

DIRECT STUDY OF MULTICOMPONENT ADSORPTION USING MOLECULAR SIMULATION

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Introduction

Experimental adsorption isotherms are usually reported as a function of the pressure and composition of the bulk fluid. Molecular methods like GCMC, traditionally employed in adsorption studies, require the knowledge of an accurate equation of state in order to relate the pressure with the applied chemical potential. Recently, a new method [1] was proposed, which replaces the chemical potential by the pressure as an input parameter, and in which the level of adsorption can be measured directly. However, for multicomponent adsorption studies the method does not offer any advantages over the established methods since the composition of the bulk fluid cannot be fixed. Here, we present a new method that overcomes these limitations.

Simulation method

Our method employs two simulation boxes, one representing the pore (P) and the other the coexisting bulk fluid (B). The volume of the pore (V_P) and the system temperature (T) are fixed, but the number of molecules of each species in the pore (N_{iP} , $i = 1, \dots, n_{SP}$) is allowed to change. Instead of fixing the total number of particles of each species ($N_i = N_{iP} + N_{iB}$), as was done in [1], only the value of each N_{iB} is fixed. Since it is difficult to know in advance the average value of N_{iP} for a given run, in [1] the value of N_i is usually oversized to guarantee that the bulk box is not emptied. This is not the case in our method, because each N_{iB} value is fixed and the N_{iP} fluctuate around the correct values due to molecule insertion/deletion moves.

In our method the bulk box can be handled in two different ways: in the isobaric ensemble (const- $N_{iB}PT$) version, a specified input pressure P is imposed in the bulk box through attempts to randomly change the value of V_B . In the canonical ensemble (const- $N_{iB}V_B T$) version, the molar density (ρ_B) (or volume, V_B) of the bulk box is specified and the code estimates the corresponding applied gas pressure P . The method accepts two sets of input parameters, corresponding to the two ensembles under which the bulk box can be simulated: $\{P, y_{iB}\}$ or $\{\rho_B, y_{iB}\}$, where y stands for either mole or mass fraction. If the set of input parameters is $\{\rho_B, y_{iB}\}$, the method estimates the value of P based on

a numerical calculation of the derivative of the free energy with respect to volume [2]. The main advantage of the proposed method is that it computes the adsorbed phase composition $\{\rho_P, y_{iP}\}$ directly for a specified composition of the coexisting bulk fluid, y_{iB} .

To enhance the sampling of chain molecules we employ configurational-bias techniques [3], in which a molecule is inserted segment by segment such that conformations with favorable energies are preferred. The bias introduced in finding an improved conformation for the molecule is then accounted for by changing the acceptance criterion. The basis for the computational implementation of our method were the GCMC and GIBBS codes developed by Errington and Panagiotopoulos [4,5].

Trial moves

The potential energy of each molecule is divided into two additive contributions: the bonded intramolecular energy (u^{bond}), and the external energy (u^{ext}) that contains the intermolecular fluid-fluid and solid-fluid interactions and the nonbonded intramolecular interactions.

Molecule insertion/deletion in the pore box

The donor box is selected at random, let it be denoted by 'd'. A molecule is selected at random in this box. For each segment i of the molecule ($i = 1, \dots, n$), the external energy $u_i^{\text{ext}}(\mathbf{d})$ is calculated and $k_i - 1$ trial positions/orientations $\{\mathbf{s}\}_{k_i} = (\mathbf{s}_2, \dots, \mathbf{s}_{k_i})$ are generated with a probability

$$P_i^{\text{bond}}(\mathbf{s}_j) \propto \exp[-\beta u_i^{\text{bond}}(\mathbf{s}_j)], \quad \beta = 1/k_b T. \quad (1)$$

From these trial orientations, together with the actual orientation of segment i , we compute the factor

$$w_i^{\text{ext}}(\mathbf{d}) = \exp[-\beta u_i^{\text{ext}}(\mathbf{d})] + \sum_{j=2, \dots, k_i} \exp[-\beta u_i^{\text{ext}}(\mathbf{s}_j)]. \quad (2)$$

After retracing the entire molecule, its Rosenbluth factor is calculated:

$$W^{\text{ext}}(\mathbf{d}) = \prod_{i=1, \dots, n} w_i^{\text{ext}}(\mathbf{d}). \quad (3)$$

For the box ('r') that will receive the molecule, the following steps are performed.

