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Computation of the Heat and Entropy of Adsorption in Proximity of Inflection Points

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S *Supporting Information*

ABSTRACT: The adsorption of different heptane isomers in MFI- and MEL-type zeolites is studied to investigate the performance of molecular simulation for computing the heat and entropy of adsorption as a function of loading. It is shown that none of the conventional methods are capable of computing the heat or entropy of adsorption of bulky molecules such as 2,4-dimethylpentane around the inflection point of the adsorption isotherm. The "Energy Slope" method is introduced which outperforms the present techniques at loadings near and above the inflection point. There is a quantitative agreement between the heats of adsorption computed with the energy slope method for a butane/isobutane mixture and the ones computed by the method based on energy/particle fluctuations in the grand-canonical ensemble. This verifies that the energy slope method is a valuable and robust tool for computing the heat and entropy of adsorption for a wide range of hydrocarbon lengths and loadings.
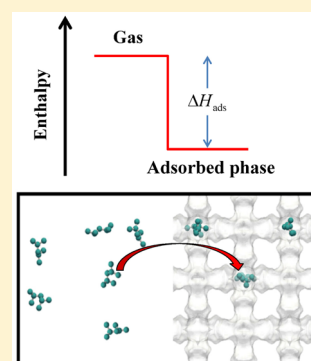
INTRODUCTION

Thermodynamic properties such as the heat of adsorption and the entropy of adsorption are crucial for the characterization of the performance of adsorption-based separation processes.[1-3] The heat of adsorption determines the thermal energy released during the adsorption step (exothermic) and the heating demand through the desorption step (endothermic).[2-4] It is well-known that the entropic differences can influence the selectivity of the adsorption process and can be used as the driving force for the separation of similar molecules.[5-7] These thermodynamic properties ultimately determine the effectiveness of a separation process. Consequently, comprehensive knowledge concerning the heat and entropy of adsorption is of great industrial importance.

Gasoline and other types of fuels are among the most consumed petroleum products (roughly, one barrel of gasoline is produced from every two barrels of crude oil). Fuels with higher concentration of branched hydrocarbons are more valuable and have a higher octane number.[8,9] However, due to the difficulties associated with the separation of hydrocarbon isomers, aromatics are conventionally added to the fuels to increase their octane number.[10,11] Recent environmental regulations have limited the concentration of aromatics in fuels, making the industrial separation of hydrocarbon isomers more important than ever.[12,13] Zeolite 5A is used for the industrial separation of linear and branched alkanes,[14] and several other zeolites are suggested by the literature for this

task.[14-17] Zeolites contain a network of pores which only allows the adsorption of molecules with sizes comparable to or smaller than the pore dimensions.[18] Zeolites usually provide different adsorption sites. As branched hydrocarbons are more bulky than their linear isomers, they are preferentially located at very specific adsorption sites.[8] As the loading increases, the molecules are eventually forced to fill the less favorable adsorption sites as well. The loading at which molecules start to fill a different adsorption site is known as the inflection point. This is due to the fact that this phenomenon is usually recognized by an inflection in the adsorption isotherm.[19,20] The thermodynamic properties of adsorbate molecules can be highly influenced by the topology of the adsorption site.[18,19] The difference between the topologies of the less favorable adsorption sites and the sites that were initially preferred by the branched molecules can cause significant changes in the adsorption properties of hydrocarbons.[7,21]

Recent advancements in computing power have made molecular simulation a powerful tool for the computation of thermodynamic properties of adsorbed molecules. Molecular simulations can provide fundamental information regarding the adsorption properties at the molecular scale.[18,22-26] Although there are several methods to compute the heat of adsorption
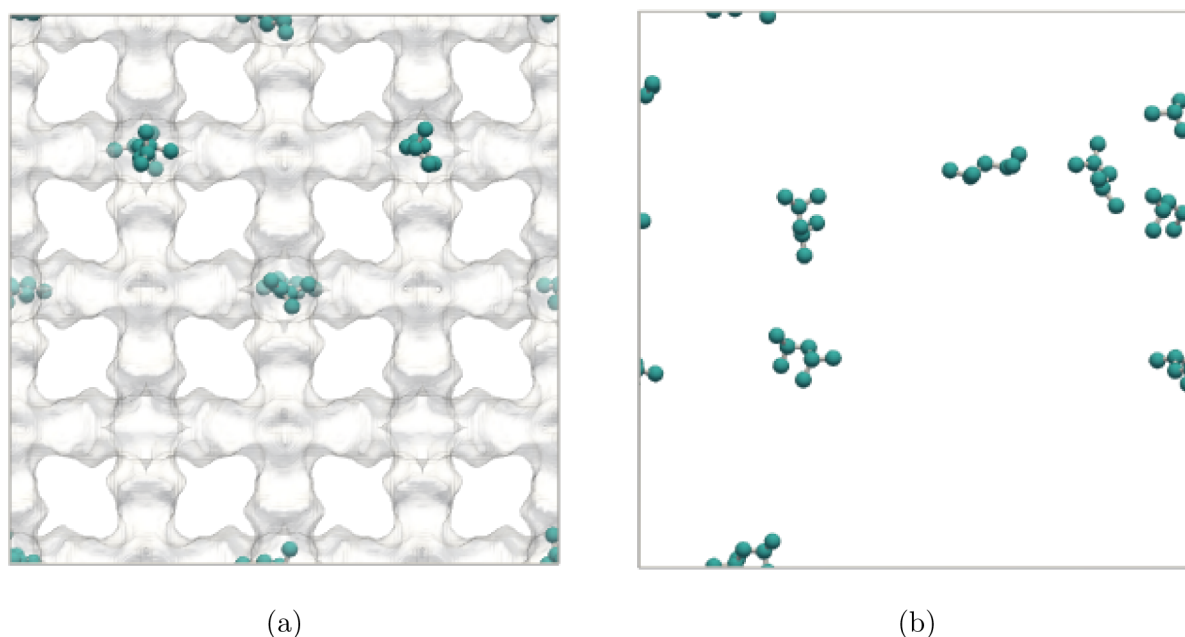
(a)

