Invited Contribution

Monte Carlo Simulation and Exact Statistical Mechanical Lattice Models as a Development Tool for Zeolite Multi-Component Adsorption Isotherm Derivation

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ABSTRACT: Developing a suitable separation and purification procedure for multi-component gas mixtures is a ubiquitous problem. Very little is known experimentally about multi-component adsorption isotherms, yet these are crucially important for designing separation processes. Multi-component adsorption isotherms over a wide range of composition, pressure and temperature are virtually unknown. Adsorption onto zeolites is widely used in adsorptive separation processes due to the unique characteristics of its structural pores which may be “engineered” to permit adsorption to take place on the basis of molecular shape and size. In this article, we discuss the methodological development of rapidly obtaining multi-component adsorption isotherms using the interplay between the essentially exact (in the statistical mechanical sense) lattice model and configurational bias Monte Carlo simulations. The latter technique has the known capability of being able to reproduce experimental isotherms reliably, but can be very time consuming and expensive. In contrast, the lattice model adsorption isotherms can be parameterized by comparing with those obtained by Monte Carlo simulation and thereafter used to cheaply and rapidly explore a very wide range of mixture concentrations and conditions. The interactions required in the lattice model are effective interaction-free energies. This approach has been applied to the adsorption isotherms of selective binary and ternary mixtures of small alkanes (methane, ethane) and carbon dioxide adsorbed in silicalite. The lattice model results are shown to have the potential, when suitably parameterized, to rapidly and cheaply reproduce the main features of the much more expensive Monte Carlo isotherms over a very wide range of mixture compositions, temperatures and pressures.

1. INTRODUCTION

Separation of short alkanes and carbon dioxide and other gases is of major importance for both environmental and economic reasons (Breck 1974; Ruthven 1984; Rees et al. 1991; Golden and Sircar 1994; Ruthven et al. 1994; Nicholson and Gubbins 1996; Fraissard and Conner 1997; Keller and Staudt 2004; Babarao et al. 2007; Dunne and Manos 2010; Krishna 2012). It is also vitally important, for example, to develop a viable adsorption method based separation technologies to reduce carbon dioxide emissions, which are regarded as the main culprit in global

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warming. The removal of carbon dioxide from natural gas and the recovery of alkanes in a sustainable and efficient way are other challenges to be addressed when developing such methods. These require knowledge of multi-component adsorption isotherms. Mixtures of simple gases can be separated by adsorption in zeolites due to the special characteristics of zeolite channels which may be designed to allow adsorption to occur selectively based on molecular size and shape. Amongst the different methods used for gas separations, adsorption processes involving the use of zeolites (Lin et al. 2012) have demonstrated an increasing importance because of their high thermal, mechanical and chemical stability. Recent exciting developments show the potential of using metal oxide frameworks for adsorptive separation processes (Getman et al. 2012), but detailed knowledge of adsorption isotherms in these materials is yet to become available.

This work focuses on zeolites and specifically silicalite (pure siliceous ZSM-5) (Olson et al. 1981), which is a highly porous material and has an intersecting two-dimensional porous network throughout its structure. ZSM-5 has two types of pores, both formed by 10-membered oxygen rings. The first set of pores is straight with an elliptical cross-section, while the second set intersects the straight pores at right angles, in a zigzag pattern and is circular in cross-section as shown in Figure 1. The straight channels of silicalite have pore size (Baerlocher et al. 2001) of 5.4 Å × 5.6 Å and the zigzag channels are 5.5 Å and the unit cell size is 20.07 Å × 19.92 Å × 13.42 Å.

![Figure 1. Pore structure of silicalite.](image)

