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Molecular Simulation of Gas Separation by Equilibrium-Based Adsorption Processes

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Abstract. A new molecular simulation method is proposed to solve the governing equations of a multicomponent, isothermal batch adsorber under equilibrium-controlled conditions. The technique is formulated in the Gibbs ensemble, but is more appropriately viewed as a hybrid of a molecular simulation and continuum modelling. Our approach employs a basic idea behind the Gibbs-Duhem Integration and pseudo-ensemble Monte Carlo methods: a macroscopic model is established based on the differential material balances to the adsorption unit and a series of molecular simulations is conducted that integrate along the path described by the model. If an analytical equation of state for the fluid phase is known, the simulation procedure acquires many characteristics of a Monte Carlo simulation conducted in the grand canonical ensemble. The usefulness of the technique is demonstrated through application to a gas separation problem encompassing the major steps of practical value to batch adsorption processes.

Keywords: molecular simulation, adsorption processes, GEMC, GCMC, hybrid modelling

1. Introduction and Problem Formulation

The adsorption system under consideration is sketched in Fig. 1. It consists of an isothermal batch adsorber with a perfectly mixed fluidized bed operating under equilibrium-controlled conditions. These assumptions are met in practice if both the heat transfer to the environment and the adsorption kinetics are much faster than the mean residence time of the fluid in the adsorber.

The individual material balance to the ith component of an m-component mixture in the adsorber, between arbitrary states $n-1$ and n, yields

$$\eta\Delta c_i^{(n)} - (1+\eta)\eta_{\mathrm{P}}\Delta q_i^{(n)} = \Delta F_i^{(n)} - \bar{c}_i^{(n-1/2)}\Delta G^{(n)}, \tag{1}$$

where $\Delta\phi^{(n)} \equiv \phi^{(n)} - \phi^{(n-1)}$, the superscript denotes the state at which the evaluation takes place, and

$$\bar{c}_i^{(n-1/2)} = \frac{1}{\Delta G^{(n)}}\int_0^{\Delta G^{(n)}} c_i \,\mathrm{d}G \tag{2}$$

is the average concentration of component i in the volume $\Delta G^{(n)}$ of fluid removed in the outlet stream. If $\Delta G^{(n)}$ is small enough then a first-order implicit approximation for Eq. (2) holds,

$$\bar{c}_i^{(n-1/2)} = c_i^{(n)} + O\big[\Delta G^{(n)}\big], \tag{3}$$

and Eq. (1) can be approximated as

$$\begin{aligned}\big[\eta + \Delta G^{(n)}\big]c_i^{(n)} + (1-\eta)\eta_{\mathrm{P}}q_i^{(n)} &= \eta c_i^{(n-1)}\\ &\quad + (1-\eta)\eta_{\mathrm{P}}q_i^{(n-1)} + \Delta F_i^{(n)}.\end{aligned} \tag{4}$$

If the inlet value $\Delta F_i^{(n)}$ is an input parameter, the terms on the r.-h.-s. of Eq. (4) are known quantities; we assume that to be the case here. To simplify the notation, the r.-h.-s. of Eq. (4) is condensed into a single

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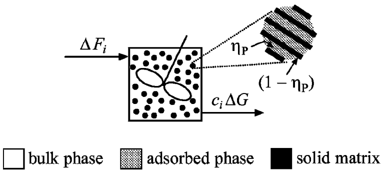

η is the bed void fraction, η_P is the internal porosity of the adsorbent; c_i and q_i are the concentrations in the bulk fluid and adsorbed phase, respectively; $F_i \geq 0$ is the amount of component i added to the adsorber in the inlet stream, and $G \geq 0$ is volume of fluid (at the conditions prevailing in the adsorber) removed in the outlet stream; both F_i and G are defined per unit volume of adsorber.