(b)

Figure 1. (a) $2 \times 2 \times 2$ unit cells of MEL-type zeolite with adsorbed 2,4-dimethylpentane at 400 K. (b) The same number of 2,4-dimethylpentane molecules as in Figure (a) at 400 K with a volume equal to $2 \times 2 \times 2$ unit cells of MEL-type, in the absence of zeolite (Reference State 2).

with Monte Carlo simulations (e.g., energy difference in canonical ensemble and energy/particle fluctuations in grand-canonical ensemble[22]), a systematic comparison of the different methods is missing. For instance, a technique that is suitable for computation of the heat of adsorption at low loadings might not be efficient or applicable for calculating the same property near the inflection point. The main focus of this study is on the calculation of the heat and entropy of adsorption at various loadings and investigation of the important aspects of each method. Although this study is focused on the adsorption of hydrocarbons by zeolites, the proposed methods are by no means restricted to this case and can be applied to other porous materials such as metal organic frameworks.

This paper is organized as follows. In section 2, the heat and entropy of adsorption are defined, and the relevant thermodynamic correlations for calculating these properties are derived. In section 3, various methods used in molecular simulations to compute the heat and entropy of adsorption for pure components and mixtures are reviewed. The advantages and disadvantages of each method are discussed. The energy slope method is introduced which outperforms the other approaches in the computation of the heat and entropy of adsorption of large molecules near the inflection point. The results of different methods for the system described in section 4 are compared in section 5. In section 6, values for the heat of adsorption of the butane/isobutane mixture computed using the energy slope method are presented. These results are compared with the ones computed by the method based on the energy/particle fluctuations for the adsorption of an equimolar gas mixture of butane and isobutane at different pressures. The main findings are summarized in section 7.

■ **ENTHALPY AND ENTROPY OF ADSORPTION**

During an adsorption process, molecules are removed from the reference state and transported into the zeolite. It is important to have a clear definition of the reference state. In this paper, the gas phase in chemical equilibrium with the adsorbed phase

is used as the reference state for the calculation of the enthalpy and entropy of adsorption.[27] Moreover, the gas phase is assumed to be ideal, only to simplify the equations. Not using this assumption results in small but trivial changes in upcoming equations.

The heat of adsorption of component i is defined as the change in the total enthalpy of the system as a molecule of component i is removed from the gas phase (which is in equilibrium with the zeolite) and transported into the zeolite at constant temperature. Here, the system includes the gas phase, zeolite, and the guest molecules. Therefore

$$\Delta H_{i,\text{ads}} = \left(\frac{\partial H}{\partial N_i}\right)_{T,N_{j\neq i},z} - \left(\frac{\partial H}{\partial N_i}\right)_{T,N_{j\neq i},g} \tag{1}$$

where H is the total enthalpy of the system and N_i and $\Delta H_{i,\text{ads}}$ are the number of guest molecules and the heat of adsorption of component i. The subscripts "z" and "g" refer to the zeolite and the gas phase, respectively. In eq 1, the heat of adsorption is divided into two contributions: the changes in the enthalpy of the zeolite with guest molecules caused by the addition of a single molecule and the change in the enthalpy of the gas phase when a molecule is removed from it. The enthalpy of adsorption can be written as the sum of the change in the internal energy and the change in product of the pressure and the volume of the system.

$$\Delta H_{i,\text{ads}} = \Delta U_{i,\text{ads}} + \Delta(PV)_{\text{ads}} \tag{2}$$

$\Delta U_{i,\text{ads}}$ is the total internal energy change of the system, due to adsorption of an additional molecule of component i. The term $\Delta(PV)_{\text{ads}}$ in eq 2 requires a closer look. The conditions under which the removal of a molecule from the ideal gas phase and its addition to the zeolite take place should be specified. Generally, the volume and the temperature of the zeolite are assumed to be constant during this process. For the gas phase, usually the pressure and the temperature are kept constant. Similar to the heat of adsorption, the $\Delta(PV)_{\text{ads}}$ in eq 2 is

expanded into an ideal gas phase contribution and an adsorbed phase contribution. The ideal gas phase contribution is computed utilizing the ideal gas law. The zeolite is acknowledged as a solid structure with microscopic openings where pressure is not defined, and the volume of adsorbate is zero.[28] With this assumption, the contribution of the adsorbed phase to the $\Delta(PV)_{ads}$ term of eq 2 would vanish, and the enthalpy of adsorption of component i can be computed from

$$\Delta H_{i,ads} = \Delta U_{i,ads} - k_B T \tag{3}$$

Here k_B is the Boltzmann factor. The entropy of adsorption is defined in a similar way, starting from the Gibbs free energy. The Gibbs free energy of adsorption of component i is the change in the total Gibbs free energy of the adsorption system when an additional molecule of component i is transferred from the ideal gas phase inside the zeolite

$$\Delta G_{i,ads} = \left(\frac{\partial G}{\partial N_i}\right)_{T,V,N_{j\neq i},z} - \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i},g} \tag{4}$$

where G is the total Gibbs free energy of the system. The first term on the right-hand side of eq 4 is, by definition, equal to the chemical potential of component i in the adsorbed phase, and the second one is the chemical potential of component i in the ideal gas phase. Chemical equilibrium implies that the chemical potential of component i in the adsorbed phase is equal to the one in the gas phase. Consequently, at equilibrium, the Gibbs free energy of the adsorption system remains unchanged. Then, the entropy of adsorption of component i is given by

$$\Delta G_{i,ads} = \Delta H_{i,ads} - T\Delta S_{i,ads} = 0 \tag{5}$$

$$\Delta S_{i,ads} = \frac{\Delta H_{i,ads}}{T} \tag{6}$$

In eq 6, the gas phase in equilibrium with the adsorbed phase (denoted by Reference State 1) is used as the reference state for the calculation of the entropy of adsorption.[27] However, sometimes a different reference state is used: the gas phase with the temperature and number density equal to the adsorbed phase (denoted by Reference State 2).[29−31] In this approach, the entropy of the adsorbate molecules inside the zeolite is compared to the entropy of the adsorbate molecules in the absence of the zeolite (Figures 1a and 1b). In this case, the Helmholtz free energy is the natural starting point for the computation of the entropy of adsorption. The change in the total Helmholtz free energy of the system is given by