Because of the difficulty in performing adsorption experiments, no adsorption isotherms have been published for methane/ethane/carbon dioxide ternary mixtures adsorbed onto zeolites over a wide range of gas phase composition. In this article, fast and efficient ways to generate adsorption isotherms of pure methane, ethane, carbon dioxide and their binary and ternary mixtures in silicalite are discussed using an interplay between Monte Carlo simulation (Siepmann and Frenkel 1992; Frenkel and Smit 1996; Catlow et al. 2004; Gallo et al. 2006; Dunne and Manos 2010) and statistical mechanical lattice models (McCoy and Wu 1973; Nicholson and Parsonage 1982; Huang 1987; Dunne et al. 2009). Once the Monte Carlo isotherms have been generated, the lattice model may be parameterized against them which allows for the entire state space to be rapidly explored. Previous efforts (Smit 1995; Du et al. 1998; Maris et al. 1998; Vlugt et al. 1998; Catlow et al. 2004; Cruz and Müller 2009; Keil 2010) have established that these types of simulations can reproduce the details of the
experimentally determined single-component adsorption characteristics in zeolites. Mixture isotherms can exhibit novel and surprising features and this does not appear to be widely recognized. For example, ethane/carbon dioxide mixtures display adsorption preference reversal at high coverage (Khettar et al. 2002). Orientation effects of molecules adsorbed in tubes similar to that observed by Müller (Müller 2008) are also possible here. The configurational bias grand canonical Monte Carlo simulation technique was used to compute adsorption isotherms for mixtures of methane, ethane and carbon dioxide at various temperatures ranging between 250 and 353 K, and over a wide range of compositions and pressures up to 200,000 kPa. For a wide range of interaction parameters, the lattice model gives unusual features in the shape of adsorption isotherms similar to those observed in Monte Carlo simulations. For the lattice model, the grand partition function for the mixture adsorbed in a zeolite channel is calculated exactly using a previously described matrix method (Dunne et al. 2003). Approximate treatments, such as mean-field theory, are well known as being incorrect in one-dimensional systems (Huang 1987) by erroneously predicting phase transitions which may show up as spurious steps in adsorption isotherms and, therefore to have confidence in our results, an accurate statistical mechanical treatment of the one-dimensional adsorbed phase is required. In the results presented below, Figures 2–9 show Monte Carlo simulation isotherms expressed as a ratio of number of moles adsorbed per unit mass of silicalite (mmol/g). However, the lattice model isotherms (Figures 10–17) are shown as fractional coverage. In pure component isotherms at high pressure, we assumed that the maximum loading in Monte Carlo simulation would correspond to a fractional coverage approaching 1 in the lattice model, at least for the molecules considered here.

The main achievement of this work is that it provides a design tool for the engineer scientist who wishes to quickly and cheaply explore the likely adsorption behaviour in a zeolite of a multi-component system under particular conditions.

There are many development possibilities for the future such as mixtures of molecules of widely different sizes and a range of microporous media.

2. MONTE CARLO SIMULATIONS OF MIXTURES IN SILICALITE

The Monte Carlo method for the preparation of mixture was described in a previous publication (Du et al. 1998). In this article, the united atom model was used with all of the mixtures being represented as spherical pseudo-atoms (Siepmann et al. 1997), which interact via Lennard-Jones potentials given by:

\[
U(r_{ij}) = \begin{cases} 
4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} & \text{if } r_{ij} < R_c \\
0 & \text{if } r_{ij} \geq R_c
\end{cases}
\]

where \( r_{ij} \) is the distance between united atoms i and j, \( \varepsilon_{ij} \) is the energy parameter (depth of the potential well), \( \sigma_{ij} \) is the size parameter (collision diameter) and \( R_c \) is the cut-off radius of the potential. In this work, the cut-off radius is 13.8 Å. The contribution of the atoms beyond the cut-off radius to the total energy is estimated using the usual tail corrections. The interaction parameters between different united atoms i and j are calculated using the Lorentz–Berthelot (Jorgensen et al. 1984) mixing rules, given by
To avoid the use of a prohibitively large amount of computer time, carbon dioxide is modelled as an effectively spherical molecule whose Lennard-Jones parameters for interactions inside the silicalite cage were determined by fitting (Frenkel and Smit 1996) the experimental adsorption isotherms of pure carbon dioxide to that produced by Monte Carlo simulation shown in Figure 2. The well-depths and collision diameters are given in Table 1.

\[ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad \text{and} \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (2) \]

Figure 2. Experimental (Exp) isotherms for adsorption of CO₂ in silicalite at various temperatures compared with those generated by Monte Carlo simulation (MCS) with the parameters given in Table 1 (Copyright Elsevier, Dunne et al. 2009).

| Lenard-Jones parameters | Well depth (k/K) | Collision diameter (Å) |
|-------------------------|-----------------|-----------------------|
| CO₂–CO₂                 | 125.3           | 3.04                  |
| CH₃–CH₃                 | 98.1            | 3.77                  |
| CH₄–CH₄                 | 148.0           | 3.73                  |
| CO₂–O (silicalite)      | 120.0           | 3.60                  |
| CH₃–O (silicalite)      | 80.0            | 3.60                  |
| CH₄–O (silicalite)      | 96.5            | 3.60                  |

2.1. Methane–Carbon Dioxide and Ethane–Carbon Dioxide Mixtures

The simulations were carried for various temperatures ranging from 250 to 353 K and over a wide range of pressures up to 200,000 kPa and at several concentrations.

