,5-trichlorobenzene to reorient and reduce its footprint within the channels allowing this isomer to reach a higher saturation capacity (Figure S5). In Figure 6.7b the CB/CFCMC simulated mixture isotherms of an equimolar mixture of trichlorobenzene isomers are presented. The reorientation into a pile of 1,3,5-trichlorobenzene leads to a very efficient separation, especially under saturation conditions.

6.4 Conclusions

When in a mixture of components only one of them has the right size to rotate inside the channels, this mechanism can lead to important differences in saturation capacities. Therefore, highly selective separations can be achieved by proper choice of one-dimensional channel sizes at saturation conditions. Our CB/CFCMC and breakthrough simulations clearly underscore the potential of adopting separation strategies that relies on differences in molecular footprints, rather than adsorption strengths.

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CHAPTER 7

Entropic Separation of Styrene/Ethylbenzene Mixtures *

7.1 Introduction

Styrene is an important feedstock in the petrochemical industry. The reactivity of its vinyl group makes styrene easy to polymerize and copolymerize and therefore it serves as raw material for the production of a great variety of materials, the two most important being polystyrene and rubber. [1] Although styrene appears in small quantities in nature, the global consumption (of the order of millions of tons per year) requires its commercial production. There are two main methods to obtain styrene: dehydrogenation of ethylbenzene and co-production of styrene and propylene oxide via hydroperoxidation of ethylbenzene. Direct dehydrogenation of ethylbenzene to styrene accounts for the majority of the production. The conventional method involves two steps: the alkylation of benzene with ethylene to produce ethylbenzene and the dehydrogenation of the ethylbenzene to produce styrene. Complete conversion is not achieved in the reactor and therefore the product stream contains a large fraction of ethylbenzene that has to be removed.

The preferred technology for the ethylbenzene/styrene separation nowadays is extractive distillation [2] and vacuum distillation [3, 4] together with inhibitors like phenylene-diamines or dinitrophenols to avoid styrene polymerization.

However, because of the similarity in the boiling point of styrene (418 K) and ethylbenzene (409 K), this process is energetically expensive and most of the energy needed for the production of styrene is used in the separation process. The

^{*}Based on: A. Torres-Knoop, J. Heinen, R. Krishna and D. Dubbeldam, *Entropic Separation of Styrene/Ethylbenzene Mixtures by Exploitation of Subtle Differences in Molecular Configu*ations in Ordered Crystalline Nanoporous Adsorbents, Langmuir, 31(12), **2015**, 3771-3778.

process is even more complicated due of the presence of side products like toluene, o-xylene and benzene.

An alternative energy-efficient separation strategy involves utilizing the molecular, chemical and geometrical differences by means of adsorptive separation with nanoporous materials like metal-organic frameworks and zeolites. Ahmad et al. [5] performed liquid chromatography separation using HKUST-1($Cu_3(BTC)_2$) a metal-organic framework with open Cu(II) sites and 1.3.5-benzenetricarboxylate (BTC) linkers. They found that styrene is preferentially adsorbed in the structure because of the coordinative interaction of styrene with the Cu(II) in a π complexation mechanism. Maes et al. [6, 7] and Remy et al. [8] reported results on MIL-47(V) and MIL-53(Al), showing both structures are capable of separation in the liquid phase. They found that in MIL-47(V) styrene selectivity is related to styrene capacity for packing, while for MIL-53(Al) styrene selectivity is related to adsorption enthalpy (interaction with the carboxylate). For competitive adsorption in static conditions, they reported separation factors of 3.6 and 4.1 for MIL-47(V) and MIL-53(Al), respectively, and for an equimolar mixture in dynamic conditions (breakthrough experiments using a column filled with crystallites in an HPLC apparatus) they found separation factors of 2.9 and 2.3. They also observed that if a more realistic mixture is taken into account (with toluene and o-xylene) in MIL-53, o-xylene and toluene are retained even longer, which makes the material good for impurity removal. Yang et al. [9] conducted experiments on stationary phase HPLC with MIL-101(Cr), a material built from a hybrid supertetrahedral building unit formed by terephthalate ligands and trimeric chromium octahedral clusters. Similar to HKUST-1, they reported a higher affinity towards styrene due to the π - π interactions with the metal-organic framework walls and the unsaturated metal sites. They also reported the efficient separation of impurities like o-xylene and toluene.

Separation based on adsorption relies on either adsorption or diffusion characteristics. At low loadings (i.e. the Henry regime), the selectivity is mainly driven by enthalpic effects, and favors the molecule with the strongest interaction with the framework. Selectivity is therefore strongly related to adsorbent and adsorbate properties such as dipole moment, polarizability, quadrupole moment and magnetic susceptibility. At saturation conditions (industrial set-up) the selectivity is driven by either enthalpic effects and/or entropic effects, like:

- commensurate freezing [10], which favors molecules which efficiently pack in intersecting-channels structures;
- size entropy [11, 12], which favors the smallest molecules;
- *length entropy* [11, 13–15], which favors the molecules with the shortest effective length (footprint) in one-dimensional channels;
- commensurate stacking [16], which favors molecules with stacking arrangements that are commensurate with the dimensions of one-dimensional channels;

• *face-to-face stacking* [17], which favors molecules that, when reoriented, significantly reduce their footprint in one-dimensional channels.

The various separation strategies for exploitation of molecular packing effects have been reviewed recently. [18]

Styrene and ethylbenzene are very similar molecules, the main difference being that styrene is a flat molecule whereas ethylbenzene is not. Finding structures with selective adsorption for styrene is not easy. In this work we present a screening study for the separation of styrene and ethylbenzene at liquid conditions. We propose to separate on the basis of a difference in saturation loading because it is more cost-efficient and utilizes the pore volume most efficiently.

7.2 Methodology

The systems were modeled using classical force fields. The adsorbates were modeled with OPLS-AA force field for organic liquids [19]. In previous work [16] we have shown that the use of these force fields is in good agreement with experiments. Because we were interested in the selectivity of planar/non-planar molecules and not in their conformational changes, adsorbates were described as multisite rigid molecules with properties and configurations shown in Figure 7.1. The parameters for the interaction of the adsorbates (Lennard-Jones and electrostatic interactions) together with a schematic representation of the molecules showing the atom types are presented in Table 7.1. Cross-interactions with other molecules and the framework were computed using Lorentz-Berthelot mixing rules.



Figure 7.1: Styrene (top) and ethylbenzene (bottom) configurations. The figure shows the typical properties of the modeled adsorbates. Distances are "molecular shadow lengths" [20] from Materials Studio [21]. Besides small differences in the charges, the main difference between these molecules is their height (planarity).

$\operatorname{atom/group}$	$q [e^-]$	σ [Å]	$\epsilon \; [\text{kcal mol}^{-1}]$	H1 H
С	-0.115	3.55	0.070	
C1	-0.115	3.55	0.076	
C2	-0.005	3.50	0.066	
C3	-0.180	3.50	0.066	
C4	-0.000	3.55	0.076	Н
C5	-0.115	3.55	0.076	
C6	-0.148*	3.55	0.076	
Η	0.115	2.42	0.030	
H1	0.060	2.42	0.030	
H2	0.074^{*}	2.42	0.030	

Table 7.1: OPLS-AA force field parameters for styrene and ethylbenzene [19]. The vinyl group charges (*) were taken from Shirley et al. [22].

The frameworks were modeled as rigid with atom positions taken from crystallographic experimental data. Most MOFs were further optimized using VASP [23, 24] with the cell fixed to the experimentally determined unit cell size and shape (PBE [25, 26] exchange-correlation functional with dispersion corrections [27] was used and the PAW method was applied to describe the core atoms; convergence criteria of the ionic forces was set to -1×10^{-3} Å/eV). The metal-organic frameworks were modeled using the DREIDING force field [28] and Van der Waals parameters not found in DREIDING were taken from the universal force field (UFF) [29]. DREIDING and UFF force fields were designed to be very generic, so that broad coverage of the periodic table, including inorganic compounds, metals, and transition metals, could be achieved. UFF was tailored for simulating molecules containing any combination of elements in the periodic table. For the zeolites the TraPPE [30] force field was used. This force field was specifically developed for zeolites.

The charge-charge interactions were computed using the Ewald summation (relative precision 10^{-6}). Charges for the frameworks were computed by minimizing the difference of the classical electrostatic potential and a quantum mechanics electrostatic potential over many grid points using the REPEAT method [31, 32].

7.3 Adsorption isotherms

To compute the adsorption isotherms we perform Monte Carlo simulation in the grand-canonical ensemble (or μ , V, T ensemble). In this ensemble, the number of adsorbates fluctuates until equilibrium conditions are reached: the temperature and chemical potential of the gas inside and outside the adsorbent are equal. Because in confined systems the fraction of successful insertions and deletions is very low, reaching equilibrium with conventional Monte Carlo methods can be very time consuming. In this study we used the Configurational Bias Continuous Fractional Monte Carlo (CB/CFCMC) [33] method to enhance the success rate of

insertions and deletions. The method is a combination of the Configurational Bias Monte Carlo (CBMC) [34–36], where molecules growth is biased towards favorable configurations and Continuous Fractional Component Monte Carlo (CFCMC) [37] in which molecules are gradually inserted or deleted by scaling their interactions with the surroundings. We have shown in previous work [33] that the results obtained with this method do not differ from CBMC calculations but the efficiency is higher.

Using the dual-site Langmuir-Freundlich fits of the pure component isotherms, breakthrough calculations were carried out by solving a set of partial differential equations for each of the species in the gas mixture [38, 39]. The molar loadings of the species at any position along the packed bed and at any time were determined from Ideal Adsorbed Solution Theory calculations. Video animations of the breakthrough behavior as a function of time of selected structures are provided as web-enhanced objects online.

7.4 Results

We perform a screening study of several zeolites and metal-organic frameworks for the separation of styrene/ethylbenzene mixture focusing on saturation conditions. Under these conditions, differences in the saturation capacity of the mixture components strongly dictate the separation.

In systems with small pores, like MRE and MTW zeolites, molecules are forced to adsorb parallel to the channels. The saturation capacity is determined by the effective length per molecule in the channel (*footprint*). Because of the similarity in the length of styrene and ethylbenzene, the difference in saturation capacities is almost negligible, making systems with small pores unsuitable candidates for the separation.

In structures with cavities or channels much larger than styrene and ethylbenzene molecular dimensions, like IRMOF-1 and Zn-DOBDC, molecules do not present any particular packing. The observed difference in the saturation capacities is a consequence of the natural packing of the molecules in liquid phase ($\rho_{Eb} = 0.8665 \text{ g/mL}, \rho_{St} = 0.909 \text{ g/mL}$). This makes these materials also unsuitable for the separation process.

We have identified a few materials where styrene has a higher saturation capacity than ethylbenzene. In the following we describe how this difference arises from the previously mentioned entropic mechanisms and we highlight their applicability for the separation process.

Size exclusion is observed in MFI-para [40]. MFI-para is a ZSM-5 zeolite which structure is a combination of interconnected straight and zigzag channels. The straight channels have a diameter of 5.3×5.6 Å and the zigzag channels have a diameter of 5.1×5.5 Å. In Figure 7.2b the simulated single component isotherms of styrene and ethylbenzene in MFI-para at 433 K and snapshots of styrene and ethylbenzene at 1×10^9 Pa and 433 K are presented. At low loadings molecules

preferentially adsorb in the straight channels, the difference in loadings arise from a stronger interaction of styrene with MFI-para. At saturation conditions, styrene can obtain almost twice the loading of ethylbenzene because of a size exclusion effect in the zig-zag channels in which ethylbenzene does not fit due to its height. When an equimolar styrene/ethylbenzene mixture is considered, the difference in loadings at saturation conditions is even larger (Figure 7.2c).



Figure 7.2: (a) Snapshots of ethylbenzene (top) and styrene (bottom) at 1×10^9 Pa and 433 K. (b) Single component isotherms of styrene (red) and ethylbenzene (blue) in MFI-para at 433 K (lines are dual-site Langmuir-Freundlich fits of the pure components, points are the pure component isotherms from CB/CFCMC simulations). (c) Mixture component isotherms for an equimolar mixture in MFI-para at 433 K.

Face-to-face stacking occurs in MAZ [41] and AFI [42] zeolites. MAZ and AFI are 1D-channel zeolites with dimensions that allow a molecular reorientation of ethylbenzene and styrene.