Figure 1. Schematic representation of an isothermal batch adsorber.

parameter, which we denote by w_i, and the superscripts are dropped. Eq. (4) becomes

$$(\eta + \Delta G)c_i + (1 - \eta)\eta_P q_i = w_i. \tag{5}$$

The m material balances given Eq. (5) are constrained by the conditions of thermodynamic equilibrium for an isothermal adsorption system (equality of chemical potentials between the phases), and require a closure equation involving either ΔG or the pressure P at the new state. Typically, the closure condition is simply assigning a value to ΔG or P. Table 1 outlines the two distinct problem formulations that can arise. Provided that the correct specification variables are selected, Eq. (5) encompasses all possible operating modes of the adsorber.

In this work we show that the problem formulated above can be solved in the framework of statistical mechanics by a hybrid of the grand Canonical (GCMC) and Gibbs ensemble (GEMC) Monte Carlo methods.

2. Simulation Method

Molecular studies of adsorption usually employ the GCMC method (Frenkel and Smit, 1996). The chemical potentials (as well as V and T) are specified in advance and the equilibrium number of adsorbed particles is calculated as an ensemble average. However, in process modelling one is often interested in other views of the phase behavior, such as Eq. (5), beyond that of the traditional adsorption isotherm provided by the GCMC method. A breakthrough in molecular simulation of phase equilibria was the invention of the GEMC method (Panagiotopoulos et al., 1988), which gives the same type of phase coexistence information obtained from a flash calculation. The method has been used, for example, to determine capillary condensation (Panagiotopoulos, 1987; Jiang and Gubbins, 1995) and liquid-liquid phase diagrams (Gozdz et al., 1995) in confined systems. In the GEMC method the two phases are simulated as two separate boxes, thereby avoiding problems with the direct simulation of the interface between the two phases. The system temperature T is specified in advance and the number of molecules of each species i in the adsorbed phase, N_{iP}, and in the bulk, N_{iB}, may vary according to the constraint $N_{iB} + N_{iP} = N_i$, where N_i is fixed.

Table 1. Input parameters and output variables for each type of problem formulation.

Type	Input parameters	Output variables
I	$w_i, \Delta G$	P, c_i, q_i
II	w_i, P	$\Delta G, c_i, q_i$

To solve Eq. (5) using a Monte Carlo method, it is convenient to reformulate it in terms of N_{iB} and N_{iP}. The resulting expression is

$$N_{iB} + N_{iP} = C_i \equiv \frac{N_{Av} V_P}{(1 - \eta)\eta_P} w_i, \tag{6}$$

where N_{Av} is avogadro's number and V_P is the volume of the box simulating the adsorbed phase. Note that C_i has been expressed as a function of V_P and not as a function of the volume V_B of the box simulating the bulk fluid. The reason for this is that V_P is always fixed, whereas, as we shall see below, V_B must be allowed to fluctuate during the course of the simulation when the pressure is an input parameter. Since Eq. (6) is a restatement of Eq. (5) at molecular scale, V_B and V_P must preserve the bulk to internal porosity ratio of the macroscopic system, i.e.,

$$V_B/(\eta + \Delta G) = V_P/(1 - \eta)\eta_P. \tag{7}$$

Although for a binary mixture it is possible to size V_B and V_P according to Eq. (7) so that each C_i is an integer, that is no longer the case for more complex mixtures. For an arbitrary multicomponent mixture, the total number of molecules of each species is allowed to fluctuate around the target value C_i so that the ensemble average gives

$$\langle N_i \rangle = C_i. \tag{8}$$

To get the best statistics, N_i must fluctuate with the smallest amplitude around the target value C_i. This happens when N_i can only take the two integer values $\mathrm{int}(C_i)$ or $\mathrm{int}(C_i) + 1$, where $\mathrm{int}(C_i)$ denotes the integer obtained by truncating the value of C_i and corresponds to the maximum value of N_i that does not exceed the material balance imposed by Eq. (6). It is straightforward to derive that for Eq. (8) to hold, the probability density of finding the system in one of the two configurations must be

$$\begin{aligned} \mathcal{N}\{N_i \to \mathrm{int}(C_i)\} &\propto 1 - \delta_i, \\ \mathcal{N}\{N_i \to \mathrm{int}(C_i) + 1\} &\propto \delta_i, \end{aligned} \tag{9}$$