Figures 3–6 show adsorption isotherms calculated by Monte Carlo simulation for methane–carbon dioxide and ethane–carbon dioxide mixtures in silicalite for the gas phase
Figure 3. Monte Carlo adsorption isotherms of the equimolar binary mixtures (50% each in the gas phase) of carbon dioxide–methane in silicalite at 334 K.

Figure 4. Monte Carlo adsorption isotherms of the binary mixtures of 10% carbon dioxide–90% methane in silicalite at 333 K.
Figure 5. Monte Carlo adsorption isotherms of the binary mixtures of 80% carbon dioxide–20% methane in silicalite at 300 K.

Figure 6. Monte Carlo adsorption isotherms of the equimolar binary mixtures (50% each in the gas phase) of carbon dioxide–ethane in silicalite at 313 K.
compositions and conditions given in the captions. In Figure 6, it can be seen that carbon dioxide displaces ethane at higher coverage (adsorption preference reversal) which has important implications for practical separation processes, while this does not occur with methane–carbon dioxide mixtures (Figures 3–5). At all temperatures, carbon dioxide adsorbed more strongly than methane as expected because of the stronger interaction between carbon dioxide and the zeolite surface.

2.2. Methane–Ethane Mixtures

The adsorption isotherms of methane–ethane were calculated for their equimolar binary mixtures (50% molar each in the gas phase) (Figure 7). As expected ethane is much more strongly adsorbed than methane due to its higher adsorption enthalpy, which is about 1.5 times greater than that of methane. As the pressure increases, the adsorbed amount of ethane reaches a plateau and starts to decline, while the adsorption of methane continues to increase. A similar observation has been reported by Du et al. (Du et al. 1998).

2.3. Monte Carlo Adsorption Isotherms of Ternary Mixtures, Methane–Ethane–Carbon Dioxide

We have also investigated the adsorption isotherms for ternary mixtures of methane–ethane–carbon dioxide. The study of these ternary components is of great interest especially for the natural gas industry. The simulations were conducted for equimolar mixtures of methane–ethane–carbon dioxide, 33.3% each in the gas phase (Figure 8) and a mixture of 85% methane–10% ethane–5% carbon dioxide (Figure 9).
Figure 8. Monte Carlo adsorption isotherms for ternary equimolar mixtures (33.3% each in the gas phase) of methane–ethane–carbon dioxide in silicalite at 298 K.

Figure 9. Monte Carlo adsorption isotherm for a ternary mixture of 85% methane–10% ethane–5% carbon dioxide at 298 K in silicalite.
At lower pressures, ethane is initially preferentially more adsorbed, while at higher pressures the other two components start to displace ethane. In the adsorption of the equimolar gas mixture, the increasing adsorption of carbon dioxide causes the adsorbed ethane amount to level off and start declining. At even higher pressures, the highest adsorbed component is carbon dioxide. Methane remains as the lowest adsorbed component for the entire pressure range employed in the experiment. Figure 9 illustrates an adsorption isotherm for a ternary mixture of 85% methane–10% ethane–5% carbon dioxide at 298 K. This composition is very close to a typical composition of raw natural gas which typically includes the following composition: CH₄ (70–90/95%), C₂H₆ (about 10%), CO₂ in the range of 0–8%. Despite the gas-phase ethane being only 10%, it is still the strongest adsorbed component at low pressures. However, methane displaces ethane first in the silicalite structure because of its high concentration in the gas phase, explaining its higher chemical potential. The pressure at which the adsorbed molar amount of methane surpasses that of ethane is around 20,000 kPa. At even higher pressures, around 200,000 kPa, the adsorbed methane amount is surpassed by the adsorbed carbon dioxide, while adsorption of ethane continues to decline after its maximum adsorption at around 1000 kPa.