In Figure 7.3 we present the simulation results for the single component isotherms of ethylbenzene and styrene in AFI zeolite at 433 K. At low loadings molecules are mostly adsorbed flat on the walls (parallel to the channels axis), adsorption is dictated by enthalpy effects, which favors ethylbenzene. As the loading increases, the molecules undergo a molecular reorientation from a configuration parallel to the channel axis to a "pile" configuration with the phenyl groups facing each other. This new configuration (face-to-face stacking) reduces styrene's footprint more than ethylbenzene's footprint (Figure 7.6a) because of the nonplanarity of ethylbenzene, allowing styrene to obtain higher saturation loadings.

For MAZ zeolite a similar behavior is observed however, because MAZ zeolite has smaller channels than AFI, the angle at which molecules can reorient has a smaller effect on the reduction of the molecule's footprint in the channels (Figure 7.6b). When an equimolar mixture is considered both AFI and MAZ zeolites are styrene selective at saturation conditions as shown in Figures 7.4a and 7.4b where the simulated mixture component isotherms at 433 K are presented.



Figure 7.3: Single component isotherms of styrene and ethylbenzene in AFI at 433 K. Inset: snapshots of styrene (top) and ethylbenzene (bottom) at 1×10^3 Pa and 1×10^9 Pa. At low loadings both molecules are adsorbed with the phenyl group parallel to the channel axis. At higher pressures styrene can arrange in a tilted face-to-face stacking configuration, which reduces its footprint and allows for a higher saturation capacity. The difference in saturation capacities ensures the selectivity of AFI towards styrene at saturation conditions in the mixture.



Figure 7.4: Mixture component isotherms for and equimolar mixture of styrene and ethylbenzene at 433 K in (a) AFI zeolite and (b) MAZ zeolite.

Face-to-face stacking is also observed in DON zeolite. DON [43] is a structure with 1D-channels slightly larger than AFI and MAZ zeolites. This increase in dimensions favors ethylbenzene to undergo a molecular reorientation into a face-to-face stacking configuration but also, because the diameter of the channels are larger than the length of styrene, it induces styrene to adopt a *commensurate stacking* configuration where the stacking of two molecules with their phenyl groups facing each other is commensurate with the channel dimensions (Figures 7.5a). This is also observed in MIL-53 [44], a metal-organic framework with lozenge-shaped rhombohedric channels of approximately 0.85 nm, as show in Figure 7.5b



Figure 7.5: (a) Snapshots of styrene (left) and ethylbenzene (right) in DON zeolite at 1e9 Pa and 433 K.(b) Snapshots of styrene (left) and ethylbenzene (right) in MIL-53 at 1e9 Pa and 433 K. Color code: carbon (cyan), hydrogen (white).

where snapshots of styrene and ethylbenzene at 1×10^9 Pa and 433 K are presented. Because of styrene and ethylbenzene dimensions, styrene with commensurate stacking can obtain higher saturation capacities than ethylbenzene with face-to-face stacking as shown schematically in Figure 7.6c. This is also seen in DON and MIL-53 single component isotherms (Figure 7.7a). Mixture isotherms (Figures 7.7b) and breakthrough curves (Figure 7.7c) further confirm that DON and MIL-53 are styrene selective structures.

Commensurate stacking for both styrene and ethylbenzene is observed in MIL-47 [45] and MAF-X8 [46]. MIL-47 is a metal-organic framework with lozengeshaped rhombohedric channels which size (slightly larger than MIL-53) allows for ethylbenzene to also have commensurate stacking. In Figure 7.8 we present the simulated single component adsorption isotherms of ethylbenzene and styrene in MIL-47 at 433 K and snapshots of styrene and ethylbenzene at 1×10^6 Pa and 1×10^9 Pa. At 1×10^9 Pa both molecules have commensurate stacking, but in order for ethylbenzene to have commensurate stacking the phenyl groups have to be slightly shifted due to the non-planar ethyl group. This shift affects the amount of ethylbenzene molecules that can be adsorbed (as compared to styrene) and therefore, causes a difference in the saturation capacity of styrene and ethylbenzene. Interestingly, commensurate stacking occurs at lower loading for styrene than for ethylbenzene. We can see in Figure 7.8 that at 1×10^6 Pa styrene already presents commensurate stacking while ethylbenzene seems to have more of a face-to-face stacking. In a mixture, this will favor styrene adsorption even more. In Figure 7.9 simulated mixture adsorption isotherms for an equimolar mixture in MIL-47 at 433 K are presented. MIL-47 is a styrene selective structure. Our results are in good qualitative agreement with Maes et al. [6]. Breakthrough simulations further confirm that MIL-47 is a styrene selective structure at saturation conditions. In MAF-x8, a metal-organic framework with square channels of approximately 1nm,



Figure 7.6: Schematic representation of different entropic effects occurring in the separation of styrene and ethylbenzene in nanoporous materials. (a) The reduction of the molecule's footprint in the channels because of a reorientation into a face-to-face stacking configuration. (b) Effect of the channel size on the reorientation and therefore molecule's footprint reduction. (c) Comparison of the channel length needed for two molecules of styrene to have commensurate stacking *vs.* two molecules of ethylbenzene to have face-to-face stacking.



Figure 7.7: Simulated isotherms and breakthrough curves of styrene and ethylbenzene in MIL-53 (top) and DON (bottom) at 433 K. (a) Pure component isotherms (lines are dual-site Langmuir-Freundlich fits of the pure components, points are the pure component isotherms from CB/CFCMC simulations). (b) Mixture component isotherms for an equimolar mixture. The IAST results are in good agreement with the mixture isotherms. (c) Simulated step-type breakthrough at 1e6 Pa total fugacity.



Figure 7.8: Single component adsorption isotherms for styrene and ethylbenzene at 433 K in MIL-47. Inset: styrene (top) and ethylbenzene (bottom) snapshots at 1×10^6 Pa and 1×10^9 Pa. Styrene has commensurate stacking at lower pressures than ethylbenzene. Because of the out of plane ethyl group, ethylbenzene molecules have to be slightly shifted in order to have commensurate stacking and therefore less ethylbenzene molecules can be adsorbed in MIL-47 channels at saturation conditions.



Figure 7.9: Styrene/ethylbenzene separation using MIL-47 at 433 K (a) equimolar mixture isotherms and Ideal Adsorption Solution Theory (IAST) prediction based on pure component isotherms, (b) simulated step breakthrough at 1×10^6 Pa total fugacity. The IAST prediction is in excellent agreement with the mixture simulations. The mixture and breakthrough simulations show a high styrene selectivity and loading in the mixture.

it is easier for ethylbenzene to have commensurate stacking than in MIL-47. The single component isotherms of both molecules behave very similar. The topology of the structure seems to induce a shift between parallel styrene molecules and allows for the ethyl group of ethylbenzene to stick in the channel "pockets" (Figure 7.10). This might be the reason for the smaller difference in saturation capacities of styrene and ethylbenzene compared to MIL-47.



Figure 7.10: Snapshots of (a) styrene and (b) ethylbenzene in MAF-X8 at 1e9 Pa and 433 K. Both styrene and ethylbenzene have commensurate stacking. Color code: carbon (cyan), hydrogen (white). (c) Simulated single component isotherms of styrene and ethylbenzene in MAF-X8 at 433 K.

Combination/competition of mechanisms is observed in structures with a more complex topology. An example of this is MOF-CJ3 metal-organic framework [47]. The wide segment of the channels are big enough to allow for both styrene and ethylbenzene to form two parallel rows (commensurate stacking), however the shape of the channels forces ethylbenzene molecules to adopt a configuration where the ethyl group is pointing to the channel "pockets". Styrene has more freedom and molecules can arrange in a way that an extra styrene can be adsorbed in the protracted segments in a configuration perpendicular to the channel (face-to-face stacking) (Figure 7.11). The interplay between different mechanisms rarely makes the separation better. Even when all the mechanisms favor a specific molecule, the competition between them can induce enough disorder to destroy the selectivity one could achieve with a "pure" mechanism.



Figure 7.11: Snapshots of styrene (top) and ethylbenzene (bottom) at 1×10^9 Pa and 433 K in MOF-CJ3.

7.5 Discussion

There are two important factors to consider when using adsorption for separation processes at industrial conditions, namely selectivity and capacity. A high selectivity ensures that less cycles are needed to achieve a high degree of purity in the separation, but a high capacity implies that the regeneration time is longer. For a binary mixture the adsorption selectivity is defined as

$$S_{\rm ads} = \frac{q_1/q_2}{f_1/f_2} \tag{7.1}$$

and the capacity is defined as the styrene loading in the adsorbed phase of a binary mixture.

$$Capacity = q_1 \tag{7.2}$$

In Figure 7.12, the relationship between these two properties for different structures is presented. Structures with the same separation mechanism are plotted with the same color. An ideal structure for the separation would be located at the right top corner.



Figure 7.12: Selectivity as a function of styrene loading (capacity) in a binary mixture at 433 K and 1×10^6 Pa total fugacity. The structures are divided in different colors depending on the selectivity mechanism observed. Color code: Size exclusion (red), face-to-face stacking (purple), commensurate stacking (blue), commensurate stacking/face-to-face stacking (green), mixed(orange). The dotted red line corresponds to the ratio styrene/ethylbenzene at liquid conditions. There is a natural trade-off between selectivity and loading, finding structures in the top right corner is not feasible. The black dashed line (guide to the eye) denotes the inverse relationship between selectivity and capacity. MIL-47 is a styrene selective material with a high capacity, therefore a good candidate for the styrene/ethylbenzene separation.

In structures where the separation is driven by size-exclusion (MFI-para), the selectivity is high because there is an adsorption site available only for styrene (zig-zag channels) but the capacity is rather low since for size-exclusion to occur among similar molecules, there has to be a very tight fit between the molecules and the adsorbent, usually associated with small pore systems.

In structures where the separation is driven by face-to-face stacking the selectivity relies on the increase of the molecule's footprints difference, consequence of a reorientation and piling. Ideally, only one of the mixture components should be able to reorient but in the case of styrene and ethylbenzene the similarity in their length and width makes no significant difference in the pore size needed for the reorientation. The selectivity relies thus in how favorable the reorientation and piling are.

In MAZ and AFI both molecules can reorient but the reorientation is restricted by the pore size, forcing a tilting in the face-to-face stacking configuration that is unfavorable for ethylbenzene to form a pile but it is favorable for styrene. This allows styrene to obtain higher saturation loadings and ensures MAZ and AFI styrene selectivity at saturation conditions.

However, face-to-face stacking only occurs at high loadings. In Figure 7.12 the selectivity is presented at 1×10^6 Pa. At this fugacity, MAZ is not yet styrene selective and AFI selectivity is almost negligible. The effect of face-to-face stacking in styrene selectivity can only be observed at higher loadings as shown in Figure 7.13, where the selectivity as a function of styrene loading for higher fugacities is presented.



Figure 7.13: Selectivity (q_{st}/q_{eb}) in an equimolar mixture at 3 different fugacities. The dashed red line corresponds to the liquid phase ratio. For all the cases styrene loading increases with the fugacity (shift to the right of the plot). The selectivity also increases in most of the cases with the fugacity (shift upwards) except for MFI-para, JUC-77, MIL-47 and Cu-BTC.

Face-to-face stacking can only occur when the reoriented molecules are commensurate with the channel diameter. This has an important restriction in the pore size and therefore in the capacity.

In structures where styrene has commensurate stacking an ethylbenzene has face-to-face stacking (as observed in MIL-53 and DON), the difference in saturation capacities arises because the channel length needed to accommodate molecules of styrene in commensurate stacking is smaller than the channel length needed to accommodate molecules of ethylbenzene in face-to-face stacking. When an equimolar mixture is considered, styrene will be favored even more because it does not have to undergo any reorientation to achieve higher loadings. Structures with pore sizes that allow styrene to have commensurate stacking, but not ethylbenzene, are styrene selective and have a higher saturation capacity than structures that present face-to-face stacking or size exclusion.

In structures where both, styrene and ethylbenzene can have commensurate stacking (MIL-47 and MAF-X8), the selectivity will depend on the efficiency in which the molecules can stack. In Figure 7.14 we present schematic commensurate stacking configurations of styrene and ethylbenzene. For ethylbenzene to have commensurate stacking the "minimal length", the "packing length" or both have to be larger than for styrene. At saturation conditions, this implies that more styrene molecules can be adsorbed than ethylbenzene ones, favoring the adsorption of styrene over ethylbenzene in a mixture. Commensurate stacking enhances the dimensional differences of styrene and ethylbenzene as "pairs" of molecules. Because commensurate stacking occurs in structures with larger pores, high capacity can be attained.



Figure 7.14: Schematic differences of the channel dimensions needed for commensurate stacking. Because styrene is a planar molecule, commensurate stacking can occur in smaller channels. Commensurate stacking is a powerful separation mechanism for planar/non-planar molecules.