where $\delta_i = C_i - \mathrm{int}(C_i)$. To sample this probability distribution, a new type of trial move must be performed which consists of an attempt to change the system to a configuration with $\mathrm{int}(C_i)$ or $\mathrm{int}(C_i) + 1$ particles. The box for insertion or removal of the molecule must be selected with a fixed probability, which may be different for each box. In fact, we advocate that insertions and removals take place only in the bulk box, except for the infrequent case that $N_{i\mathrm{B}}$ becomes zero after a successful transfer of a particle to the adsorption box. This choice is most suited to adsorption from the gas phase where, in general, the bulk phase is much less dense than the adsorbed phase and, therefore, more permeable to particle insertions.

The proposed algorithm is heuristic because the probability density defined by Eq. (9) is independent of the molecular configuration of the system. For example, Eq. (9) does not provide any guidance on how to select the molecule to be removed from the system nor the location for insertion of a new molecule. However, as shown recently (Mota and Esteves, 2004), this fact is irrelevant when an analytical equation of state for the fluid phase is known and the system is cycled between configurations with $\mathrm{int}(C_i)$ and $\mathrm{int}(C_i) + 1$ particles by adding and removing particles solely in the bulk box. If an analytical equation of state for the fluid phase is known, the potential energy of a given configuration in the bulk box is determined solely by the integer vector $N_\mathrm{B} = [N_{1\mathrm{B}}, \ldots, N_{m\mathrm{B}}]$, which holds the number of molecules of each species in volume V_B. This is the only state variable of the bulk box that must be updated during the course of the simulation. The resulting method can be viewed as a hybrid Monte carlo method, which incorporates features of both the GCMC and GEMC techniques. Only the more relevant aspects of the method are reviewed here; the reader is referred to the original reference for further details.

Regardless of the type of problem (either type I or II) being solved, thermodynamic equilibrium between the two subsystems is achieved by allowing them to undergo configurational and particle transfer moves. For an attempted change of the internal configuration of volume V_P (molecule displacement, rotation, or conformational change), the probability of acceptance is the same as for a conventional canonical simulation (Frenkel and Smit, 1996).

To satisfy equality of chemical potentials, transfers of particles between the two boxes are attempted. The probability of accepting a move in which a particle of type i is transferred from the bulk fluid to the adsorbed phase is

$$\begin{aligned} &\mathrm{acc}(N_{i\mathrm{P}} \to N_{i\mathrm{P}} + 1; N_{i\mathrm{B}} \to N_{i\mathrm{B}} - 1) \\ &\quad = \min\left\langle 1, \frac{\alpha_-(N_{i\mathrm{P}} + 1)}{\alpha_+(N_{i\mathrm{P}})} \frac{\beta \hat{f}_{N_{i\mathrm{B}}} V_\mathrm{P}}{N_{i\mathrm{B}}} \right. \\ &\qquad \left. \times \exp\{-\beta \Delta U_\mathrm{P}(\mathbf{r}^{N_{\mathrm{iP}+}} 1)\} \right\rangle, \end{aligned} \tag{10}$$

where $\Delta U_\mathrm{P}(\mathbf{r}^{N_{i\mathrm{P}}+1})$ is the potential energy change in the adsorbed phase resulting from the particle transfer, $\alpha_\pm(N_{i\mathrm{P}})$ is the probability of changing the system from a state with $N_{i\mathrm{P}}$ particles to a new state with $N_{i\mathrm{P}} \pm 1$ particles, and $\hat{f}_{N_{i\mathrm{B}}+k}$ is the fugacity of species i at temperature T in the gas mixture of number density $\rho_{N_\mathrm{B}+k} = (N_\mathrm{B} + k)/V_\mathrm{B}$ and mole-fraction composition

$$\begin{aligned} y_1 = N_{1\mathrm{B}}/(N_\mathrm{B} + k), \ldots, y_i = (N_{i\mathrm{B}} + k)/(N_\mathrm{B} + k), \\ \ldots, y_m = N_{m\mathrm{B}}/(N_\mathrm{B} + k). \end{aligned} \tag{11}$$