To insert each segment i of the molecule, k_i trial positions/orientations $\{\mathbf{s}\}_{k_i} = (\mathbf{s}_1, \dots, \mathbf{s}_{k_i})$ are generated with a probability given by eq. 1.

For each of these trial orientations, the external energy $u_i^{\text{ext}}(\mathbf{s}_j)$ is calculated together with the factor

$$w_i^{\text{ext}}(\mathbf{r}) = \prod_{j=1, \dots, k_i} \exp[-\beta u_i^{\text{ext}}(\mathbf{s}_j)]. \quad (4)$$

Out of these k_i trial positions/orientations, one is selected with probability

$$P_i^{\text{ext}}(\mathbf{s}_j) = \exp[-\beta u_i^{\text{ext}}(\mathbf{s}_j)] / w_i^{\text{ext}}(\mathbf{r}). \quad (5)$$

Once the entire molecule is grown, the Rosenbluth factor of the molecule is calculated:

$$W^{\text{ext}}(\mathbf{r}) = \prod_{i=1, \dots, n} w_i^{\text{ext}}(\mathbf{r}). \quad (6)$$

The move is then accepted with probability

$$\text{acc}(d \rightarrow r) = \min \left\{ 1, \frac{N_i(d)V(r)}{[N_i(r) + 1]V(d)} \frac{W^{\text{ext}}(r)}{W^{\text{ext}}(d)} \right\}. \quad (7)$$

However, unlike the usual configurational-bias Gibbs ensemble simulation, the acceptance of the transfer move changes only the number of molecules N_{iP} in the pore box; those in the bulk box (N_{iB}) are not affected.

Molecule displacement/rotation

A molecule is randomly selected in one of the boxes and is given a random displacement/rotation. The move [old (o) \rightarrow new (n)] is accepted using the usual Metropolis scheme:

$$\text{acc}(o \rightarrow n) = \min(1, \exp\{-\beta[U(n) - U(o)]\}). \quad (8)$$

Volume change of the bulk box (const- $N_{iB}PT$ version)

An attempted volume change of the bulk box from $V_B(o)$ to $V_B(n)$ is accepted with a probability

$$\text{acc}(o \rightarrow n) = \min(1, \exp\{-\beta[U_B(n) - U_B(o) + P(V_B(n) - V_B(o)) - N_B k_B T \ln(V_B(n)/V_B(o))]\}). \quad (9)$$

Molecule regrow

Part of a molecule is regrown starting from a random segment. The move is accepted with a probability

$$\text{acc}(o \rightarrow n) = \min \left(1, \frac{W^{\text{ext}}(n)}{W^{\text{ext}}(o)} \exp\{-\beta[u^{\text{ext}}(n) - u^{\text{ext}}(o)]\} \right). \quad (10)$$

Simulation details

The volume change is attempted approximately once per MC cycle (a cycle consists of $N_B + N_P$ attempted displacement/reorientation moves and several molecule insertion/removal attempts). The insertion/removal move is attempted N_{ins} times per cycle, with N_{ins} varied to ensure that at least 3% of the molecules are inserted in every cycle.

A typical run starts with an equilibration phase consisting of approximately 2×10^6 moves. During this phase the maximum displacement, rotation, and volume change are altered to give a 50% acceptance rate. After the equilibration phase a production phase of about 3×10^6 moves begins during which the thermophysical properties are averaged.

Application example

To illustrate the capabilities of the code, we report some results of single and multicomponent adsorption of n -alkanes on nonporous carbon, covering both sub- and supercritical adsorption. The results show clearly the impact of T/T_c on the shape of the adsorption isotherm.