$$\Delta A_{i,ads} = \Delta U_{i,ads} - T\Delta S_{i,ads} \tag{7}$$

$\Delta A_{i,ads}$ is the total change in the Helmholtz free energy of the system, subjected to adsorption of an additional molecule of component i. The value of $\Delta A_{i,ads}$ in eq 7 is given by the difference in the chemical potential of component i in the adsorbed phase and in the gas phase. Due to the choice of the reference state, the chemical potentials are not identical. The chemical potential can be expressed as the sum of the ideal gas part and the excess part. The ideal gas part is defined by the number density. Since the number densities of the Reference State 2 and the adsorbed phase are equal, the ideal gas parts cancel each other out. Assuming ideal gas behavior at Reference State 2, the excess chemical potential of component i in the Reference State 2 would be zero. Therefore, the total changes

in the Helmholtz free energy of the system can be estimated by the excess chemical potential of component i in the adsorbed phase. The Widom's test particle method is conventionally used to compute the excess chemical potential in molecular simulations. For chain molecules, conformation of a test chain is normally generated using the Rosenbluth algorithm.[32] Using Widom's test particle method with the Rosenbluth algorithm, the excess chemical potential of component i in the adsorbed phase and, therefore, the total change in the Helmholtz free energy of the system are given by

$$\Delta A_{i,ads} = \mu_{i,ex,z} = -k_B T \ln \frac{\langle W_{i,z}\rangle}{\langle W_{i,id}\rangle} \tag{8}$$

where $\langle W_{i,z}\rangle$ is the average Rosenbluth factor of a test chain of component i in the adsorbed phase and $\langle W_{i,id}\rangle$ is the average Rosenbluth factor of an isolated chain of component i. $\mu_{ex,z}$ is the excess chemical potential of component i in the adsorbed phase. Using eqs 7 and 8, considering the fact that the chemical potential of the Reference State 1 (not Reference State 2) and the chemical potential of the adsorbed phase are equal, the entropy of adsorption for component i, using Reference State 2, can be computed from eq 9.

$$\Delta S_{i,ads} = \frac{\Delta U_{i,ads}}{T} - k_B \ln \frac{\rho_{i,ref.1}}{\rho_{i,ref.2}} \tag{9}$$

where $\rho_{i,ref.1}$ and $\rho_{i,ref.2}$ are the number densities of component i in the Reference State 1 and Reference State 2. As reflected in eqs 3, 6, and 9, choosing different reference states can lead to different expressions for the entropy of adsorption. However, the difference between these expressions is only caused by the entropy difference between the reference states (last term on the right-hand side of eq 9 and a term $k_B T$). Therefore, the values computed by the two approaches can be compared after including the entropy difference between the reference states.

The computational steps needed to compute the entropy of adsorption and the enthalpy of adsorption are identical. Therefore, in the remainder of this paper, to compare various computational methods, only the enthalpy of adsorption is considered explicitly.

■ COMPUTATIONAL METHODS

The partial derivative of the total internal energy of an ideal gas phase with respect to the number of molecules of component i is independent from the pressure. This value is equal to the average internal energy of a single isolated molecule of component i at the corresponding temperature and needs to be calculated only once. As a result, the heat of adsorption is given by

$$\Delta H_{i,ads} = \left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j\neq i},z} - \langle U_{g,i}\rangle - k_B T \tag{10}$$

in which $\langle U_{g,i}\rangle$ is the average internal energy of a single isolated molecule of component i in the gas phase. There are various methods for computing the change in the total internal energy of the zeolite and adsorbates upon the adsorption of an additional molecule (the partial derivative in eq 10) in molecular simulations. In this section, the most commonly used methods are reviewed, and their advantages and disadvantages are discussed. The "Energy Slope" method is also introduced as an improved method to compute the partial

derivative in eq 10. The subscript "z" is skipped for the partial derivatives, and they all apply to the zeolite phase.

1. Energy/Particle fluctuations in the grand-canonical ($\mu V T$) ensemble:

The partial derivatives with respect to chemical potential can be expressed as a function of averages in the grand-canonical ensemble.[33−36] Consequently, for a single-component system, the partial derivative in eq 10 is computed from

$$\left(\frac{\partial U}{\partial N}\right)_{T,V,z} = \frac{\left(\frac{\partial U}{\partial \mu}\right)_{T,V,z}}{\left(\frac{\partial N}{\partial \mu}\right)_{T,V,z}} = \frac{\langle UN\rangle_\mu - \langle U\rangle_\mu\langle N\rangle_\mu}{\langle N^2\rangle_\mu - \langle N\rangle_\mu\langle N\rangle_\mu} \quad (11)$$

where $\langle...\rangle_\mu$ presents an average in grand-canonical ensemble. The heat of adsorption of a single-component system is therefore expressed as[22,36,37]

$$\Delta H_{ads} = \frac{\langle UN\rangle_\mu - \langle U\rangle_\mu\langle N\rangle_\mu}{\langle N^2\rangle_\mu - \langle N\rangle_\mu\langle N\rangle_\mu} - \langle U_g\rangle - k_B T \quad (12)$$