Analogously, if a particle of type i moves from the adsorption box to the bulk cell, the acceptance probability is

$$\begin{aligned} &\mathrm{acc}(N_{i\mathrm{P}} \to N_{i\mathrm{P}} - 1; N_{i\mathrm{B}} \to N_{i\mathrm{B}} + 1) \\ &\quad = \min\left\langle 1, \frac{\alpha_+(N_{i\mathrm{P}} - 1)}{\alpha_-(N_{i\mathrm{P}})} \frac{N_{i\mathrm{B}} + 1}{\beta \hat{f}_{N_{i\mathrm{B}}+1} V_\mathrm{P}} \right. \\ &\qquad \left. \times \exp\{-\beta \Delta U_\mathrm{P}(\mathbf{r}^{N_{i\mathrm{P}}-1})\} \right\rangle. \end{aligned} \tag{12}$$

If the density of the fluid is sufficiently low, such that it behaves as an ideal gas mixture, the fugacity $\hat{f}_{N_{i\mathrm{B}}}$ can

Table 2. Alternative methods of implementing the particle exchange step and corresponding probability ratios.

Method	Description	$\frac{\alpha_-(N_{i\mathrm{P}}+1)}{\alpha_+(N_{i\mathrm{P}})}$	$\frac{\alpha_+(N_{i\mathrm{P}}-1)}{\alpha_-(N_{i\mathrm{P}})}$
a	A phase is chosen with equal probability, then a species is chosen with a fixed (but otherwise arbitrary) probability, and finally a molecule of that species is randomly selected for transfer to the other phase.	$\frac{N_{i\mathrm{B}}}{N_{i\mathrm{P}}+1}$	$\frac{N_{i\mathrm{P}}}{N_{i\mathrm{B}}+1}$
b	A phase is chosen with equal probability, then a molecule is randomly selected for transfer to the other phase regardless of its species.	$\frac{N_\mathrm{B}}{N_\mathrm{P}+1}$	$\frac{N_\mathrm{P}}{N_\mathrm{B}+1}$
c	A species is chosen with a fixed (but otherwise arbitrary) probability, then a molecule of that species is randomly selected regardless of its phase and is transferred.	1	1
d	A molecule is chosen regardless of its phase or species, and is transferred.	1	1

be replaced by the partial pressure $P_{N_{i\mathrm{B}}} = \beta^{-1} N_{i\mathrm{B}}/V_\mathrm{B}$. As expected, this simplification is equivalent to setting $\Delta U_\mathrm{B} = 0$ in the acceptance criteria for particle exchange in a conventional GEMC simulation.

The method of employing $\mathbf{N}_\mathrm{B}$ and the equation of state to compute $\hat{f}_{N_{i\mathrm{B}}}$ depends on the type of problem being solved. For a type I problem, V_B is fixed during the course of the simulation and the gas mixture is further specified by its number density $\rho_{N_\mathrm{B}} = N_\mathrm{B}/V_\mathrm{B}$. If, on the other hand, P is fixed (type II problem), its value defines the state of the mixture. In this case, the volume V_B fluctuates so that on average the fluid contained within it is at the desired pressure. Once the ensemble average $\langle V_\mathrm{B}\rangle$ is determined, the value of ΔG follows from Eq. (7):

$$\Delta G = (1-\eta)\epsilon_\mathrm{P} \frac{\langle V_\mathrm{B}\rangle}{V_\mathrm{P}} - \eta. \qquad (13)$$

As listed in Table 2, the particle exchange step can be done in one of four ways, each corresponding to a different method of selecting the particle to be transferred and, consequently, to a different expression for $\alpha_\pm(N_{i\mathrm{P}})$. The choice between the various methods is a matter of convenience. For example, methods (*a*) and (*c*) allow the transfer to be restricted to selected species only, which would be appropriate when simulating adsorption in materials with molecular sieving properties. The simulation results presented in this work were obtained with method (*a*).