Force-field model

The interaction parameters for the n -alkanes are taken from the TraPPE model [6] (see Table 1). It is based on an united-atom description: CH₄, CH₃ and CH₂ groups are taken as single interaction centers. The non-bonded interactions are described by LJ potentials. Bond-bending is modeled by a harmonic potential and changes in the torsional angles are controlled by the OPLS potential [7]. The surface of the nonporous carbon is assumed to be represented by the basal plane of graphite. The fluid solid interaction is modeled using the usual 10-4-3 potential [8]:

$$u_{iS}(z) = 2\pi\rho_S\epsilon_{iS}\sigma_{iS}^2\Delta \left[\frac{2}{5}(\sigma_{iS}/z)^{10} - (\sigma_{iS}/z)^4 - \frac{1}{3}\sigma_{iS}^4\Delta^{-1}(0.61\Delta + z)^{-3} \right]. \quad (11)$$

The parameters modeling a graphite surface are [8]:

$$\begin{aligned} \sigma_{SS} &= 0.340 \text{ nm}, & \epsilon_{SS}/k_b &= 28.0 \text{ K} \\ \Delta &= 0.335 \text{ nm}, & \rho_S &= 114 \text{ nm}^{-3} \end{aligned}$$

The cross parameters for fluid-fluid and solid-fluid interactions are calculated by using the Lorentz-Berthelot combining rules.

Table 1. Details of the n -alkanes model.

	Potential function	Parameters
Non-bonded interactions	$u_{LJ}(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right]$	$\sigma_{\text{CH}_4} = 3.73 \text{ \AA}$ $\sigma_{\text{CH}_3} = 3.75 \text{ \AA}$ $\sigma_{\text{CH}_2} = 3.95 \text{ \AA}$ $\epsilon_{\text{CH}_4} = 148 \text{ K}$ $\epsilon_{\text{CH}_3} = 98 \text{ K}$ $\epsilon_{\text{CH}_2} = 46 \text{ K}$
Bond bending	$u_{\text{bend}}(\theta) = \frac{1}{2}k_\theta(\theta - \theta_o)$	$k_\theta = 62500 \text{ K rad}^{-2}$ $\theta_o = 114^\circ$
Angle torsion	$u_{\text{tors}}(\phi) = a_1(1 + \cos \phi) + a_2(1 - \cos 2\phi) + a_3(1 + \cos 3\phi)$	$a_1 = 355.03 \text{ K}$ $a_2 = -68.19 \text{ K}$ $a_3 = 791.32 \text{ K}$