Commensurate stacking is the best mechanism for the separation of ethylbenzene and styrene. It offers a geometrical solution to the separation problem that ensures a high selectivity and it occurs in open pore structures ensuring a high capacity. The channel topology can facilitate or impede the selectivity.

In the case of MIL-47, the almost planar walls force ethylbenzene molecules to be shifted increasing the difference in "length" per pair of molecules in the channel as compared to styrene. This makes MIL-47 a highly styrene selective material and the best candidate for the separation of styrene/ethylbenzene from the structures we screened.

7.6 Conclusion

Styrene and ethylbenzene are very similar molecules and finding structures that can discriminate between them is not easy. At liquid conditions, the success in the separation process is strongly related with difference in saturation capacities of the mixture components which in turn is strongly dictated by the underlying entropic mechanisms occurring in the nanoporous material. Commensurate stacking offers the best trade-off between saturation capacity and selectivity and is therefore a very efficient mechanism for the separation of styrene and ethylbenzene. Among the different structures we studied, MIL-47, a styrene selective structure, is the best candidate for the adsorptive separation of styrene/ethylbenzene mixture in nanoporous materials. Commensurate stacking offers a geometrical solution to the separation of planar/non-planar molecules, this enables a convenient approach to designing materials for the separation.

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Associated Content

This material provides (a) structural details of various materials investigated (b) pure component and mixture adsorption data, (c) dual-Langmuir-Freundlich fits parameters for unary isotherms (d) transient breakthrough simulation results for various materials. http://pubs.acs.org/doi/abs/10.1021/acs.langmuir.5b00363.

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CHAPTER 8

Exploiting Large-Pore Metal-Organic Frameworks for Separations using Entropic Molecular Mechanisms*

8.1 Introduction

Nanoporous materials such as zeolites [1, 2], metal-organic frameworks (MOFs) [3– 7], and zeolitic imidazolate frameworks (ZIFs) [8] offer great potential as energyefficient alternatives to conventional separation processes like distillation, absorption, and extraction. Besides being industrially relevant, they are scientifically very interesting to gain understanding of the fundamentals of the separation mechanisms governing adsorbed molecules in confinement. Separation in nanoporous materials relies on adsorption [9] and diffusion [10], and can be achieved by size/shape exclusion (steric separation), by differences in the adsorbate-adsorbent interactions and by adsorbate packing (thermodynamic equilibrium effect) and by differences in the diffusion rate of adsorbates within the adsorbent channels.

Zeolites and aluminosilicates are produced commercially and have relatively high thermal and chemical stabilities. These materials are based on TO_4 tetrahedra (where T is an aluminum or silicon atom), which results in 3-dimensional networks when all four corners of the tetrahedral are shared. The tetrahedra are primary building blocks, which form secondary building blocks (*e.g.* 4-rings, 6rings, double 6-rings, etc.). These secondary units join together to form the about 225 different zeolite topologies we know today. In Figure 8.1 two well-known zeolites are shown: faujasite (FAU) and Mobile Five (MFI). For FAU we can see the 6-6, 6-2, 6, 4-2, 1-4-1, and 4 secondary building blocks forming a supercage. The nomenclature can be found in the zeolite atlas, but for example 6-6 stands

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Figure 8.1: Two well-known zeolites: (a) Faujasite (FAU), and (b) Mobile Five (MFI). The Faujasite family of zeolites is composed of sodalite cages linked through double 6-rings into an hexagonal layer. Color code: aluminum (green), silicon (yellow), extra-framework cation site I, I', II and II' (red), site III (blue, pink, yellow). MFI is a 3-dimensional network consisting of linear channels ('L'), zig-zag channels ('Z') and intersections ('I'). The unit cell has dimensions of $20.022 \times 19.899 \times 13.383$ Å; per unit cell there are 4 intersections, 2 zig-zag channels, and 2 linear channels. The channels are shown as an adsorption surface (inside as 'gold', outside view as 'blue'), with hexane molecules adsorbed in the linear and zig-zig channel.

for a double 6-ring of T-atoms. FAU-type zeolites are widely used in separation processes and catalysis. There are many forms of the FAU topology, *e.g.* Ba-X, Na-X, Na-Y, siliceous Na-Y, and SAPO-37, which differ in their chemical composition. The FAU-type pore structure consists of sodalite cages arranged in 1.2 nm wide supercages accessible through 0.72 nm windows. MFI is a typical example of a three-dimensional channel structure with intersections at the crossing of the channels, and has been the focus of the pioneering computational zeolite work, starting with the works of June *et al.* [11, 12] and Snurr *et al.* [13]. The channels of MFI are wide enough to adsorb *e.g.* C6, C7, and C8 isomers, including benzene and xylenes.

In aluminosilicates, the ratio between aluminum and silicon determines the charge of the framework. This charge is compensated by the presence of extra-framework cations like Na^+ , Li^+ , K^+ , Ba^{2+} and Ca^{2+} which are distributed among different sites in order to maximize their interactions with the framework oxygens and minimize the cation-cation repulsion. Zeolites have relatively high framework densities, low surface areas, and low pore volumes, and in general show high selectivities because strong confinement allows for higher discrimination between adsorbing species.

MOFs are novel materials that, relative to zeolites, have moderate stability, high void volumes, and well-defined tailorable cavities of uniform size. These materials consists of building blocks that self-assemble into crystalline materials that, after evacuation, can find applications in adsorption, separations, air purification, gas storage, chemical sensing, and catalysis [14–17]. MOFs possess almost unlimited structural variety because of the many combinations of building blocks that can be imagined [18–20]. The clear advantage of MOFs is their very high pore volumes and surface areas. For development of next-generation porous materials it is highly desired to combine the high selectivity of zeolites with the large pore capacities of MOFs. Another scientifically extremely appealing property of MOFs is design. Düren et al. developed 'in silico MOF design', *i.e.* using information obtained from computer simulation these authors proposed a new, not yet synthesized, MOF with enhanced methane storage capabilities [21]. Sarkisov and Kim reviewed how the information obtained from computational characterization can be used in screening protocols to identify the most promising materials for a specific application before any costly and time consuming experimental effort is committed [22].

There is a conceptual difference between adsorption of small versus larger molecules. In contrast to larger molecules, small gas molecules such as CO_2 , O_2 , N_2 , CH_4 , etc. have little or no shape/size differences relative to the framework. They behave more like a fluid inside large pores of nanoporous materials [23]. The possible separation mechanisms are therefore limited to either small pore systems, or for larger pores limited to reduced separation selectivities. It is inherently hard for these systems to combine high selectivity with high pore volumes, because only the surface-adsorbed molecules "feel" the framework (while the remainder of the molecules interact mainly with other molecules). Selectivity therefore originates from the low loading regime where a few molecules interact with strongly selective sites, but selectivity is lost at higher loadings. This is unfortunate, because many industrial processes operate at saturation conditions (*e.g.* liquid-phase separations).

Separation mechanisms that are effective at saturation conditions have (in general) to be *entropic* in nature (saturation corresponds to the high-pressure part of adsorption isotherms). For molecules that have a bulky size and shape (relative to the framework) it is possible to exploit entropy effects to induce a difference in saturation loading. Molecules that fall into this class are for example alkanes (chain-like) and aromatics (flat in shape). For example, xylene isomers have the same mass and similar boiling points, and are also close in shape. The similarity of these properties is why they are so difficult to separate via traditional methods. Xylene isomers have a bulkiness of the shape and size of MOF cavities. If one specific isomer can stack or pack two molecules per channel-length, but the other isomers only one, then a significant difference in saturation loading leads to a very efficient separation. In this case, high selectivity *can* be combined with high pore volumes. Here, we will focus on systems of this type and on the methodologies to achieve this. Our focus lies heavily on computational work because in simulations all molecular level information is readily available and a wide range of



Figure 8.2: Typical geometric properties of MOFs, COFs, ZIFs, and zeolites. NU-110 has the highest geometric surface area (7400 m2/g), while COF-108 has the highest pore volume (5.46 cm3/g) and void fraction (93.1 %). Figures adapted from Ref. [24].

thermodynamic conditions can be examined.

8.2 Nanoporous materials for separations

Surface area, pore volume, and porosity have become the main characterization properties for bench-marking porous materials [24]. Geometric surface areas can be calculated using a simple Monte Carlo integration technique in which a nitrogen probe molecule is rolled along the surface [21, 25]. The obtained values usually compare well to BET surface areas once the appropriate consistency criteria are met [26]. For sorption applications, these molecular surface areas are physically more meaningful than e.g. Connolly surface areas [27]. The crystal volume per mass is a property directly computable from the crystallographic data of a nanoporous material, but it is the *accessible* volume (the volume accessible to the adsorbates per volume or mass of framework) that is the appropriate adsorption metric. The porosity can be computed using a methodology proposed by Talu and Myers [28], where the volume is probed with a non-adsorbing helium atom. An alternative is to use the $r \to 0$ limit of the pore size distribution function to determine the void fraction [24]. Once the helium void fraction and the crystal volume per mass are known, then the accessible pore volume or pore capacity can be calculated (by multiplying the two). The pore capacity is the volume accessible to adsorbates per framework mass and it takes the framework density and porosity into account. Relevant accessible pore volumes should not include volumes that are not accessible (from the main channel).

In Figure 8.2 we plot surface areas and pore capacities as a function of the porosity for a wide range of MOFs, zeolites, COFs, and ZIFs. Note that the y-axes are in log-scale. The structures have been selected on the premise that



Figure 8.3: Two examples of MOFs: (a) An iron-based MOF with triangular 1D channels running in the z-direction. The linker molecule is 4,4-bis(1H-pyrazol-4-yl)biphenyl. The topology of the MOF is the same as $Fe_2(BDP)_3$ but has an additional phenyl-group in the linker. The channels are large enough to accommodate aromatics. (b) UiO-66 consisting of two types of cages in an alternating arrangement (left-view: small type cavities, right-view: large type cavities). We show a snapshot of 2,3-dimethylbutane at high loading at 433 K in $2 \times 2 \times 2$ unit cells. Each edge length of the unit cell is 20.7 Å.

their pores should be large enough to accommodate hexane molecules. In general, the pore capacities and surface areas of MOFs are an order of magnitude larger than for zeolites. MOFs therefore have the potential to revolutionize storage [29–31], CO₂ capture and adsorption [32–34], adsorption[35], separations [36], and catalysis[37–41], and to become just as widespread as zeolites.

Figure 8.3 shows two examples of MOFs: (i) an iron-based MOF with triangular channels and (ii) UiO-66 containing cavities accessible through windows. The iron-based MOF has iron-metal corners that are bridged by 4,4-bis(1H-pyrazol-4yl)biphenyl linkers, creating a one-dimensional, triangular channel structure. The openness of the structure is striking. In contrast to zeolites, which are much denser, every MOF framework atom is in contact with the channel and the wall thickness is one atomic layer. The channels are large enough to accommodate aromatics without diffusion limitations. The UiO-66 pore system consists of two types of cages per unit cell that alternate: 4 octahedral cages of 1.1 nm in diameter and 8 smaller tetrahedral cages 0.8 nm in diameter [42]. About 50% of the structure is void. The UiO-66 structure is capable of efficiently separating hexane isomers [43].

What is also evident (beside noting the high pore volume) is that the structures are not as thermally stable as zeolites. MOFs consist of a coordinating metal atom (or cluster of atoms) with one or more ligands attached to it by so-called 'coordination bonds'. These bonds (between 50 kJ/mol and 200 kJ/mol) are weaker than covalent bonds and its force is acting on a relevant distance of 1.5-2.5 Å. The strength of covalent bonds is about 200-800 kJ/mol and the force operates over shorter distances of the order of 1-2 Å [44]. In addition, and likely related to this, the structures are less water-stable than zeolites. The principles of designing water-stable MOFs are not yet well understood. Solvents, left over from synthesis, need to be removed, usually by heating and vacuum. But the temperatures that are attainable before thermal decomposition are not as high as for zeolites. And similar to zeolites, there are also issues of (partial) pore collapse and imperfections and stacking faults during crystal growth. However, the last years much progress has been made in the synthesis of (water-)stable MOFs [45].