3. ONE-DIMENSIONAL LATTICE MODEL OF SMALL ALKANE–CARBON DIOXIDE BINARY MIXTURES IN SILICALITE

The matrix method used in this work evaluates the grand canonical partition function for a mixture and allows for conformational transitions wherever appropriate. The vapour phase is modelled as an ideal gas mixture in equilibrium with the adsorbed phase with reference chemical potential $\mu_i^0$ for component “i” given by equation (3) (Hill 1960)

$$\mu_i^0 = -kT \ln \left( \frac{2\pi \hbar^2 kT}{\hbar^2} \right)^{3/2}$$

Here we extend our earlier treatments using matrix methods to embrace the adsorption of a mixture of these components in a zeolite pore. The model chosen is effectively that of one-dimensional chains of sites, which may be occupied by molecules in various states. This is not an exact representation of the zeolite structure, but is thought to mimic the silicalite lattice realistically. As in the Monte Carlo simulations, a carbon dioxide molecule is modelled as a rapidly rotating effectively spherical molecule and is assumed to occupy a single lattice site. A methane molecule can occupy a single lattice site, but the model allows for two possible conformations of an ethane molecule, lying down and standing up. We denote the potential energy of an adsorbed molecule in a defined orientation by $U_i$. Pairs of ethane molecules in the lying down configuration on neighbouring sites are assumed to interact with a strong repulsion which is equivalent to occupying two sites by each lying-down ethane molecule.

3.1. Exact Matrix Method for Mixture Grand Partition Function

Matrix methods for statistical mechanical treatment of one-dimensional lattice fluid problems have been discussed by us previously. The grand partition function – for the alkane–carbon dioxide mixture in the adsorbed phase on the zeolite lattice with N sites may be written as the sum of the products of N factors given by
where \( n \) is the number of possible species (including vacancies or holes) which can occupy a lattice site. Here \( n = 5 \) corresponding to holes, CO2, methane and ethane in two orientations.

As usually defined in this matrix method, the terms in equation (4) are as follows:

\[
A_{\mu\nu} = \left( \phi_\mu \phi_\nu \right)^{1/2} \cdot \phi_{\mu\nu}
\]  

(5)

The factors in \( A_{\mu\nu} \) are given by

\[
\phi_i = \exp\left( \frac{\mu_i - U_i}{kT} \right)
\]  

(6)

\[
\phi_{\mu\nu} = \exp\left( -\frac{J_{\mu\nu}}{k \cdot T} \right)
\]  

(7)

The parameter \( J_{\mu\nu} \) is the interaction energy between pairs of species \( \mu, \nu \) on the nearest neighbour sites at the separation of the lattice sites. \( \mu_i \) and \( U_i \) are the chemical potential and potential energy of species “i”. The chemical potential and energy of vacant site or “hole” are evidently zero. The separation distance of the adsorbed nearest neighbour pairs of molecules may differ from the optimal distance of separation for pairs of free molecules. By making the parameter \( J_{11} \) strongly repulsive, pairs of ethane molecules, both in the lying-down configuration, can be made to behave effectively as dimers occupying two lattice sites each.

Using the inner product rule for matrix multiplication of a pair of conformable matrices \( B \) and \( C \), the grand partition function given in equation (4) can be expressed as:

\[
\Xi = \sum_{\alpha=1}^{n} \left( A^{N} \right)_{\alpha\alpha} = \text{Trace} \left( A^{N} \right) = \sum_{i=1}^{N} \left( \lambda_{i} \right)^{N}
\]  

(8)

where \( \lambda_1, \lambda_2, \lambda_3, \lambda_4 \ldots \lambda_n \) are the eigenvalues of the matrix \( A \) given below:

\[
\begin{pmatrix}
A_{11} & A_{12} & \cdots & A_{1n} \\
A_{21} & A_{22} & \cdots & A_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
A_{n1} & \cdots & \cdots & A_{nn}
\end{pmatrix}
\]

For large values of \( N \), we then obtain

\[
\Xi = \left( \lambda_{\text{max}} \right)^{N}
\]  

(9)
where $\lambda_{\text{max}}$ is the largest eigenvalue of the matrix $A$. Therefore, we have an evaluation of the grand partition function for the mixture in the quasi-one dimensional zeolite pores. The mean density $\rho_a$ of the adsorbed species “a” is given by

$$\rho_a = kT \left( \frac{\partial}{\partial \mu_a} \ln (\lambda_{\text{max}}) \right)$$

(10)

and similarly for all other species.