The energy/particle fluctuations in the grand-canonical ensemble can also be used to compute the heat/entropy of adsorption of gas mixtures. In this case, the partial derivative in eq 10 is given by[37]

$$\left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j\neq i},z} = \sum_{k=1}^{N_C}\left(\frac{\partial U}{\partial \mu_k}\right)_{T,V,\mu_{j\neq k}}\left(\frac{\partial \mu_k}{\partial N_i}\right)_{T,V,N_{j\neq i}} \quad (13)$$

where N_C is the number of components in the gas mixture. As the partial derivatives in eq 10 indicate, the change in the total internal energy of the adsorbed phase should be calculated. This value should be computed while only the loading of component i is changed and the loadings of all other components are unchanged. The change in the chemical potential of component i results in changes in the chemical potentials of all other components and, therefore, their loadings. Consequently, as shown in eq 13, the chemical potentials of all other components should change in such a way that their loadings remain constant. To find the correct values for the last term on the right-hand side of eq 13, a system of linear algebraic equations should be solved. For the most simple case of a binary mixture, the system of equations can be written as[37]

$$\begin{bmatrix} \left(\frac{\partial N_1}{\partial \mu_1}\right)_{T,V,\mu_2} & \left(\frac{\partial N_2}{\partial \mu_1}\right)_{T,V,\mu_2} \\ \left(\frac{\partial N_1}{\partial \mu_2}\right)_{T,V,\mu_1} & \left(\frac{\partial N_2}{\partial \mu_2}\right)_{T,V,\mu_1} \end{bmatrix}\begin{bmatrix} \left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,V,N_2} & \left(\frac{\partial \mu_1}{\partial N_2}\right)_{T,V,N_1} \\ \left(\frac{\partial \mu_2}{\partial N_1}\right)_{T,V,N_2} & \left(\frac{\partial \mu_2}{\partial N_2}\right)_{T,V,N_1} \end{bmatrix} = I \quad (14)$$

Here I is the identity matrix. As mentioned before, the partial derivatives with respect to the chemical potential can be written as a function of averages in the grand-canonical ensemble

$$\left(\frac{\partial U}{\partial \mu_k}\right)_{T,V,\mu_{j\neq k}} = \langle UN_k\rangle_\mu - \langle U\rangle_\mu\langle N_k\rangle_\mu$$

$$\left(\frac{\partial N_i}{\partial \mu_k}\right)_{T,V,\mu_{j\neq k}} = \langle N_iN_k\rangle_\mu - \langle N_i\rangle_\mu\langle N_k\rangle_\mu \quad (15)$$

The main disadvantage of this method is that calculating the energy/particle fluctuations is computationally very expensive, requiring many successive particle insertions/removals. The acceptance rate for the complete insertion of branched molecules can be quite low, even when advanced sampling methods, such as the Configurational-Bias Monte Carlo (CBMC), are used. Generally, the fraction of accepted trial moves decreases as the loading increases and near the inflection point, where all the suitable adsorption sites are already filled. Therefore, significantly long simulations are needed to obtain accurate statistics.

2. Energy difference of two simulations in canonical ensemble:

The partial derivative in eq 10 can be estimated by

$$\left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j\neq i},z} = \langle U\rangle_{N_1,N_2,...,(N_i+1),...,N_C} - \langle U\rangle_{N_1,N_2,...,(N_i),...,N_C} \quad (16)$$

where $\langle U\rangle_{N_1,N_2,...,(N_i),...,N_C}$ denotes the average total internal energy of the zeolite plus $N_T = \sum_{k=1}^{N_C} N_k$ adsorbate molecules at constant temperature, volume, and loading of all N_C components. $\langle U\rangle_{N_1,N_2,...,(N_i+1),...,N_C}$ is the average total internal energy when the loadings of all the components are the same as the former case, except for the component i. As a result, the total number of adsorbed molecules in this case is $N_T + 1$. The canonical ensemble is the natural choice for calculating these averages. The heat of adsorption can be computed by substituting eq 16 in eq 10. This method is mostly used to estimate the heat of adsorption at zero loading. Usually, rigid zeolite structures are used in simulations;[38] therefore, the average internal energy of zeolite without any guest molecule is zero. At zero loading, only one simulation in the NVT ensemble is needed to compute the partial derivative in eq 10.[15,39,40] This approach is rarely utilized for the calculation of the heat of adsorption at higher loadings. The reason behind this is that as the loading increases the values of the two average internal energies in eq 16 increase. At higher loadings, these values can become significantly larger than their difference. Therefore, even a small relative error in the calculation of average internal energies can cause a noticeable relative error in the energy difference and eventually in the calculated value for the heat of adsorption.

3. Widom's test particle in canonical ensemble:

In principle, the two averages on the right-hand side of eq 16 can be computed in a single simulation in the canonical ensemble. Using Widom's test particle method with the Rosenbluth algorithm, $\langle U\rangle_{N_1,N_2,...,(N_i+1),...,N_C}$ is computed in the NVT simulation with N_T adsorbate molecules

$$\langle U\rangle_{N_1,N_2,...,(N_i+1),...,N_C} = \frac{\langle (U+u_i^+)W_i\rangle_{N_1,N_2,...,(N_i),...,N_C}}{\langle W_i\rangle_{N_1,N_2,...,(N_i),...,N_C}} \quad (17)$$
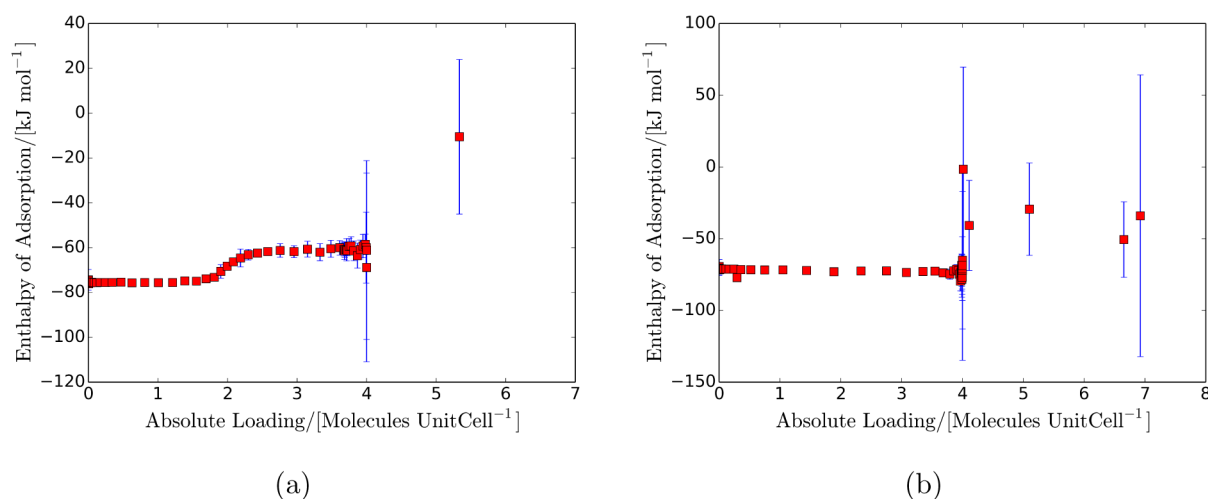
Figure 2. Enthalpy of adsorption of 2,4-dimethylpentane computed using energy/particle fluctuations in the grand-canonical ensemble at 400 K. (a) MEL-type and (b) MFI-type zeolite. The error bars indicate the 95% confidence interval.