There are several works that discuss guidelines and objective criteria for which the adsorptive delivery should be optimized [46, 47], taking the entire adsorptiondesorption cycle into account (in a practical pressure range of 1-30 bar). A too strong affinity of adsorbates with the framework makes it very energetically costly to desorb, whereas a too low affinity leads to poor delivery. For example, for methane an optimal enthalpy value of around 20 kJ/mol has been found (at 254 K). Most small pore structures (like zeolites) have a significantly stronger interaction. MOFs seem to have an ideal adsorption behavior for many adsorbates, except perhaps for hydrogen adsorption (MOFs are still well below the DOE targets for hydrogen storage although progress is made [48]). For example, the record holder for methane-storage is a MOF [49]. However, because the building blocks of MOFs are expensive, it would be very costly to use MOFs for storage applications. For separation and catalysis applications the material can be immediately reused and the cost of the material itself is less of an issue (especially if the MOFs are very stable). The open structure of MOFs means that there are little or no diffusion limitations [50]. A wish list for a next-generation adsorbent would therefore be:

- sufficient thermal- and water-stability,
- high adsorption selectivity,
- large pore capacity,
- heats of adsorption that are not too low or too high,
- a diffusion selectivity that enhances the adsorption selectivity even further (or at least does not hamper the adsorption selectivity).

Operating at saturation conditions using large pore capacities is benificial because then more fluid can be treated in a single adsorption-desorption cycle, thereby reducing the amount of cycles (and hence the costly desorption step). Especially for membrane applications, it is the product of both the diffusivity and adsorption selectivities that determines the efficiency. This creates an inherent difficulty, because usually (but fortunately not always) an increase in affinity decreases the diffusion rate.

8.3 Adsorption thermodynamics

The thermodynamics of physi-sorption of gases in porous solids is well developed (see refs. [51–53] and references therein). Excess adsorption is defined as "the difference between the number of moles of gas present in the system (sample cell
containing porous solid) and the number of moles that would be present if all the accessible volume in the system (both inside and outside the pores) were occupied by the adsorbate gas in its bulk state at the same temperature and pressure" [54]. Although experiments measure excess adsorption, it is much more convenient (and even necessary) to describe the theoretical framework in terms of absolute adsorption [54]. Simulations always compute absolute adsorption $n_{\rm a}$, but (knowing the accessible pore volume $V_{\rm pore}$ of the framework) $n_{\rm a}$ can be converted to excess adsorption $n_{\rm exc}$:

$$n_{\rm exc} = n_{\rm a} - \frac{pV_{\rm pore}}{zRT} = n_{\rm a} - \rho\left(p, T\right) V_{\rm pore} \tag{8.1}$$

R = 8.31451 J/mol/K is the gas constant, z the compressibility in the bulk fluid phase, and ρ is the density of the bulk fluid phase at temperature T and pressure p.

The affinity of a molecule with the framework can be expressed as the binding energy, or more general, as the enthalpy of adsorption at infinite dilution ΔH [55]:

$$\Delta H = \Delta U - RT = \langle U_{hg} \rangle - \langle U_h \rangle - \langle U_g \rangle - RT$$
(8.2)

where ΔU is the internal energy, and $\langle U_{hg} \rangle$, $\langle U_h \rangle$, and $\langle U_g \rangle$ are the average energy of the guest molecule inside the host-framework, the average energy of the host-framework, and the average energy of the guest-molecule, respectively. In simulations a common approximation is to assume the framework is rigid, and in this case the enthalpy of adsorption at infinite dilution can be understood to be the difference in internal energy of a single molecule outside and inside the confinement of the host framework. In the limit of zero temperature, the enthalpy of adsorption becomes the binding energy. Infinite dilution enthalpy of adsorption ΔH is related to the Henry's coefficient K_H as

$$\Delta H = -\frac{\partial \ln K_H}{\partial \beta} \tag{8.3}$$

where $\beta = 1/(k_B T)$ is the inverse temperature, and k_B the Boltzmann's constant. The Henry's coefficient is the slope of the isotherm at zero pressure/loading.

The Helmholtz free energy ΔA of adsorption can be computed using Widom test-particle insertion. At infinite dilution the Gibbs free energy is related to the Helmholtz free energy by

$$\Delta G = \Delta A - RT \tag{8.4}$$

The entropy difference of a molecule outside and inside the framework is given as

$$\Delta S = \frac{\Delta U - \Delta A}{T} = \frac{\Delta H - \Delta G}{T} \tag{8.5}$$

The Gibbs free energy of adsorption consists of a change in enthalpy ΔH and a (temperature) change in entropy $T\Delta S$

$$\Delta G = \Delta H - T \Delta S \tag{8.6}$$

So, when a molecule adsorbs it transitions from the free fluid phase to an adsorbed phase with two common contributions:



Figure 8.4: Thermodynamic adsorption properties of (a) hexane (nC6) and (b) 2,2dimethylbutane (22DMB) as a function of channel size. The zeolites are in order of smallest to largest: MTW, VET, SPE, BEA, SSZ-31, MOR, CON, OFF, GME, AFI, CFI, MAZ, ADR, DON, AET, MEI, LTL, and FAU. Lines are guides to the eye. Data taken from Ref. [56].

- 1. it (usually) gains favorable energy (ΔH is negative) because of attractive interactions with the framework, and
- 2. the molecule has an increased confinement compared to the gas phase, thereby loosing entropy (ΔS is negative, $-T\Delta S$ is positive, leading to increased and less favorable ΔG).

Adsorption will occur only when ΔG is negative and this is possible only if $\Delta H < T\Delta S$. The process is (usually) exothermic ($\Delta H < 0$). Figure 8.4 plots ΔG , ΔH , and $-T\Delta S$ as a function of pore size at 533 K. The data is taken from Schenk *et al.* [56]. For hexane, the adsorption strength ΔG is stronger in the tighter MTW channels, even though the hexane molecule is more confined, as this is offset by a larger enthalpy-gain with the structure. For hexane the ΔG nicely correlates with the channel diameter, but for 2,2-dimethylbutane there is an optimal channel width somewhere in between FAU and MTW (*i.e.* AFI with pore size of 7.3 Å) [56, 57]. In general, the interplay of enthalpy and entropy is difficult to predict.

As another example, we show in Table 8.1 the values of ΔH , ΔG and $-T\Delta S$ for hexane isomers in UiO-66. At low loading, the hexane isomers prefer the smalltype cages in UiO-66 and at high loading also occupy the large-type cages. The branched hexane isomers are preferred in these small cages over the mono-branched and linear hexane. At 300 K, the 2,3-dimethylbutane is preferred, while at higher temperatures 2,2-dimethylbutane is preferred. This is exclusively due to entropy. In structures like UiO-66 the molecules are well separated in small cavities and inter-molecular interactions for hexane isomers are low. In general, because there are two types of cavities in UiO-66, molecules of a certain type can preferentially adsorb in one of the two types of cage (or transition between them) depending on temperature and loading [58]. Entropy differences between components in a

T[K]	adsorbate	$\Delta G \; [\rm kJ/mol]$	$\Delta H \; [\mathrm{kJ/mol}]$	$-T\Delta S \; [kJ/mol]$	$\Delta S ~[\text{J/mol}]$
300	22DMB	-50.6	-71.9	21.3	-70.8
300	23DMB	-55.7	-77.5	21.8	-72.8
300	2MP	-44.8	-70.4	25.6	-85.3
300	3MP	-48.8	-72.8	24.0	-80.2
300	nC6	-37.2	-64.0	26.8	-89.2
400	22DMB	-56.0	-71.5	15.5	-38.9
400	23DMB	-46.1	-77.3	31.2	-78.0
400	2MP	-35.3	-69.1	33.7	-84.3
400	3MP	-42.3	-71.8	29.4	-73.6
400	nC6	-23.0	-62.8	39.8	-99.4
500	22DMB	-51.3	-71.3	20.0	-40.0
500	23DMB	-39.8	-77.0	37.2	-74.4
500	2MP	-28.1	-67.8	39.7	-79.4
500	3MP	-36.0	-71.0	35.0	-70.0
500	nC6	-15.3	-61.4	46.0	-92.0

Table 8.1: Thermodynamic adsorption properties of hexane isomers at infinite dilution in UiO-66 at 300, 400 and 500 K. The structure of UiO-66 is shown in Figure 8.3.

mixture can be substantial, even at low loading, and mixture simulations can be driven by rotational entropy [43, 59].

At the start of an adsorption process, $\Delta H < T\Delta S$ and $\Delta G < 0$, and the process transfers molecules in the direction of lower free energy (which results in adsorption). As the adsorption process continues the ΔH and $T\Delta S$ terms change until $\Delta H = T\Delta S$ and $\Delta G = 0$, and equilibrium is achieved. At finite loading, the enthalpy of adsorption ΔH can be computed in the grand-canonical ensemble μVT (fixed chemical potential μ , fixed volume V and fixed temperature T) from a fluctuation formula [60, 61]:

$$\Delta H = \frac{\langle U \times N \rangle_{\mu} - \langle U \rangle_{\mu} \langle N \rangle_{\mu}}{\langle N^2 \rangle_{\mu} - \langle N \rangle_{\mu}^2} - \langle U_g \rangle - RT$$
(8.7)

The chemical potential in the adsorbed μ_a and gas phase μ_g are defined as

$$\mu_a = \left(\frac{\partial G_a}{\partial n_a}\right)_{T,p} \tag{8.8}$$

$$\mu_g = \left(\frac{\partial G_g}{\partial n_g}\right)_{T,p} \tag{8.9}$$

When equilibrium is reached, the chemical potential of the adsorbed phase becomes equal to the gas phase chemical potential

$$\Delta G = (\mu_a - \mu_g) \ dn_a = 0 \to \mu_a = \mu_g \tag{8.10}$$

Adsorption is usually described through isotherms, *i.e.* the amount of adsorbate on the adsorbent at constant temperature as a function of pressure or fugacity. A common, generic isotherm-model is the *n*-site Langmuir-Freundlich (LF) model (also known as 'Sips' model):

$$q(x) = \sum_{i}^{n} q_{i,\text{sat}} \frac{b_i x^{\nu_i}}{1 + b_i x^{\nu_i}}$$
(8.11)

where x can be pressure or fugacity, n is the number of types of sites, and $q_{i,\text{sat}}$ (the saturation loading for site i), b_i and ν_i are fitting constants. The constant ν is often interpreted as the heterogeneity factor [62]. Values of unity indicate a material with homogeneous binding sites and Eq. 8.11 reduces to the n-site Langmuir model.

Our knowledge on the peculiarities of isotherm behavior has grown tremendously the last two decades. Hexane and heptane in MFI show inflections in the isotherms due to 'commensurate freezing' [63]. The length of these molecules is commensurate with the length of the zig-zag channels. In Figures 8.5(a) and 8.5(b) we show the density of hexane atoms in the MFI structure. The pictures can be considered an average over millions of snapshots. Hexane fits very snugly, and packs nicely in the zig-zag channels without sticking out into the intersections. Only the hexane molecules that are in the linear channels can stick out into the intersection.

By fitting the isotherms to a model and by examining simulation snapshots of the system a lot of information can be obtained [24]. Branched alkanes in MFI can be described by the dual-site Langmuir model [64], which signals the absence of significant inter-molecular interactions. In Figure 8.5(c) we show the adsorption isotherms of linear alkanes [65] and their dual-site LF fits (Table 8.2). The model describes the isotherms well. Linear alkanes smaller than hexane have a lot of rotational freedom (*i.e.* several molecules can fit at the channels and intersections) and there is much heterogeneity. For small molecules the intersections are comparatively unfavorable owing to a high potential energy and low entropy [66]. Adsorption in the straight or zig-zag channels have very similar potential energies, but the zig-zag channel is slightly more favored due to its higher entropy [66, 67]. Hexane is the most commensurate with the zig-zag channel and is the onset of the behavior for longer alkanes, all of which have large inflections. They are no longer 'hidden' inside the zig-zag channels, and after 4 molecules per unit cell have to interact with each other. The magnitude of the inflection increases for lower temperatures (which signals an energetic origin),

In hindsight, almost all isotherms in nanoporous materials have inflections. The underlying cause of inflections is an energetic and entropic difference between sites in the structure. If the sites differ greatly in the energetics, then first the lowest energy site is filled up before the next site is (example: branched alkanes in MFI), and this second filling requires significantly more pressure. For smaller energy differences, the adsorption occurs concurrently, but is mostly in favor of the lowest energy site. The magnitude of an inflection is so strongly related and so sensitive to



Figure 8.5: Commensurate freezing of hexane and heptane in MFI: (a) front-view of the density of hexane atoms in MFI, (b) top-view of the density of hexane atoms in MFI, (c) single component isotherms of linear alkanes in MFI at 303 K. The solid lines are dual Langmuir-Freundlich fits through the isotherm data. For hexane, a dashed line shows the fit of a single Langmuir-Freundlich fit (there is a small difference at 7.5 molecules per unit cell). The simulation were run long enough to make sure the error bar was smaller than the symbol size [65].

	site A			site B			
	$q_{i,A,\text{sat}}$			$q_{i,B,\text{sat}}$			
	[molec. uc^{-1}]	$b_{i,A} \left[\mathrm{Pa}^{-\nu_{i,A}} \right]$	$\nu_{i,A}$ [-]	[molec. uc^{-1}]	$b_{i,B} \left[\mathrm{Pa}^{-\nu_{i,B}} \right]$	$\nu_{i,B}$ [-]	
nC4	7.83	$2.08 imes 10^{-3}$	1.34	2.35	$2.20 imes 10^{-2}$	0.42	
nC5	7.56	1.01×10^{-1}	1.30	1.28	1.06×10^{-1}	0.27	
nC6	7.57	1.34×10^0	0.86	0.43	9.04×10^{-4}	1.42	
nC7	4.02	$1.55 imes 10^2$	1.15	2.97	8.20×10^{-3}	1.38	
nC8	3.97	4.73×10^3	1.16	2.02	$5.50 imes 10^{-3}$	0.64	
nC9	4.00	5.92×10^4	1.10	1.00	3.25×10^{-2}	0.96	

Table 8.2: Dual-site Langmuir-Freundlich parameters for pure component linear alkanes at 303 K in MFI.

the energy difference between the sites that very accurate force field parameters can be obtained by fitting molecular models to adsorption isotherms with inflections [68]. Also large pore MOFs show inflections, even for small molecules. Walton *et al.* showed that the pressure of the pore filling shifts toward the bulk condensation pressure with increasing pore size (IRMOFs-1, -10, -16) [23]. This means that the original fluid behavior is largely retained for small adsorbates in large pore MOFs, and inflections of this type are due to effects already present in the fluid-phase.