Extraction of the largest eigenvalue and subsequent differentiations were performed straightforwardly using the Mathcad mathematical software package. Thus for a given gas-phase composition, adsorption isotherms for an exact one-dimensional model can be constructed.

The chemical potential of a component in an ideal gas mixture is given by equation (11) as follows:

$$\mu_i = \mu_i^0 + kT \ln X_i P$$

(11)

where $\mu_i^0$ is the standard chemical potential given by equation (3) described earlier. $P$ is the total pressure and $X_i$ is the mole-fraction of component $i$ in the gas phase.

Isotherms are constructed using the above equations for a given set of variables $X_a$, $X_b$, total pressure $P$ and temperature $T$. The shape of the isotherms shown in Figures 10–17 quite remarkably reproduce all of the essential features of the Monte Carlo isotherms (Figures 2–9). The parameters required to produce this effect are given below:

![Figure 10. Lattice model adsorption isotherms of carbon dioxide in silicalite at 353 K (compare with Figure 2). The parameters are given in the text.](image-url)
Figure 11. Lattice model adsorption isotherms of the binary mixtures of 50% carbon dioxide–50% methane in silicalite at 334 K (compare with Figure 3). The parameters are given in the text. The solid line represents methane and the dashed line represents carbon dioxide.

Figure 12. Lattice model adsorption isotherms of binary mixtures of 10% carbon dioxide–90% methane in silicalite at 333 K (compare with Figure 4). The parameters are given in the text. The solid line represents methane and the dashed line represents carbon dioxide.
Figure 13. Lattice model adsorption isotherms of binary mixtures of 80% carbon dioxide–20% methane in silicalite at 300 K (compare with Figure 5). The parameters are given in the text. The solid line represents methane and the dashed line represents carbon dioxide.

Figure 14. Lattice model adsorption isotherms of binary mixtures of 50% carbon dioxide–50% ethane in silicalite at 313 K (compare with Figure 6). The parameters are given in the text. The dotted line represents ethane and the dashed line represents carbon dioxide.
Figure 15. Lattice model adsorption isotherms of binary mixtures of 50% methane–50% ethane in silicalite at 308 K (compare with Figure 7). The parameters are given in the text. The solid line represents methane, dotted line represents ethane and the dashed line represents carbon dioxide.

Figure 16. Lattice model adsorption isotherms of ternary mixtures of 33.3% methane–33.3% ethane–33.3% CO₂ in silicalite at 298 K (compare with Figure 8). The parameters are given in the text. The solid line represents methane, dotted line represents ethane and the dashed line represents carbon dioxide.
The best fit we obtained for the lattice model $U_i$ parameters to enable the Monte Carlo isotherms to be reproduced is as follows (in units of $10^{-20}$ J):

$U_{CH_4} = -5.55$, $U_{C_2H_6,up} = -7.2$, $U_{C_2H_6,down} = 10.0$ and $U_{CO_2} = -6.84$. The $\{J_{ij}\}$ values are given in Table 2.

Table 2, except for $\{J_{ij}\}$ values, all the other parameters are zero. The set $\{J_{\mu\nu}\}$ must be interpreted as effective interaction-free energy parameters. These values are largely positive and it would appear that in order to simulate the Monte Carlo behaviour, repulsive entropic interactions (Israelachvili 2011) are required in the lattice model. The interpretation of the shape of the isotherms can be readily deduced from the lattice model parameters. For example, Figure 14 shows the lattice model adsorption isotherms of binary mixtures of 50% carbon dioxide–50% ethane in silicalite at 313 K (compare with Figure 6), where ethane is preferentially adsorbed at low coverage, but is displaced by carbon dioxide at high pressures. At low coverage the free energy of adsorption is such that ethane is preferred to carbon dioxide at low coverage. However,
at high pressures, interactions must be included leading to a crossover in the energetics whereby carbon dioxide is preferentially adsorbed. Similar arguments apply to the other isotherms as well. Future work should go beyond spherical carbon dioxide molecules and consider conformational transitions in these molecules too. In summary, we have shown how a combination of Monte Carlo simulations and lattice model calculations have the potential, when suitably parameterized, to enable multi-component mixture adsorption isotherms to be generated over a very wide range of mixture compositions, temperatures and pressures. In the future, such an approach may make some contribution to design tools for natural gas separation processes.

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