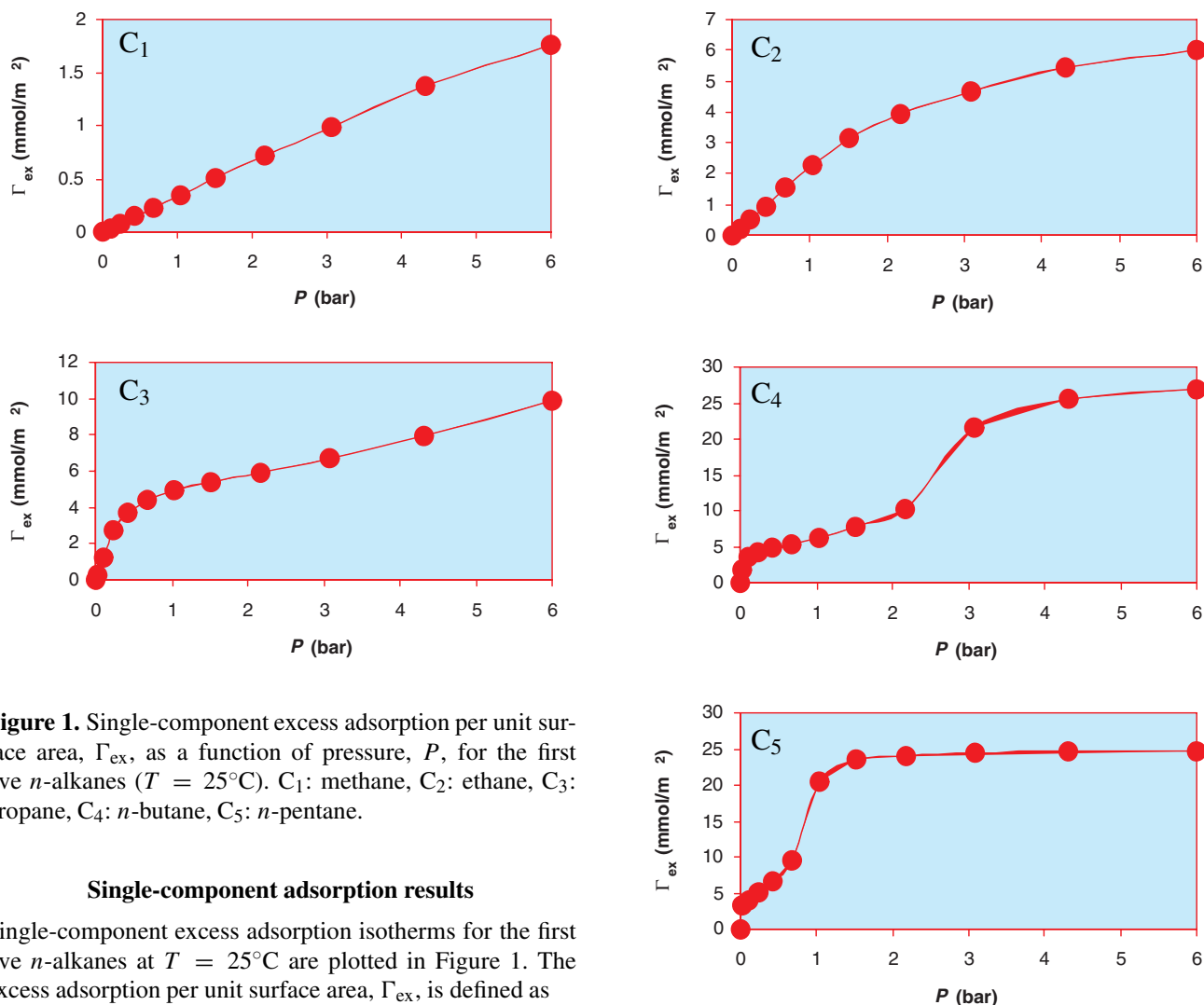


Figure 1. Single-component excess adsorption per unit surface area, Γ_{ex} , as a function of pressure, P , for the first five n -alkanes ($T = 25^\circ\text{C}$). C_1 : methane, C_2 : ethane, C_3 : propane, C_4 : n -butane, C_5 : n -pentane.

Single-component adsorption results

Single-component excess adsorption isotherms for the first five n -alkanes at $T = 25^\circ\text{C}$ are plotted in Figure 1. The excess adsorption per unit surface area, Γ_{ex} , is defined as

$$\Gamma_{\text{ex}} = h_P(\rho_P - \rho_B), \quad (12)$$

where h_P is the height of the pore box. The system temperature is slightly below the critical temperature of ethane ($T_c = 305.4 \text{ K}$), which makes the methane (C_1) adsorption data supercritical and all the other isotherms subcritical. Since the sharpness of the steps of the isotherm depends on $\beta u(z)$, the steps become less pronounced as T/T_c becomes higher, which for a fixed system temperature is equivalent to reducing the chain length of the n -alkane.

Multicomponent adsorption results

Figure 2 shows multicomponent adsorption equilibrium data for an equimolar mixture ($y_{iB} = 1/5$) of the first five n -alkanes on nonporous carbon at $T = 25^\circ\text{C}$ and pressures up to 6 bar. The total excess adsorption per unit surface area is plotted in Figure 2(a), whereas Figure 2(b) shows the mole fraction composition.

Figure 3 is a snapshot of the pore box for one of the multicomponent runs carried out at $P = 1 \text{ atm}$ and $T = 25^\circ\text{C}$,

each type of molecule is identified by a different color. The predominant color is cyan, corresponding to n -pentane molecules. Much less molecules of n -butane (blue) and propane (green) can be seen; only two ethane molecules appear in the snapshot, and methane cannot be seen at all. This is a very nice illustration of the displacement of lighter adsorbates from the adsorbed phase by the stronger ones. As depicted in Figure 2(b), the mole fraction in adsorbed phase is seen to increase roughly linearly with the logarithm of the number of carbons in the adsorbate.