8.4 Enthalpic separation mechanisms

Most studies aim to improve the separation (and storage) efficiency of materials focusing on tuning the enthalpy of adsorption, because it is much harder to elucidate the entropy contribution as a function of topology. The entropy effects can (in general) up to date only be studied by doing explicit simulations, and is one of the reasons for performing 'screening' studies in which a large dataset of structures is examined for adsorption performance. The tuning of the heat of adsorption involves changing the affinity of an adsorbate with an adsorption site, which is easier to reason about and think in terms of design rules. For storage the affinity should be relatively high, but not too high or else the adsorbate component will be very hard to desorb. For mixture separations, there should be (in addition to lying in a limited range of enthalpies of adsorption) also be a large difference in affinity between the components. Before turning to the entropic effects, which is the main focus, we briefly review some examples of how affinities of adsorbates with the framework might be adjusted. We will only discuss a few physisorption examples (and not chemisorption).

The larger polarizability and quadrupole moment of CO_2 over N_2 , H_2 , COand CH_4 , allows for its separation by selective binding of CO_2 with either the unsaturated metal atoms (M) of Cu-BTC[69, 70], Cu-TDPAT[71], M-MOF-74[72-77], the extra-framework cations of NaX zeolite [78] and rho-ZMOF[79] (a charge framework) or with the functional groups (-NH₂, -OH, CH₃, Cl, F, Br, CN) in the MOFs linkers [80–82]. D'Alessandro et al. and Zhang and co-workers have given excellent reviews on CO_2 capture and separations [83, 84]. Differences in the quadrupole moments of N_2 and O_2 favor N_2 adsorption in both LTA-4A and LTA-5A [85] and also in $C_3(BTC)_2$, Fe(DOBDC)[86] and Cu-BTC[87]. Differences in their magnetic susceptibilities are believed to be responsible for the higher affinity of O_2 over N_2 in MOF-177[88]. Hydrogen bonds are responsible for the selective adsorption of $CHCl_3$, MeOH and H_2O in Zn_2 (bptc), but not hexane or pentane [89]. More effective van der Waals interaction between C_2H_2 in M(HCO)₂ (M=Mg,Mn) could be responsible for the separation of C_2H_2 from CO_2 , CH_4 , N_2 , O_2 and H_2 [90]. π - Interactions between the metals and the double bonds of alkenes are responsible for the separation of alkane/alkenes mixtures. Wang et al. [69] showed separation of ethylene over ethane in Cu-BTC, which is a consequence of the interactions between the π -electrons in ethylene double bond and the positive charge of the Cu(II) sites in the framework. Yoon et al. [91] and Lamia et al. [92] showed separation of propylene over propane in Cu-BTC and Hartmann et al. [93] showed separation of isobutene and isobutane in Cu-BTC.

MOFs differ from zeolites in that they can possess unsaturated (also called 'open') metal-sites. These sites can be very strong and selective, and have opened up a promising future for MOFs as catalysts. Zeolites on the other hand, can possess strong electric field gradients when cations are incorporated. Zeolites that are used in industry usually contain cations, *e.g.* Na-X, Ba-X, Na-Y, and LTA-4A (sodium ions) and LTA-5A (sodium and calcium ions). Introducing cations in MOFs can lead to increased affinity for certain adsorbates. For example, several studies used lithium-doping as a method to increase the affinity of hydrogen with the MOF [94–96], to provide the desired binding enthalpies in the range of 20-30 kJ/mol for hydrogen. Mulfort and Hupp [95] reasoned that framework reduction might increase affinity by: (a) increasing the polarizability of organic struts, thereby strengthening adsorbate/ framework van der Waals interactions,



Figure 8.6: Elucidating enthalpy vs. entropy: (a) Enthalpy of adsorption and average energy in MFI at 433 K for hexane and 2,3-dimethylbutane, (b) Average energies (total, adsorbate-host, and adsorbate-adsorbate energy [intra-molecular energy not shown]).

(b) introducing charge-compensating cations capable of binding gas molecules via charge/ quadrupole or more specific interactions, and (c) coulombically displacing interwoven frameworks, thereby enhancing accessible surface area.

8.5 Entropic separation mechanisms

8.5.1 Entropy

In a mixture, one component can drive another out at high pressures. Differences in adsorption loading of a mixture can be caused by energetic difference in the affinity of the components and by entropic effects. There are several tests to get to the root-cause of the expulsion effect:

• Examine the heat of adsorption and compare to the average energy (as a function of loading).

Each point of the isotherm is equilibrium and hence $\Delta H = T\Delta S$. At infinite dilution, the enthalpy is directly related to the difference in internal energy (see Eq. 8.2). So when one plots ΔH as a function of loading (at constant temperature) any sudden changes signals a sudden change in entropy. And when compared to $\langle U_{hg} \rangle - \langle U_h \rangle - \langle U_g \rangle - RT$ the effect of enthalpy can be examined. By comparing the difference in behavior one can elucidate whether the effect is enthalpic or entropic. For example, in Figure 8.6a we plot the enthalpy of adsorption as a function of loading for hexane and 2,3-dimethylbutane in MFI. For hexane, energetics and entropy goes hand-in-hand: the hexane molecules at loadings higher than 4 molecules per unit cell have significant favorable inter-molecular interactions which confines the molecules more and more. The dibranched molecule adsorbs in the intersec-



Figure 8.7: Elucidating enthalpy vs. entropy: component loading of an equimolar C2,C4,C6-mixture in TON-type zeolite at (an approximately) fixed total loading of 0.9 mol kg⁻¹ (dashed line) as a function of temperature.

tions of MFI first (see Figure 8.1b for the structure of MFI), and as soon as these are filled (4 molecules per unit cell), the dibranched molecules are pushed into the linear and zig-zag channels, thereby creating an additional adsorption lattice that was not energetically favorable before. Doubling of the amount of available sites causes a sudden jump in the entropy. The creation takes a large additional driving force (as the channel sites are energetically unfavorable for the branched isomers) leading to large inflections in the isotherms. We will discuss this further in the section 'configurational entropy'. Note the large scatter in ΔH at high loading. The fluctuation method relies on the efficiency of insertion and deletions of the particle during the simulation, and therefore generally fails close to saturation loadings.

- Change the interaction model of the atoms to a hard-sphere model [97]. If the attractive part of the Lennard-Jones potential is removed from the framework-adsorbate and adsorbate-adsorbate interactions and the repulsion term is extremely strong then the atoms are treated as impenetrable spheres that cannot overlap in space. Such a 'hard sphere' model has no energy scale and the only driving force is entropy. If in a mixture, one of the components is driven out at high pressures, then this *must* be because of entropy.
- Investigate the effect as a function of temperature. The lower the temperature, the more energetics dominates. Vice versa, entropy becomes increasingly important at high temperatures. In Figure 8.7 we show the component loading in a C2,C4,C6 equimolar mixture in TONtype zeolite at constant total loading. As can be observed, with an increase in temperature and hence $T\Delta S$, the smallest component will win (this will be further discussed in 'size entropy' and 'length entropy'.)

Molecules may be separated by selective adsorption on the basis of differences

in their molecular shape [98]. Krishna *et al.* reviewed entropy effects affecting the adsorption of mixtures of alkanes [99] and packing effects in microporous materials [100]. Smit and Maesen reviewed adsorption and shape selectivity in zeolites [101, 102].

For alkanes three entropy effects were discovered: (i) size entropy [103], (ii) length entropy [103], and (iii) configurational entropy [64, 97, 104]. The prominent geometric property that characterizes linear alkanes is the chain-length. Branched alkanes, compared to its linear isomer, exhibit a decreased length but also an increased width. Recently two new entropic effects were found for adsorption of a mixture of aromatics. The typical characteristic of aromatics is their relatively small 'height' compared to their width and length (*i.e.* the aromatic ring is *flat*). We will first discuss the closely related 'size entropy' and 'length entropy' effects. Next, we will discuss 'configurational entropy', and afterwards we will discuss two more recently discovered entropic mechanisms: 'commensurate stacking' and 'face-to-face stacking' (*i.e.* 'pringling').

8.5.2 Size entropy

Size entropy favors smaller molecules over larger molecules [103, 105]. At low loadings, the larger molecules adsorb the strongest (highest adsorption strength and Henry coefficients) but at high loadings, because the smaller molecules can fill the vacant sites more easily, their saturation loading is usually significantly higher than for longer molecules, in terms of molecules per unit cell (uc). The entropy gain is so strong that replacing one C6 by two C2 is favorable, even though the number of carbon atoms becomes less (so it is misleading to think of entropy in terms of *e.g.* the total amount of carbon atoms). The higher saturation capacity of the smaller molecules increases the entropy of the system (and reduces the Gibbs free energy) favoring the adsorption of smaller molecules over larger molecules at saturation conditions. This has been observed for alkane mixtures that differ in chain-length (and hence in molecular volume) in MFI at saturation conditions [106–108]. In all cases, the more bulky component adsorbs the strongest at low loading but is eventually overtaken by the smallest one.

Table 8.3: Molecular properties of hexane isomers: surface area (vdW), volume (vdW), and shadow lengths [109], calculated using Materials Studio [110] by projecting the molecular surface on three mutually perpendicular planes. The molecules are first rotated to align the principal moments of inertia with the X, Y and Z axes.

adsorbate	surface area $[{\rm \AA}^2]$	volume $[Å^3]$	L_x [Å]	\mathcal{L}_y [Å]	L_z [Å]
23DMB	116.35	86.81	6.71	6.21	4.04
22DMB	111.71	84.16	7.11	5.71	5.44
3MP	114.83	86.10	7.83	6.00	3.43
2MP	116.14	85.4	8.24	5.87	3.98
nC6	116.28	85.26	9.85	4.42	3.64



Figure 8.8: Size entropy in TON: (a) Mixture components isotherms for an equimolar mixture of C2/C4/C6 in TON zeolite at 300 K, (b) Snapshots of a 3-components equimolar mixture of C2/C4/C6 linear alkanes at 300 K in TON.

In Figure 8.8 we show this behavior for an equimolar C2/C4/C6 mixture of linear alkanes in TON-type zeolite. The TON-type zeolite is a one-dimensional channel zeolite consisting of apertures of 8-rings of about 5.7 Å in diameter. At low loadings, C6 has the strongest affinity (heat of adsorption at infinite dilution and 300 K are C2=-50 kJ/mol, C4=-77 kJ/mol, C6=-100 kJ/mol) and highest Henry coefficient because it has more carbon atoms. However, as the fugacity increases, C6 molecules are replaced by C4 molecules and afterwards by C2 molecules. This is because at saturation conditions the dimensions of TON channels restrict the adsorption of C6 to two molecules per unit cell, of C4 to five molecules per unit cell and of C2 to ten molecules per unit cell (as shown in Figure 8.8b) which increases the overall entropy of the system. The size entropy effect counters the energetic effect of the larger number of carbon-atoms which favors the adsorption of the larger molecule and the adsorption of C6 in TON is eventually overtaken at higher fugacities by the smallest component C2.