u_i^+ and W_i are the internal energy and the Rosenbluth factor of a test chain of component i in the adsorbed phase. Substituting eq 17 into eq 16 leads to the following expression for the partial derivative in eq 10

$$\left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j\neq i},z} = \frac{\langle (U + u_i^+)W_i\rangle_{N_1,N_2,\ldots,(N_i),\ldots,N_C}}{\langle W_i\rangle_{N_1,N_2,\ldots,(N_i),\ldots,N_C}}$$

$$- \langle U\rangle_{N_1,N_2,\ldots,(N_i),\ldots,N_C} \quad (18)$$

In eq 18, the adsorbed phase contribution to the variation of the total internal energy of the adsorption system is computed in a single simulation. The same parameter is computed with two different simulations using the energy differences in the *NVT* ensemble.

4. Energy slope method:

It is shown in the next section that by increasing the number of adsorbed hydrocarbon chains the enthalpy of adsorption of C_7 isomers in MFI- and MEL-type zeolites remains roughly constant. The sizable variations in the enthalpy of adsorption only occur when the more energetically favorable adsorption sites are filled and additional molecules are located in the less energetically favorable adsorption site. This observation has been used to develop the energy slope method for computing the heat and entropy of adsorption. For the adsorption of C_7 isomers in MFI- and MEL-type zeolites, it is assumed that the enthalpy of adsorption is not a function of the loading as long as the hydrocarbon chains are adsorbed in the particular adsorption sites. By increasing the loading, as soon as the most favorable adsorption site is completely filled and the next molecule is forced to sit within the less favorable adsorption site, the heat/entropy of adsorption suddenly changes to a new value. Considering the partial derivative in eq 10, this assumption suggests that while the molecules are filling a particular adsorption site the total internal energy of the zeolite plus the guest molecules should be a linear function of the loading. In the energy slope method, the partial derivative in eq 10 is estimated by the slope of the line describing the variation of the total internal energy of the zeolite plus the guest molecules as a function of the loading. When the most favorable adsorption site is completely filled (molecules are forced to fill the second favorable adsorption site), the slope of this line is expected to suddenly change to a new value. This

new value corresponds to the zeolite contribution to the enthalpy of adsorption associated with the second adsorption site. The fact that the enthalpy of adsorption of C_7 isomers in MFI- and MEL-type zeolites is a piecewise constant function of loading is the main reason for using a straight line to describe the changes in the total internal energy of the zeolite as a function of loading. However, in general, any analytical function that nicely fits into the total internal energy of the zeolite as a function of loading can be used in the energy slope method. In summary, to compute the heat and entropy of adsorption using the energy slope method the total internal energy of zeolite and adsorbed molecules should be calculated as a function of loading. This can be easily done by simulations in a canonical ensemble. An analytical function which accurately describes the variations in the total internal energy of zeolite and adsorbed molecules as a function of loading should be fitted to the data. The partial derivative in eq 10 as a function of loading is obtained by computing the derivative of the fitted analytical function with respect to the number of adsorbed molecules.