This set of results illustrates the cause for the decrease of storage capacity of carbon adsorbents with the number of cycles in vehicular and large-scale storage applications of Adsorbed Natural Gas. As seen in Figure 2(b), the higher molecular-weight hydrocarbons are more strongly adsorbed than methane, especially in the low-pressure region. If the higher molecular-weight hydrocarbons are not prevented

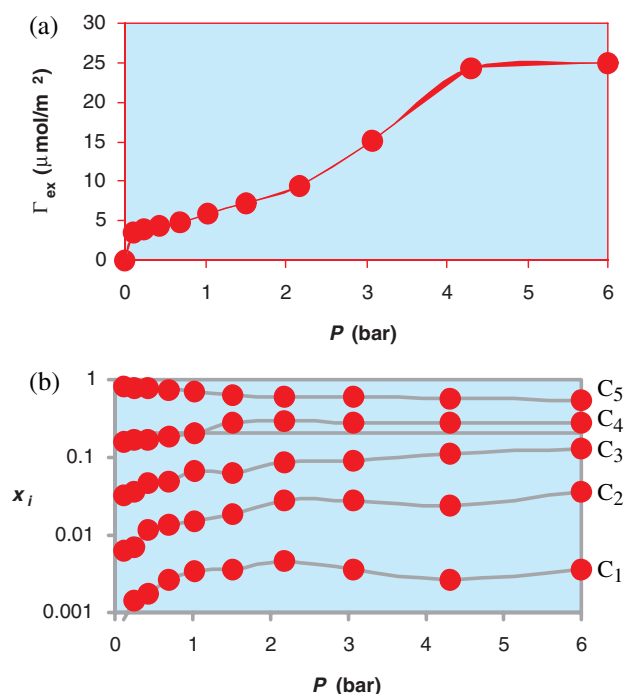


Figure 2. Adsorption of an equimolar mixture ($y_{iB} = 1/5$) of n -alkanes at $T = 25^\circ\text{C}$ and pressures up to 6 bar: (a) total excess adsorption per unit surface area, Γ_{ex} ; (b) mole fractions in adsorbed phase, y_{iP} . C₁: methane, C₂: ethane, C₃: propane, C₄: n -butane, C₅: n -pentane.

from entering the storage tank during charge, they adsorb preferentially and tend to accumulate from cycle to cycle until adsorption/desorption equilibrium is reached. This can lead to a significant decrease in adsorbent storage capacity on extended operation [9]. The storage-capacity deterioration in onboard storage is driven by the unfeasibility of operating the storage reservoir under sub-atmospheric pressure, since excessive compression hardware would be necessary to extract and boost the fuel pressure [10]. In large-scale storage the costs associated with the compression equipment required to swing the pressure between sub- and super-atmospheric values are prohibitive.

Although the results presented here apply to adsorption on a nonporous carbon, the method can be easily applied to slit-shaped pores. In particular, it can be a useful tool in defining the optimum characteristics of active carbons for guard-bed applications [11] or Evaporative Loss Control Devices [12].

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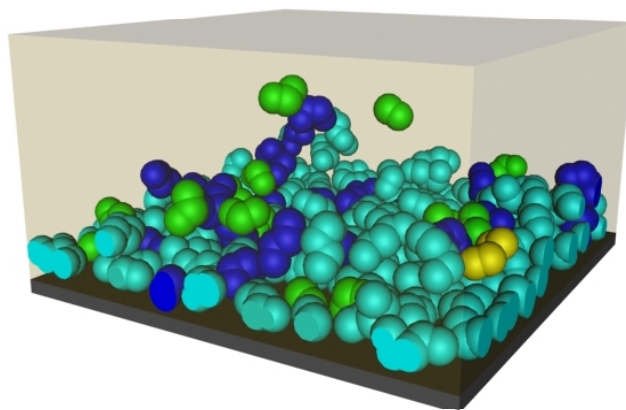


Figure 3. Snapshot of the pore box for an equimolar multicomponent run carried out at $P = 1$ atm and $T = 25^\circ\text{C}$. Each type of molecule is identified by a different color. Magenta: methane, yellow: ethane, green: propane, blue: n -butane, cyan: n -pentane (unfortunately methane does not show up in the picture).

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