In Figure 8.7 the loading of C2, C4 and C6 at a total mixture loading of 1.5 molecules per unit cell as a function of temperature is presented. We can see that at low temperatures TON is C6 selective, but with increasing temperature the system becomes more C2 selective. This means that C2 is entropically favored over C4 and C6 and (C4 over C6). If the temperature increases, the entropic effects become dominant over the enthalpic effects.

The size entropy separation mechanism requires a difference in the molecular volume of the components. For example, when we examine the same equimolar C2/C4/C6 mixture of linear alkanes in FAU-type zeolite (which has a large, roughly spherical cavity) we observe the same behavior: the smallest C2 molecule wins at high pressures. It does not depend on the topology of the framework but on the differences in saturation loading. In Table 8.3 we list geometric properties of hexane isomers; and in Figure 8.9 we show the pure component adsorption of hexane isomers in FAU-type zeolite. As can be seen, because the hexane isomers have similar molecular surface areas and volumes (with the exception of



Figure 8.9: Single components isotherms of C6 isomers at 300 K in FAU.

2,2-dimethylbutane), size entropy is of no use here. For this, we need to turn to 'length entropy' which makes use of differences in the length-direction of the isomers(' L_x ' in Table 8.3).

8.5.3 Length entropy

Although 'size entropy' is not able to separate a mixture of hexane isomers in a large pore structure like *e.g.* FAU (hexane isomers have more or lees the same volume, see Table 8.3), it is possible to modify the *effective* size of a molecule. For example, by lining up the hexane isomers in one-dimensional channels, the dominant effective size that comes into play is its length (Table 8.3 shows that length L_x of the hexane isomers are significantly different). The length entropy concept is schematically depicted in Figure 8.10. Basically, in one-dimensional channels *size* is best described in terms of *length*. Length entropy has been highlighted by Talbot [103] and the term is derived from the decreasing linear dimension of the

adsorbate	L [Å]	L [Å]	L [Å]	infinite dilution properties in kJ/mol		
	0 Pa	10^4 Pa	10^8 Pa	ΔG_0	ΔH_0	$-T\Delta S_0$
23DMB	6.54	5.35	4.67	-33.8	-49.3	15.5
22DMB	6.63	6.33	6.29	-31.0	-46.3	15.3
3MP	7.59	6.32	4.74	-30.9	-46.9	16.0
2MP	8.12	7.39	6.33	-30.5	-47.2	16.6
nC6	9.28	8.62	6.85	-28.9	-44.8	16.0

Table 8.4: Molecular properties of hexane isomers in AFI at 300 K: molecular projected lengths along the channel axis at different fugacities, enthalpy of adsorption at infinite dilution. The lengths are the end-to-end distance taken along the channel-axis with 3.76 Å added for vdW radius of CH_3 .



Figure 8.10: Length entropy of C6 isomers in one-dimensional channels. The projected lengths size are nC6>2MP>3MP>22DMB>23DMB. In a mixture it is entropically more favorable to adsorb more molecules with a smaller effective size. In one-dimensional channels (when all the isomers are able to fit in), the isomer with the smallest effective length will be preferentially adsorbed at saturation conditions. Note that 3MP has two configurations that are very close in energy (less than 1 kJ/mol difference in the gas phase in favor of the isomer in brackets), but that the more compact isomer is favored in adsorption due to more favorable vdW interactions.

molecule [111].

We use AFI as an example of a length-entropy system. Following Schenk *et al.* [57], we first measure the effective length of hexane isomers. The results are provided in Table 8.4 and at infinite dilution these lengths agree very well with the molecular shadow length given in Table 8.3. These differences in channel-occupation translate immediately to different saturation loadings, with the most compact molecule having the highest saturation loading. The pure component isotherms of hexane isomers in AFI are shown in Figure 8.11. If a structure has channels large enough to accommodate di-branched isomers while still inducing a parallel adsorption arrangement of the adsorbates, then the sorption hierarchy of that structure will be di-branched>mono-branched>linear. This is simply because the linear isomers will occupy the largest segment of the channel, as compared to the other isomers, while the di-branched isomers (the most compact ones) can arrange a larger number of molecules in the same given channel segment [99, 112, 113].

Note that the concept of length entropy is limited to small pores and that the effective length depends on pressure. By compressing the molecules more and more, for example in AFI at 10^8 Pa (see Table 8.4), the adsorbates reoriented and also can change their internal configuration [57]. If the isotherms in Figure 8.11 would be extended to higher pressure, then *e.g.* 3-methylpentane would win over 22DMB. Jiang and Sandler studied the length and configurational effects in carbon nanotubes as a function of channel size [114]. In the smallest channel, only the linear alkane can adsorb, excluding all branched molecules. In slightly larger channels the adsorption order was neoC5 > iC5 > nC5 due to length entropy. But for even larger channels the order is nC5 $\geq i$ C5 > neoC5.

Length entropy occurs when there is a difference in the saturation loading arising from the difference in the effective length of the molecules in the structure. It relies on molecules being restricted to adsorb only in certain configuration, and therefore a one-dimensional channel confinement is a requirement. Some typical



Figure 8.11: Single components isotherms of C6 isomers at 300 K in AFI.

examples of one-dimensional nanoporous materials that can accommodate linear and branched alkanes are AFI, FER, MAZ, MOR, and LTL. Schenk et al. computed thermodynamic properties (ΔG , ΔH , and ΔS) for (branched) alkanes in many one-dimensional channel systems and showed that length entropy drives the isomerization reaction toward the effective most compact isomer [56]. These entropy (stacking) effects only occur at high loadings, in which adsorbate-adsorbate interactions are important. These authors provided a thermodynamic explanation for the high branched-paraffin yield in n-C16 hydroconversion. Adsorption entropy not only affects the activity, but also the selectivity of many zeolite-catalyzed conversions. Shape selectivity states that molecules will not (trans-)form if they are too bulky to fit inside a channel of a zeolite. Inverse shape selectivity was proposed by Santilli et al. [115] to explain the high yield of dibranched alkanes in AFI-type of zeolites, and states that those molecules form that have an optimal fit within the channels. Schenk et al. demonstrated that the molecular basis of inverse shape selectivity is related to entropic effects inside the zeolite pores under conditions where the zeolites are (almost) fully saturated [57].

8.5.4 Configurational entropy

Knowledge on branched alkanes in silicalite was limited in the 90's, although a few experimental studies were published [116–119]. The peculiar isotherms shapes of especially branched alkanes in MFI were highlighted by Vlugt *et al.* [104] using simulations. This is mainly because in the range of experimentally accessible pressures the longer dibranched alkanes do not exceed the 4 molecules per unit cells. The simulations could cover a range up to very high pressures and unearthed the generic shape of the isotherms. These authors provided a molecular mechanism (using snapshots): the dibranched molecules sit in the intersections of MFI, and



Figure 8.12: Configurational entropy of hexane isomers in MFI at 300K: (a) pure component isotherms (b) components loadings in an 5-component equimolar mixture as a function of loading.

it requires significant additional pressure to push them into the zig-zag and linear channels. It was soon realized that this entropy effect could be exploited to separate linear from mono-branched alkanes in the C5-C7 carbon range [64], and more generally to separate linear, mono-branched and di-branched molecules [97]. In a mixture, the branched molecules are 'squeezed out' from the silicalite and replaced by linear alkanes. This 'squeezing out' effect was found to be entropic in nature; the linear alkanes have a higher packing efficiency. This configurational effects was later studied in more detail [112, 120–122] and also experimentally verified.

The MFI zeolite is a 3D channel system with two types of channels: (i) linear channels and (ii) zig-zag channels, and (iii) intersections (see Figure 8.1b). The zig-zag channel is slightly wider than the linear channel; the zeolite atlas list the maximum diameter of a sphere that can diffuse through the zig-zag channel as 4.70 Å, and the diameter of the linear channel as 4.46 Å, respectively [123]. The linear, mono-branched, and di-branched molecules have very different interactions with each of the three types of adsorption sites. The channels of MFI are 10-rings, but can expand somewhat upon adsorption allowing more bulky molecules like di-branched alkanes and even aromatics to adsorb. However, a linear alkane is at the channel-site energetically and entropically favored over a mono-branched molecules and even more strongly favored over a di-branched molecule. Vlugt *et al.* confirmed the entropic origin by performing simulations using a hard-sphere model [97]. Figure 8.6a shows that the replacement of branched molecules by linear molecules is mostly due to entropy, but also (albeit much less) due to the energetics.

In Figure 8.12 we show the pure-component and 5-component equimolar mixture isotherm for hexane isomers in MFI. The inflections at 4 molecules per unit cell in the pure component isotherms are related to the amount of intersections (4 per unit cell). Below the inflection the adsorption sites for branched molecules are only the intersections. It takes significant pressure to 'push' them into the



Figure 8.13: Relation between enthalpy, configurational entropy and size entropy: 13component equimolar mixture of C5-C7 isomers at 433K in MFI. In the enthalpic regime the molecules do not strongly interact. In the configurational entropy regime the linear molecules start to replace the mono- and di-branched and the mono-branched start to replace the dibranched alkanes. Inevitably, size-entropy prevails at very high pressures.

linear and zig-zag channels. In a mixture, competition between the isomers drives first the di-branched molecules out with respect to the linear and mono-branched molecules. The behavior of the mono-branched molecules is right in between the linear and di-branched.

Even a mixture of C5/C6/C7 that differs in chain-length will at medium to high pressures be ordered according to degree of branching [99]. In Figure 8.13 we show a 13-component equimolar mixture of C5-C7 isomers. The molecule now differ in degree of branching *and* size, leading to three regimes:

- 1. The enthalpic regime where molecules hardly interact and the hierarchy is determined by the affinity of the molecules with the framework,
- 2. The configurational entropy regime where linear molecules replaces monoand di-branched alkanes, and mono-branched alkanes replace dibranched alkanes (the hierarchy is determined by the degrees of branching),
- 3. The size entropy regime where the molecules with the smallest size wins (the hierarchy is determined by the size of the molecules).

Note that the cross-over points are hard to determine because from the figure it is not immediately clear which species replaces another one. However, the nC5 has an inflection which is clearly caused by configurational entropy, and the start of the influence of size entropy is around the point where nC7 goes down (as this can not be caused by configurational entropy which favors linear molecules over branched species; Instead this is because C5 is smaller than C7). In the limit of high pressure, size entropy will dominate. Also note, that because of the interplay between the three different effects, the loading of a molecule in the mixture can go up, then down, and then up again.

Configurational entropy is observed in 3D structures of channels with intersections. Figure 8.6a shows that for dibranched alkanes the forced relocation from the intersection site to the channel site results in an unfavorable entropy change. The linear hexane molecule shows the opposite, and its relocation results in a favorable entropy contribution. However, configurational entropy is generic in the sense that any structures with multiple sites that strongly differ in energetics and local topology/structure (*i.e.* the volume accessible to the adsorbate) could potentially be exploited for separations.

8.5.5 Commensurate Stacking

Ortho-xylenes in MIL-47 have a very efficient stacking arrangement [124–126]. They form two layers of molecules that are sandwiched between two walls. The arrangement was later coined 'commensurate stacking' by Krishna and van Baten [127]. They also noted a similar 'bookshelf' structure is afforded by Co(BDP), and predicted that this MOF could therefore have the potential for separation of C8 hydrocarbon mixtures. The Co(BDP) channel dimension of about 10 Å is close to the length of *para*-xylene, but larger than the length of *ortho*- and *meta*-xylene. *Para*-xylenes could therefore potentially stand 'upright', like a book in a bookshelf, adsorbed at the wall and its methyl groups favorably interacting with both the 'floor' and the 'ceiling'.

Figure 8.14a shows the concept of stacking of *ortho-* and *para-*xylene in a manner commensurate with the framework. A structure with 8.5 Å channels is commensurate with *ortho-*xylene. That structure would be *ortho-*xylene selective because *para-*xylene cannot be stacked "upright". It would have to align obliquely, thereby increasing its effective size and hence have a lower saturation loading. For *para-*selective structures, we thus need a channel dimension of about 10 ÅThen, *para-*xylene is able to make use of all available pore-volume with both methyl-groups strongly interacting with the framework.