■ SIMULATION DETAILS

The adsorption of linear (heptane), monobranched (2-methylhexane), geminal dibranched (2,2-dimethylpentane), and nongeminal dibranched (2,4-dimethylpentane) C_7 isomers in MFI- and MEL-type zeolites is studied. The RASPA software is used for the simulations.[41] A cutoff radius of 12 Å is applied, and no tail corrections are used. The simulation box is made by $2 \times 2 \times 2$ rigid unit cells with periodic boundary conditions to ensure that the distance of two periodic images is at least twice the cutoff radius. The unit cell of MFI-type zeolite consists of four identical intersections connected by zigzag and straight channels, while the unit cell of the MEL-type zeolite is formed by two large intersections and two small intersections and there are only straight channels in between.[42] Simulations were performed in the grand-canonical and canonical ensemble at 400 K. At each Monte Carlo step of grand-canonical simulations an attempt is made to either displace, regrow, rotate, insert, or remove a randomly chosen hydrocarbon chain. Hydrocarbon chains are inserted/regrown using the Configurational-Bias Monte Carlo (CBMC) technique. For the simulations in the canonical ensemble, the number of hydrocarbon chains is fixed, and there is no insertion or
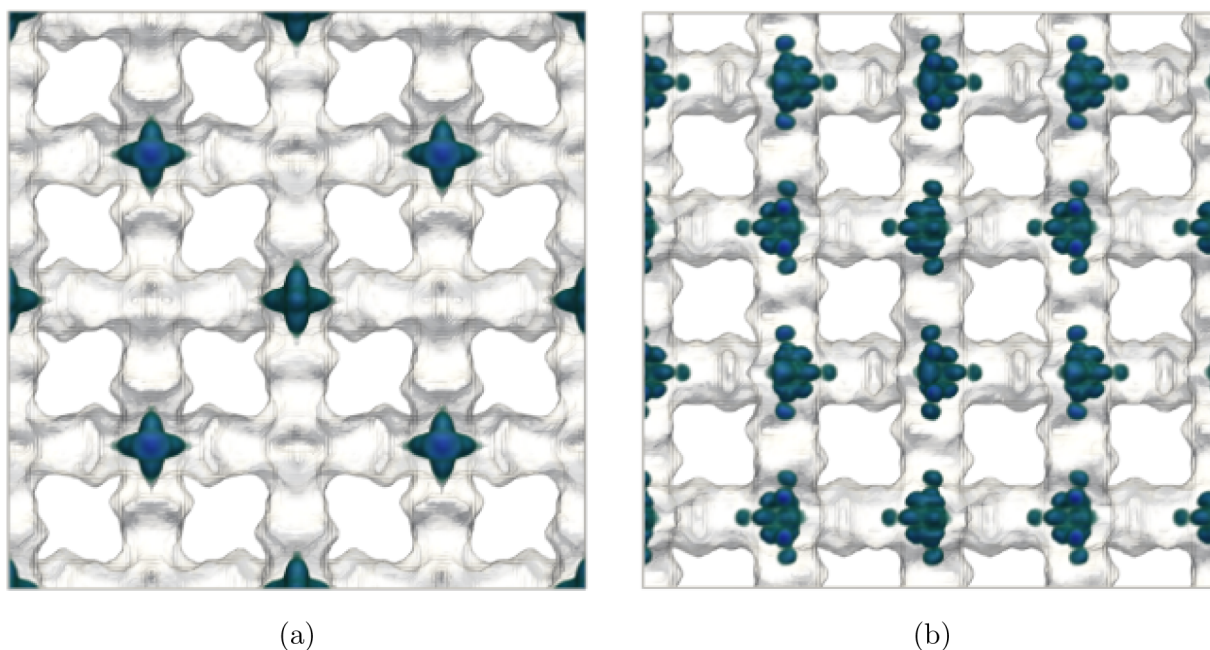
Figure 3. 3D histogram (density plot) of 2,4-dimethylpentane atomic positions at 400 K and 10 Pa in (a) MEL-type and (b) MFI-type zeolite.
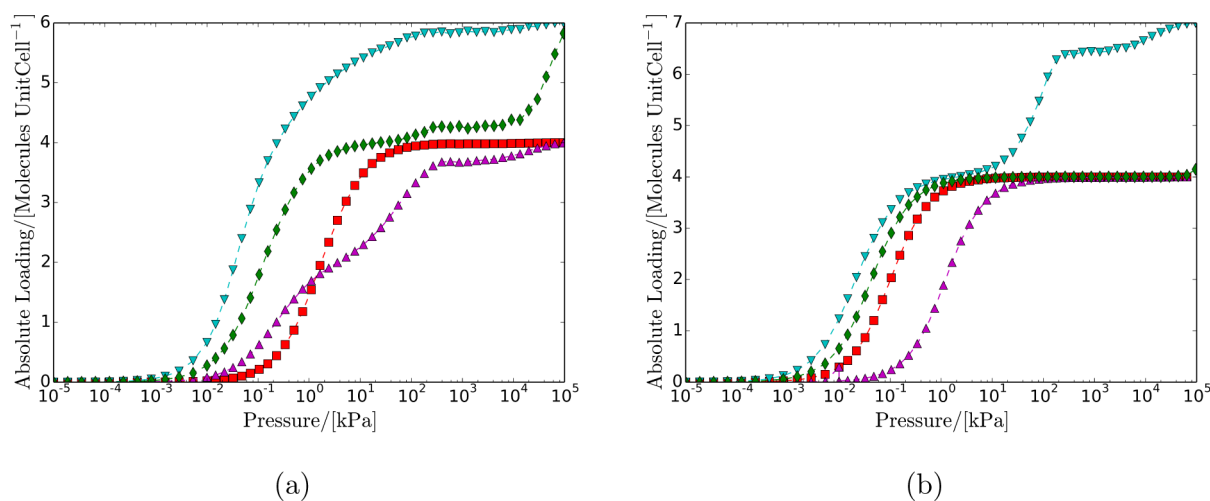

Figure 4. Adsorption isotherms of pure heptane (∇), 2-methylhexane ($\diamond$), 2,2-dimethylpentane ($\square$), and 2,4-dimethylpentane ($\triangle$) at 400 K as computed with CBMC simulations. (A) MEL-type and (B) MFI-type zeolite.

removal move. The number of Monte Carlo steps in a cycle is equal to the total current number of adsorbates in the system with the minimum of 20. Typical simulations are started with 0.2 to 0.5 million Monte Carlo cycles to equilibrate the system, followed by 0.5 to 5 million production cycles. The total production run is divided into five blocks, and the standard deviation of the block averages is used for the calculation of the error in computed properties. More details regarding the simulations can be found elsewhere.[15,43]

RESULTS

In Figures 2a and 2b, the enthalpy of adsorption of 2,4-dimethylpentane computed using the energy/particle fluctuations in the grand-canonical ensemble is plotted as a function of loading. The method works quite accurately at lower loadings; however, although all simulations have the same number of cycles, errors increase as the loading is increased. The width of the error bars expands significantly around the loading of four