3. Application Example

The simulation method has been thoroughly validated elsewhere (Mota and Esteves, 2004); here we illustrate its usefulness as a process simulation technique through its application to a gas separation problem encompassing the major steps of practical value to batch adsorption processes. For illustration purposes the adsorbent is assumed to consist of slit-shaped pores of width $h_\mathrm{P} = 15$ Å, with parameters chosen to model activated carbon. The porosity values are fixed at $\eta = 0.45$ and $\eta_\mathrm{P} = 0.6$, which are typical values for a packed bed of granular activated carbon.

The adsorbates considered in this study are hydrogen, methane and ethane. We adopted a united-atom description based on the Lennard-Jones 12-6 potential to describe the non-bonded interaction energy. The two hydrocarbons were modelled using the TraPPE (Martin and Siepmann, 1998) force field, the LJ parameters for H_2 were taken from Turner et al. (1991). Unlike interactions were computed using standard Lorentz-Berthelot combing rules. The potential cut-off was set at 14 Å, with no long-range corrections applied. The gas-phase fugacities $\hat{f}_i$ were computed from the Virial equation, truncated at the second coefficient. Pure-component and mixture interaction coefficients were estimated using the formulas given by Reid et al. (1988). The interactions with the carbon walls were accounted for using the structureless 10-4-3 potential of Steele (1974).

Each simulation run was equilibrated for 10^4 Monte Carlo cycles, where each cycle consists of N attempts to change the internal configuration of volume V_P and $N/3$ attempts to transfer a molecule between the two boxes. Each molecule transfer attempt was followed by a trial move to adjust the total number of molecules of that type according to the probability given by Eq. (9). The maximum displacements for translations and rotations in the pore box were adjusted to give a 50% acceptance rate. The production periods consisted of 3×10^4 Monte Carlo cycles. Standard deviations of the ensemble averages were computed by breaking the production runs into five blocks.

The molar composition of the feed stream is 20% H_2, 30% CH_4 and 50% C_2H_6. The operation procedure