Torres-Knoop *et al.* realized the potential for commensurate stacking but formulated stronger geometric requirements [128]. Firstly, if nothing is anchoring the molecules at the wall, then the obtained configurations will be too disordered and not exhibit the desired 'array of upright molecules'. Therefore a periodic anchoring along the channel direction commensurate with the 'width' of the xylene would be required. This anchoring should be just enough to hold the molecules in place, but not so strong to impede diffusion. Secondly, a cuboid channel allows xylene to adsorb at opposite walls, but in this arrangement the 'ceiling' and 'floor' are blocked at that channel position (only the rotated orientation can fit, but this means disorder and a larger channel-length occupation of the xylene). Since the empty space between the molecules would be wasted (and leads to too much disorder) it would be better to have a rectangular channel with the adsorbates



Figure 8.14: Schematic of "commensurate stacking" of xylenes in rectangular channels: (a) the molecule has to be of the right size, (b) an ideal *para*-xylene structure would form a double layer where the adsorbate is commensurate with the framework in all directions. The yellow arrows denote the characteristic length of the molecules, which have to be commensurate with the channel dimensions.

forming layers. An idealized stacking for *para*-xylene would schematically look like Figure 8.14b. For molecules with different dimensions (*meta-*, *ortho-*xylene, benzene and ethylbenzene) four effects occur:

- 'Wider' molecules (*e.g. ortho-*, and *meta-xylene*) will be able to stack less molecules per channel length.
- 'Longer' molecules (*e.g.* ethylbenzene) have to align obliquely and therefore also stack less molecules per channel.
- 'Shorter' molecules (*e.g. ortho-*, and *meta-xylene*) will have a less optimal interactions with the pore structure.
- More bulky and non-flat molecules (*e.g.* ethylbenzene) are unable to form commensurate layers and will therefore have a lower saturation loading. That is, commensurate stacking also provides a mechanism to separate flat from not-flat molecules. MIL-47 is particularly effective at separating styrene from ethylbenzene [129].

8.5.6 Orientational entropy ("pringling")

Aromatics have a particular shape; their height is much smaller than their respective length and width. Torres-Knoop *et al.* exploited the flatness by selecting channels of such size that one of the isomers is able to change its orientation perpendicular to the channel [130]. The other isomers remain mostly parallel to the channel and occupy more channel space per channel length. The selected component that is able to re-orient at high loading has a significantly higher saturation



Figure 8.15: Orientational entropy ("pringling"): an ideal and tightly packed arrangement of molecules that have a shape commensurate with the channel: (a) cylindrical channels for "circular" molecules (*e.g.* benzene), (b) honeycomb channel for hexagonal molecules (*e.g.* benzene), (c) triangular channels for triangular molecules (*e.g.* cyclopropane, mesitylene, aluminumhydroxide). Perhaps (d) elliptical or (e) diamond-like channels will be found that allow *para*-xylene to pringle. In pringling one of the components is able to align perpendicular, while the other isomers are unable to stack this way and have a significant lower saturation loading. This concept leads to very efficient separations especially near pore saturation conditions. Not all shapes are optimal, for example in (f) cuboid or rectangular channels have no discrimination between the parallel and perpendicular orientation and no difference in saturation loading would occur.

capacity than its isomers. The packing of this component is very reminiscent of the configuration of chips in the "pringles" snack.

The concept is explained in Figure 8.15. As long as one can avoid that molecules can pack side-by-side in the channel (as would occur in rectangular channels) the effective channel occupancy can be significantly reduced by reorienting the adsorbate. To use pringling for separations, ideally only one of the isomers must be able to reorient. Aromatics pack particular well, because there rigidity prevents internal configuration changes (as happens with flexible alkanes in length entropy). Ellipsoid or diamond-shaped channels could potentially be *para*-xylene selective.

8.5.7 Discussion entropic separation mechanisms

It is in principle always possible to separate molecules that differ in size using "size entropy". The principle does not dependent on the difference in adsorption energetics, but on the crossover point where entropy wins. Since experimental equipment and industrial setups are limited in pressure, the size entropy effect might not always be usable in practice for molecules that differ too much in size (and hence the adsorption affinity which has to be overcome).

The other entropy effects can be applied to isomers, which have usually similar adsorption affinity with the framework, but also to mixtures that differ in molecular size. The ranges to which the size can vary depend on the particular system and on the affinity of the molecules with the framework. Commensurate stacking is the most sensitive entropic effect to the low loading part, since the saturation loadings of the isomers can be the same for some of the components. It is both an enthalpic and entropic mechanism.

In nanoporous materials, the entropy is related to the amount of molecules adsorbed. The larger the amount of molecules, the larger the entropy contribution. This means that, at high pressures, the adsorption selectivity will favour the mixture component with the highest saturation capacity. In this sense, all discussed entropy effects share one important feature: the *effective* smallest one wins at high pressure because it can obtain the highest saturation capacity. Therefore, all the above mentioned entropy effects are derived from size entropy. They differ on what size means and the details of how size reduction is achieved. In size entropy, the effective smallest literally refers to the smallest component in the mixture (lower number of atoms). For length entropy, the effective smallest is the mixture component which projected length (footprint) is the smallest. For orientational entropy, the effective smallest is the component that can reorient and upon reorientation has the smallest projected length. In commensurate stacking, the effective smallest is the component that inside the structure can be "packed" in the most compact way. In configurational entropy, the difference in saturation capacities arises from the difference in "accessibility" of the mixture components to the adsorption sites. The accessibility per site is determined by a "size entropy" effect per site. If the pressure is high enough, all entropy effects reduce to size entropy and the smallest molecules are preferentially adsorbed. In order to exploit entropy effects it is therefore important not only to known in which type of systems they occur, but also in which range of pressures/loadings.

8.6 Conclusions

This review highlights the potential of adopting separating strategies that rely on the differences in effective molecular size, rather than adsorption affinity. Size entropy is not readily extendable to large pore structures because the pressure needed to reach pore saturation can be high in *e.g.* MOFs. Pore saturation is needed for a smaller component to win entropically and overcome the enthalpic penalty due to a lower affinity with the framework. Length and configurational entropy are linked to small pore frameworks such as 8-, 10-, or 12-ring channel zeolites. Because the effect is due to confinement (by the framework) it is difficult to extend to more open pores. Commensurate stacking and the orientational entropy mechanism are also due to confinement, but by the framework and by other adsorbates. Hence, these mechanisms are able to operate at saturation conditions in systems with very open pores (large capacity) while still achieving high selectivities. All the mentioned entropy effects are derived from size entropy. In all off them, the effective smallest mixture component wins at saturation conditions. The difference between the effects is how this size reduction is achieved. *Large* pore volumes of MOFs for industrial separation applications are primarily suitable for separating *large* molecules.

Simulations Methodology

The adsorption computations of single and multi-components are usually performed in the grand-canonical ensemble [131, 132]. Reference [133] reviews stateof-art adsorption simulation methodologies. The presented adsorbent/adorbate systems can nowadays accurately be modeled in full atomistic detail using calibrated classical force fields. Common force field include TraPPE [134] and OPLS [135] for adsorbates like alkanes and xylenes, respectively; and TraPPE-Zeo [136] and DREIDING [137], UFF [138] for the modeling of zeolites and metal-organic frameworks, respectively. Using the dual-site Langmuir-Freundlich fits of the pure component isotherms, breakthrough calculations can be carried out by solving a set of partial differential equations for each of the species in the gas mixture [139]. The molar loadings of the species at any position along the packed bed and at any time are determined from Ideal Adsorbed Solution Theory calculations.

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CHAPTER 9

Summary

There are many industrially relevant separation processes which are either not feasible by conventional methods (such as distillation or crystallization), or energetically very expensive. Examples are the separation of xylene isomers (important in the petrochemical industry for the production of PET), and the purification of styrene (necessary for the production of polystyrene). In these cases, separation based on adsorption in porous materials is an important alternative, from both an economic and an environmental point of view.

In industrial applications, most separations based on adsorption in porous materials are cyclic. In each cycle the mixture is passed through a column filled with an adsorbent (porous) material –chosen such that one of the components is adsorbed at a larger extent than the others– until the adsorbent material is saturated. The adsorbed molecules are then recovered or removed by desorption. In each of these cycles, the composition of the adsorbed and transmitted mixture differs from the initial (inlet) mixture, as some of the components are preferentially retained over other components. Separation is achieved by passing the mixture (either the adsorbed or the transmitted) through the adsorbent material several times, until the desired composition (purity) is achieved.

The overall performance in adsorption based separation processes in porous materials depends on (1) the degree of preference of the material for a given mixture component, the *selectivity*, and (2) the amount that the material can adsorb, the *capacity*. A large selectivity requires less cycles to achieve the desired purity, while a large capacity leads to longer cycles, since more material can be handled per cycle. In both cases, the gain in the efficiency of the separation process is due to a reduction of the desorption steps needed for the separation. Desorption is the most energetically expensive step.

This work focuses on studying and developing more economic and environmentally friendly adsorption-based separation mechanisms in porous materials for industrial applications. To fulfill this, we need separation mechanisms where both the selectivity and capacity can be combined. Most of the published literature focuses on affinity-based selectivity. In this case, the selectivity relies on one of the mixture components having a stronger interaction with the adsorbent material as compared to the other mixture components. The problem with this is that it only works at low loadings or in materials with low capacity.

In order to illustrate this, imagine we want to separate an equimolar mixture (50% component A and 50% component B). Also, lets suppose the adsorbent material prefers component A because A interacts more strongly with specific sites in the material than component B. This is what we call an *enthalpic* selectivity (or affinity-based selectivity). Then the problem is that, once all the specific sites are filled, no further selectivity can be gained. If we increase the capacity, for example by making the pores larger, the additional volume will not contribute to the selectivity. In the saturation regime, the selectivity will be lost or significantly reduced. Most relevant industrial separations work precisely in this regime to make operate cost efficiently. In this regime, the separations are *entropic* in nature.

The process described above applies to adsorption in porous materials with pore diameters of a similar size to the mixture components (in general materials with pores in the range of nanometers, 1×10^{-9} m, known as nanoporous materials). Two very promising types nanoporous materials for separations based on adsorption, due to their uniquely high surface area and porosity, are zeolites and metal-organic frameworks (MOFs). In fact, one teaspoon of zeolite can provide a surface area as large as the surface of a football field. Zeolites can be found in nature. Most of them are very stable and cheap, and they are already abundantly used in industrial applications. Unfortunately, there is a finite number of zeolite topologies and most of them are limited in pore size (and therefore in the capacity). Most metal-organic frameworks are not as stable nor as cheap as zeolites. However, their tailor-ability provides a great variety of structures, most of which posses very large pore volumes compared to other porous material. This makes metal-organic frameworks very promising alternatives for separation processes.

In order to exploit the large pore volumes of MOFs, while still ensuring a high selectivity, new entropic separation methods that do not rely on framework affinity in the low loading regime have to be envisioned. Because entropy is not easy to understand or study, less research has been done in the field as compared to enthalpy (affinity) driven separations. Several entropy effects (mechanisms) have previously been published: configurational entropy, size entropy and length entropy. However, the work in this thesis shows that none of these effects can be extended to large capacity-structures (they originate form tight confinement). Here, we present two new entropic mechanisms: commensurate stacking and faceto-face stacking, that can be used in large pore structures and therefore offer an alternative path in the design of nanoporous materials for industrial separations.

To study separation mechanisms that operate at industrial (saturation) condi-

tions, one first needs a simulation method capable of handling these types of systems. In molecular simulations, adsorption is studied by computing the equilibrium amount of adsorbed molecules at a given pressure and temperature. In thermodynamics, the pressure, or rather the chemical potential, is what is called a conjugate variable to the number of molecules. Therefore by keeping the pressure fixed, the number of (adsorbed) molecules fluctuates. To find the equilibrium loading (amount of molecules adsorbed), molecules have to be inserted and deleted. The problem is that, if the system is at saturation, inserting and deleting (and therefore sampling the fluctuations in the number of adsorbed molecules) is easier said than done. The system tends to get stuck in states that are not necessarily in equilibrium (yet), and any information we get from these states could be incorrect. To overcome this problem, we developed a method that inserts and deletes molecules in a gradual and biased way. This is done by expanding the system with a molecule whose interaction strength with the surroundings is scaled, known as a fractional molecule, and biasing its insertion towards energetically favourable configurations. The fractional molecule has a higher probability of finding a vacant spot in these highly saturated type of systems. After the fractional molecule has been inserted, we slowly increase its interaction strength with the surroundings until it becomes a fully interacting molecule. This forces the environment (the surrounding molecules) to adjust to the presence of the fractional molecule and enhances its probability to be accepted as a 'normal' molecule. The method, called Configurational-Bias Continuous Fractional Component Monte Carlo, allows the number of molecules to fluctuate even close to saturation conditions. In chapter 2, this method is described in detail and its efficiency is demonstrated.