molecules per unit cell. This is due to the fact that MC moves to place a bulky molecule like 2,4-dimethylpentane inside the narrow channels of these structures are accompanied by very unfavorable changes in the energy of the system and are rarely accepted. Therefore, when all the available intersections (four intersections per unit cell for both MFI-type and MEL-type zeolite) are filled, the acceptance rate for the insertion/removal move drops significantly. This results in poor statistics in the computation of fluctuations of eq 11 and eventually large error bars for the reported enthalpy of adsorptions. For loadings higher than four molecules per unit cell, it is not even possible to compute the fluctuations in some of the simulations even after 10 million MC cycles. It is instructive to study in more detail the variations in the enthalpy of adsorption as a function of loading. It is shown in Figure 2b that when less than four hydrocarbon chains per unit cell are present inside the MFI-type zeolite the enthalpy of adsorption of 2,4-dimethylpentane weakly depends on loading. However, in Figure 2a, there are
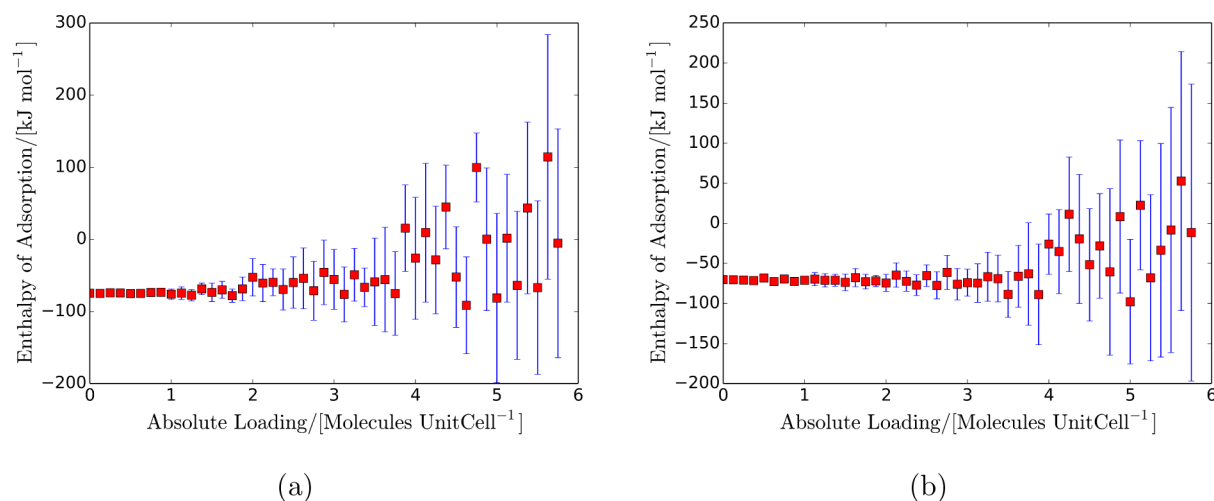
Figure 5. Enthalpy of adsorption of 2,4-dimethylpentane computed using the energy difference between two simulations in the canonical ensemble at 400 K. (a) MEL-type and (b) MFI-type zeolite. The error bars indicate the 95% confidence interval.
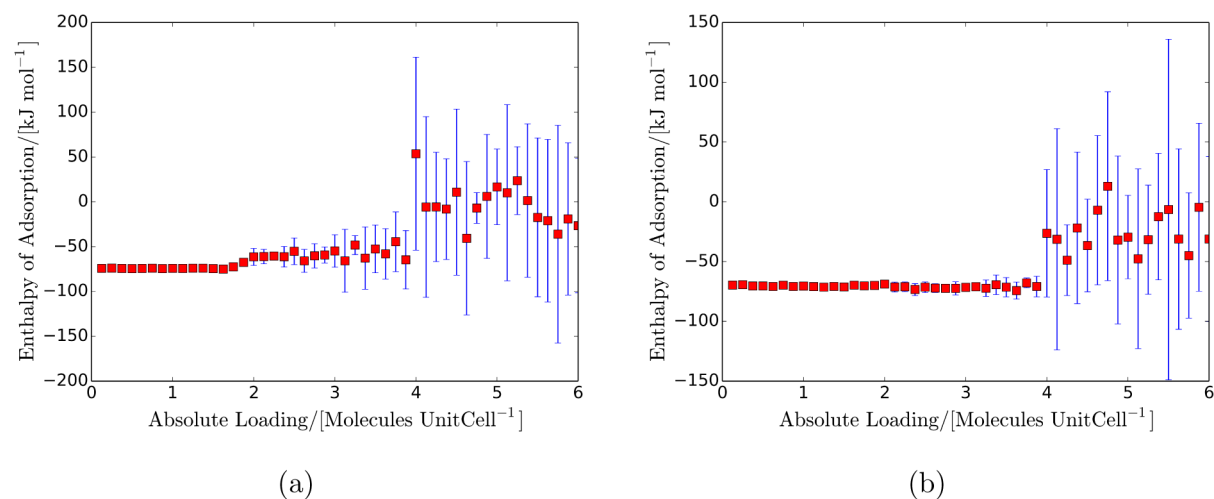

Figure 6. Enthalpy of adsorption of 2,4-dimethylpentane computed using the Widom test particle method in the canonical ensemble at 400 K. (a) MEL-type and (b) MFI-type zeolite. The error bars indicate the 95% confidence interval.

two plateaus below the loading of four molecules per unit cell. The first plateau lasts until the loading of roughly two molecules per unit cell. Then, the enthalpy of adsorption rises to the value of the second plateau and remains approximately constant up to the loading of four molecules per unit cell. The existence of only a single type of intersections in MFI-type zeolite and two different types of intersections in MEL-type zeolite is the source of different behavior. The large intersections of MEL-type zeolite are the most favorable adsorption site for the adsoption of 2,4-dimethylpentane. Therefore, the 2,4-dimethylpentane molecules are preferentially located in these intersections (Figure 3a). As soon as all the large intersections are filled (loading of two molecules per unit cell), additional molecules are forced to occupy the energetically less favorable adsorption sites (small intersections). The first plateau in Figure 2a corresponds to the adsorption in the favorable (large) intersections, and the second one is associated with the adsorption in less favorable (small) intersections. Accordingly, one can conclude that the intersections are far enough from each other that when the molecules are adsorbed only within them the adsorbate−adsorbate interactions are negligible compared to the host−adsorbate interactions.

Therefore, the enthalpy of adsorption weakly depends on loading. The enthalpy of adsorption is mainly determined by the topology of the particular adsorption site and the shape of adsorbate molecules. Consequently, the enthalpy of adsorption changes considerably only when the additional molecule is located in a new adsorption site. This explains why the enthalpy of adsorption of 2,4-methylpentane in MFI-type zeolite, with four identical intersections per unit cell, remains almost constant below the loading of four molecules per unit cell. It also explains why there are two plateaus below the loading of four molecules per unit cell in the plot of the enthalpy of adsorption versus loading of 2,4-methylpentane in MEL-type zeolite with two large and two small intersections per unit cell. The effect of this key feature of MEL-type zeolite can also be seen in the isotherm of 2,4-dimethylpentane (Figure 4a). There is a noticeable inflection in the 2,4-dimethylpentane isotherm, around the loading of two molecules per unit cell (Figure 4a). In Figures 4a and 4b, fugacity is converted to pressure using the Peng−Robinson equation of state.

