Entropy driven separations in nanoporous materials
Torres Knoop, A.

Citation for published version (APA):
Torres Knoop, A. (2016). Entropy driven separations in nanoporous materials

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Introduction

The current global chemical industry constitutes a 2.6 trillion euros a year business 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 is based on the separation and purification of metals; and in the food 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 decaffeination.

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 (secondary units) that ultimately form a 3-dimensional structure. (b) MIL-47 metal-organic framework: the metals clusters (V_{III}) 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 terephthalate), 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 TO₄ 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-
MOF          Structure      Node        Linker

ZIF-8

HKUST-1

IRMOF-1

Mg-MOF-74

Fe-MIL-101

IRMOF-3

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).
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 m$^2$/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 prop-
erties 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 differ-
ences in the diffusion rate of the adsorbates within the adsorbent channels. In this
thesis, the focus lies on separations based on adsorption (thermodynamic equilib-
rium). The amount of adsorbed molecules $\theta$ (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. Adsorp-
tion 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 ad-
sorbents 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 adsorbent-
  adsorbate interactions. They occur when the amount of gas adsorbed in-
  creases without limit as its relative saturation approaches unity. In Type III
  the heat of adsorption is less than the heat of liquefaction. As adsorption oc-
curs, additional adsorption is facilitated because the adsorbate interactions
  with an adsorbed layer are greater than the interaction with the adsorbent
  surface [23].
• 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], Tenkin [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 introduced 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 ($\Delta n$) 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:

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

$$n_e = \frac{\Delta m}{M m_s} + \rho_g v_{st} \quad (2)$$

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 physisorption, 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.
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

\[
S_{i,j} = \frac{q_i / f_i}{q_j / f_j}
\]  

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

\[
\text{Capacity} = q_i
\]
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 or-
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 $\lambda$. Molecules are inserted and deleted in the system by performing a random walk in $\lambda$-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 $\lambda$-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,N-dimethylformamide. In chapter 4, it is shown that the CB/CFCMC method can be used to compute the enthalpy of adsorption (using the energy/particle fluc-
tuation 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 metal-organic 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: face-to-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
References