In chapter 3, we further explore this methodology and use it in systems with strong and directional interactions: liquid water at low temperatures and DMF (N,N-dimethylformamide), which is a common solvent used in MOFs synthesis. In chapter 4 we study the effect of having a fractional molecule on the system's properties. We focused on the heat of adsorption for two reasons (1) is a very sensitive quantity to the number of molecules in the system and their arrangement, and (2) because it is a relevant quantity in the design of separation processes. Here, we derive the corrections needed in order to use our method for the computation of the heat of adsorption and we show that it can compute the heat of adsorption even at saturation conditions, where other methodologies fail.

With all the necessary computational tools needed to study separations at saturation conditions, we turn our attention to industrially relevant applications. This turned out to be very successful. The goal of the thesis was to find separation methods that combine high selectivity with high pore capacity, and in the process we discovered two new entropic mechanisms capable of achieving this. In chapters 5 and 6 we present these entropic mechanisms: commensurate stacking and face-to-face stacking. We show that commensurate stacking can be used to separate para-xylene and that face-to-face stacking can be used to separate benzene and ortho-xylene from other aromatics. Both of these separations are industrially relevant, as ortho and para-xylene are important raw materials for the production of plastics, rubber and PET. In chapter 7 we study the performance of several

materials for the separation of styrene/ethylbenzene mixture at saturation conditions. We analyze the entropic mechanisms taking place in the different materials and conclude that having 'pure' entropic effects enhances the selectivity. Finally, in chapter 8 we review all the entropy mechanisms published so far (to the best of our knowledge) and we reexamined the other three known entropy mechanisms and their relation. We conclude that all entropic mechanisms are actually derived from size entropy. The difference between them is what size means and how size reduction is achieved. If the pressure is high enough, all mechanisms will reduce to size entropy.

Studying and understanding entropic mechanisms at saturation conditions is crucial to the design of next generation materials for industrial separations.

CHAPTER 10

Samenvatting

Er zijn velen scheidingsprocessen belangrijk in de industrie die of niet praktisch zijn met conventionele methoden (zoals destillatie of crystallisatie), of energetisch zeer ongunstig. Voorbeeld is de scheiding van xyleen isomeren (belangrijk in de petrochemische industrie voor de productie van PET), en de zuivering van styreen (nodig voor de productie van polystyreen). In deze gevallen is de scheiding gebaseerd op poreuze materialen een belangrijk alternatief, voor economisch zowel als milieu veilig perspectief.

In industrile toepassingen werken de meeste scheidingstechnieken die gebaseerd zijn op adsorptie in poreuze materialen op iteratieve wijze. Het mengsel wordt herhaaldelijk door een absorberende kolom gehaald, die zo gekozen is dat een van de componenten meer wordt geabsorbeerd dan andere componenten, totdat het materiaal in de kolom is verzadigd. De geabsorbeerde moleculen in de kolom worden dan gewonnen en verwijderd van de kolom door desorptie. Na elke cyclus wordt hierdoor de compositie van het mengsel veranderd, en kan elke component van elkaar gescheiden worden na vele cycli.

De kwaliteit van adsorptie gebaseerde scheidingstechnieken hangt af van (1) de mate van hoe specifiek het kolommateriaal een bepaalde component kan absorberen, de selectiviteit, en (2) de hoeveelheid dat het materiaal kan adsorberen, de capaciteit. Een grote selectiviteit zorgt voor minder cycli om de gewenste zuiverheid te halen, terwijl een grote capaciteit tot langere cycli leidt, aangezien het materiaal meer kan absorberen per cyclus. In allebei de gevallen wordt de efficintie van het scheidingsproces vergroot doordat de desorptiestap in de scheiding wordt verminderd. Desorptie is namelijk vaak energetisch gezien de meest dure stap.

Hier wordt onderzoek gedaan naar meer economisch and milieuvriendelijkere

adsorptie gebaseerde scheidingsmethoden in poreuze materialen voor industrile toepassingen. Om aan deze eisen te voldoen, hebben we scheidingstechnieken nodige waar selectiviteit alsmede de capaciteit kan worden gecombineerd. Veel van de gepubliceerde literatuur focust op affiniteit gebaseerde selectiviteit. Hier echter, wordt selectiviteit gebaseerd op het feit dat een component van het mengsel een sterkere interactie heeft met het kolommateriaal in vergeleken met de andere componenten. Het probleem hiermee is dat he alleen werkt met lage ladingen of in materialen met lage capaciteit.

Om dit te illusteren, stellen we dat een equimolaire mengsel (50% component A en 50% component B) willen zuiveren. Daarnaast stellen we ook dat het kolommateriaal component A beter absorbeert, omdat A een betere interactie heeft met het materiaal dan component B. Dit noemen we een enthalpische selectiviteit (of affiniteit gebaseerd selectiviteit). Het probleem dat ontstaat is dat wanneer het materiaal is verzadigd, geen verdere selectiviteit kan worden behaald. Als we de capaciteit verhogen, door bijvoorbeeld de porin in het materiaal te vergroten, zal het vergrote volume niet toevoegen aan de selectiviteit. In dit regime van volledige verzadiging zal selectiviteit worden verloren of significant verlaagd. Meeste relevante industrile scheidingen werken precies in dit regeime wat het proces heel duur maakt. In dit regime zijn de scheikunde voornamelijk entropisch van aard.

Dit proces is van toepassing in poreuze materialen met porin die dezelfde grootte hebben als de componenten in het mengsel (in het algemeen zijn de porin ongeveer een nanometer groot, ook wel bekend als nanoporeuze materialen). Twee veel belovende typen nanoporeuze materialen voor scheidingen gebaseerd op adsorptie, door de uniek hoge oppervlakte en porositeit, zijn zeolieten en metalorganic frameworks (MOF). Ter illustratie, een theelepel zeoliet heeft een oppervlakte ter grootte van een voetbalveld. Zeolieten kunnen ook in de natuur worden gevonden. Veel van deze zeolieten zijn stabiel en goedkoop, en zijn al in meerdere industrile toepassingen te vinden. Helaas is er een eindige hoeveelheid topologieen voor zeolieten en zijn de meeste beperkt in poriegrootte (en daarom in capaciteit). Aan de andere kant zijn de meeste MOFs niet zo stabiel of goedkoop als zeolieten, maar de flexibiliteit in ontwerp biedt een grote variteit aan structuren, waarvan de meeste grote porie volumes hebben in vergeleken met ander poreus materiaal. Dit maakt MOFs een zeer belovend alternatief voor bestaande materialen in industrie.

Om gebruik te maken van de grote porie groottes van MOFs, en tegelijkertijd de selectiviteit te behouden, zullen nieuwe entropie gebaseerde scheidingstechnieken nodig zijn die niet afhankelijk zijn van affiniteit in het lage ladingsregime. Omdat entropie niet altijd intutief te begrijpen is, is er niet veel onderzoek gedaan naar entropie gebaseerd scheidings technieken in vergeleken met affiniteit gebaseerde technieken. Verschillende entropie effecten zijn gepubliceerd: configurationele entropie, grootte entropie, en lengte entropie. Hoewel dit onderzoek laat zien dat geen van deze effecten kan worden gebruikt in grote capaciteit structuren. Hier presenten we twee nieuwe scheidingsmechanismen gebaseerd op entropie: commensurate stacking en face-to-face stacking, welke allebei gebruikt kan worden in grote poor structuren en daarom ook een alternatief pad bied in de design van nanoporeuze materialen voor industriele toepassingen.

Om scheidingstechnieken theoretisch te onderzoeken zijn methoden nodig om dit soort systemen te kunnen simuleren. In moleculaire simulatie wordt adsorptie bestudeerd door de evenwichtsconstante uit te rekenen van geadsorbeerde moleculen bij een gegeven druk en temperatuur. In thermodynamica wordt de druk, of eerder de chemisch potentiaal de geconjugeerde variabele van het aantal moleculen genoemd. Daarom fluctueert het aantal moleculen terwijl de druk geluk wordt gehouden. Om het evenwicht te vinden tussen geabsorbeerde en niet geabsorbeerde moleculen, moeten moleculen worden geinserteerd en verwijderd van het systeem. Het probleem is dat het toevoegen of verwijderen van moleculen makkelijker gezegd is dan gedaan wanneer het systeem verzadigd is. Het systeem heeft de neiging om in meta-stabiele toestanden terecht te komen die niet perse de evenwichtstoestand zijn en daarom is de informatie van deze toestanden niet toepasselijk. Om dit probleem op te lossen, hebben we simulatiemethoden ontwikkeld die moleculen in een meer geleidelijke manier inserteert en verwijderd. Dit gebeurt door het systeem te vergroten en de interactiesterkte van het molecuul te schalen, zogenaamde fractionele molecuul, en dit leidt tot meer energetische gunstige toestanden. De fractionele molecuul heeft een hogere kans om een lege plek te vinden in hoog verzadigde systemen. Nadat het fractionele molecuul is toegevoegd, wordt het molecuul weer langzaam geschaald naar de normalen grootte. De forceert de omgeving zich aan te passen aan het zojuist toegevoegde molecuul en dit verbetert de kans op het accepteren van het molecuul. Deze methode, Configurational bias continuous fractional component Monte Carlo, biedt kans om het aantal moleculen te veranderen ook in verzadigde systemen. In hoofdstuk 2 wordt de methode in detail beschreven en de efficintie bewezen.

In hoofdstuk 3 onderzoeken we verder de simulatiemethoden en gebruiken we het in systemen met sterke en directionele interacties: vloeibaar water bij lage temperaturen en DMF (N,N dimethylformamide), welke een gebruikelijke oplosmiddel is in MOF synthese. In hoofdstuk 4 wordt het effect van het fractionele molecuul op de systeem eigenschappen onderzocht. Wij focussen op de warmte van adsorptie om twee redenen (1) het is gevoelig voor de hoeveelheid en indeling moleculen, en (2) omdat het een belangrijke eigenschap is in het ontwerp van scheidingsprocessen. Hier leiden we de correcties af om onze methode te gebruiken in de berekening van de warmte van adsorptie en we laten zien dat het de warmte van adsorptie kan uit rekenen in verzadigde condities waar andere technieken falen.

Met alle nodige computationele technieken om de scheidingsprocessen te onderzoeken bij hoge verzadiging, kijken we naar industriele applicaties. Dit was zeer succesvol. Het doel van deze thesis was scheidingstechnieken te vinden die selectiviteit alsmede capaciteit combineren. We hebben twee entropie gebaseerde mechanismes gevonden om dit te bereiken. In hoofdstuk 5 en 6 laten we zien dat deze entropische mechanismes: commensurate stacking and face-to-face stacking. We laten zien dat commensurate stacking gebruikt kan worden in de scheiding van para-xyleen en dat face-to-face stacking gebruikt kan worden om benzeen en ortho-xyleen van andere aromaten te scheiden. Allebei de processen zijn belangrijk voor de industrie, omdat ortho en paraxyleen belangrijke grondstoffen zijn voor de productie van plastics, rubber en PET. In hoofdstuk 7 onderzoeken we de prestatie van verschilende materialen voor de scheiding van styreen/ethylbenzen mengsels bij hoge verzadiging. Wij analyseren de entropie gebaseerde mechanismen die verantwoordelijk zijn in verschillende materialen en concluderen dat puur entropische effecten de selectiviteit verhogen. In hoofdstuk 8 beschouwen we alle entropie gebaseerde mechanismen in de literatuur. We concluderen dat alle entropie gebaseerde mechanismes eigenlijk zijn gebaseerd op entropie van groottes. Het verschil tussen de mechanismes is wat grootte betekent. Als de druk hoog genoeg is, zijn alle mechanismen grootte entropie.

Onderzoeken en het begrijpen van entropische mechanismen bij hoge verzadiging zijn cruciaal in het ontwerp in de materialen van de toekomst voor de industrie.
Chapter 11

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Author's contribution:

With the exception of chapter 1, all chapters are based on first author publications. As a first author, A. T. K. handled the write-up and submitting of the manuscripts content and performed all of the simulations (with few exceptions: the LJ-system in chapter 2, the water adsorption isotherms in chapter 3 and the breakthrough simulations in chapter 5, 6 and 7). For the later papers she also designed the research ideas. With the exception of chapter 1, she is corresponding author on all published chapters. Chapters 1,2,5,6,7,and 8 have been accepted in peer-reviewed journals, while chapter 3 and 4 are in review.

chapter 12

Curriculum Vitae

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