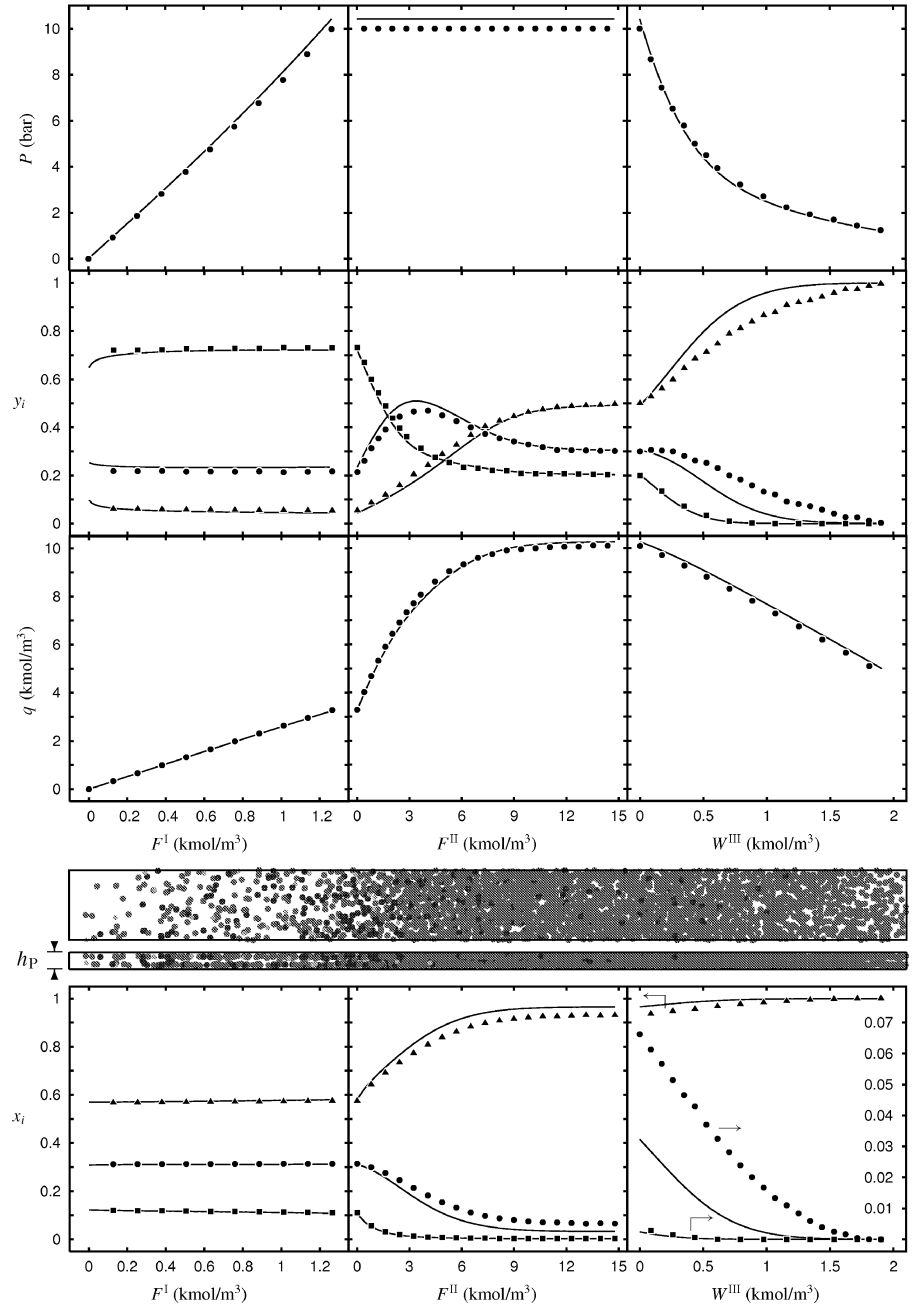

Figure 2. Simulated operation of the adsorber: (I) charge, (II) constant-pressure feed, and (III) discharge. Symbols denote molecular simulation data, whereas lines represent the profiles obtained using the multicomponent extension of the Langmuir-Freundlich isotherm model The drawing was built from a sequence of snapshots of the front and top views of the adsorption box at selected steps of the simulation (◇, H_2; ●, CH_4; ⧫, C_2H_6).

consists of the following steps: (I) charge from vacuum up to $P = 10$ bar (type I, $\Delta F_i > 0, \Delta P > 0, \Delta G = 0$); (II) constant-pressure feed (type II, $\Delta F_i > 0, \Delta P = 0, \Delta G > 0$); and (III) discharge down to $P = 1.25$ bar (type I, $\Delta F_i = 0, \Delta P < 0, \Delta G > 0$). This example encompasses the major steps of every cyclic batch adsorption process for gas separation, in which regeneration of the bed is accomplished by reducing the pressure at essentially constant temperature, as is the case in pressure swing adsorption (Yang, 1997).

The results are summarized in Fig. 2, which compares the simulated profiles obtained by the proposed method with those obtained using a classical approach based on the multicomponent extension of the Langmuir-Freundlich (LF) isotherm model. The isotherm parameters were obtained by fitting the single-component LF model to GCMC isotherm data of each component over the pressure range of the simulated operation of the adsorber. Although the two sets of results are qualitatively identical, there are some noticeable deviations, particularly in the mole fraction profiles. This simple example shows that, despite the ability of the LF isotherm model to fit the single-component adsorption data extremely well, its multicomponent extension fails to accurately predict the multicomponent adsorption equilibrium for the homogeneous microporous adsorbent of this study.

4. Conclusions

The theoretical approach presented here is an attempt to develop a computational methodology to predict the macroscopic behavior of an adsorption process from knowledge of the intermolecular forces and structural properties of the adsorbent. For simplicity, the application example presented in this work has been restricted to small molecules and to a simple pore structure. We are currently extending the methodology to handle the more general case of a nonisothermal adsorption system using a pseudo-ensemble Monte Carlo technique (Escobedo, 1998). The use of molecular simulation techniques, such as the one presented here, could grow in importance, gradually supplanting many empirical constitutive models that are used in process-scale calculations today.

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