In Figures 5a and 5b, the enthalpy of adsorption for 2,4-dimethylpentane computed from the energy difference of two simulations in the canonical ensemble is plotted as a function of
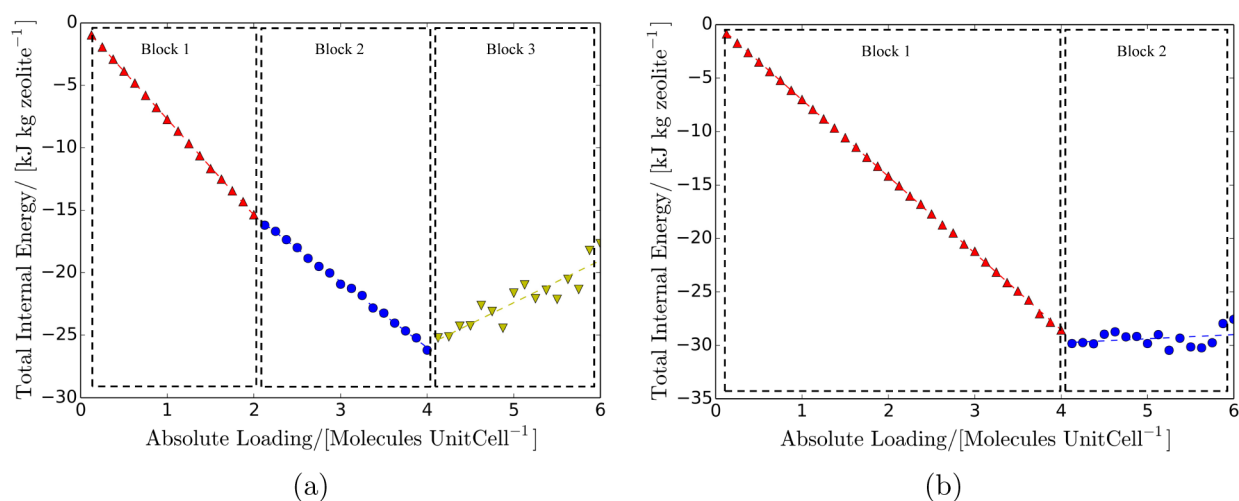
(a)   (b)

Figure 7. Total internal energy of zeolite as a function of loading of 2,4-dimethylpentane at 400 K. Different symbols (and colors) correspond to adsorption in different adsorption sites, and the dashed lines are the lines fitted to the data associated with each adsorption site. (a) MEL-type and (b) MFI-type zeolite.
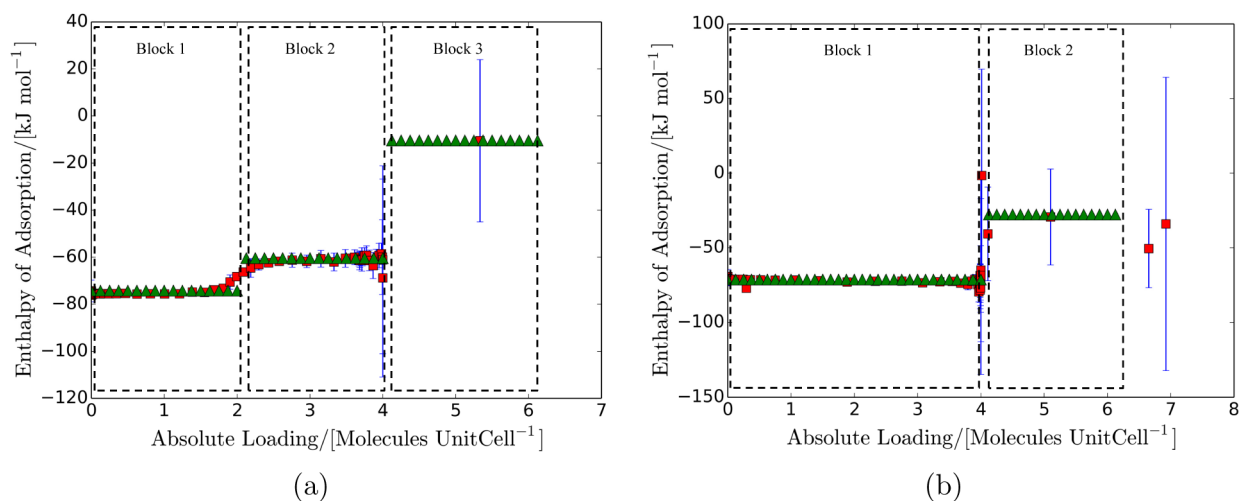

(a)   (b)

Figure 8. Comparison between the enthalpy of adsorption of 2,4-dimethylpentane computed from energy/particle fluctuations in grand-canonical ensemble (□) and using the energy slope in canonical ensemble at 400 K (△). (a) MEL-type and (b) MFI-type zeolite. The error bars indicate the 95% confidence interval.

loading. It is shown that as the loading is increased errors associated with the enthalpy of adsorption, calculated with this method, are sharply increased. As the loading rises, the difference between the two average internal energies in eq 16 becomes substantially smaller than either of them and approaches the typical fluctuations of the two averages. Hence, it is not surprising that the energy difference method performs poorly at higher loadings. Just as the method based on the energy/particle fluctuations, this method is not capable of providing an accurate estimation of the enthalpy of adsorption, at loadings that, due to lack of more favorable adsorption sites, molecules are located in the channels (the least favorable adsorption site). Due to the large error bars associated with this method, it is hardly possible to notice the change in the enthalpy of adsorption as the molecules start to fill a new adsorption site. As a result, the different adsorption regions that can be seen in Figures 2a and 2b cannot be distinguished easily when the energy difference is used instead of the energy/particle fluctuation method.

In Figures 6a and 6b, the values obtained for the enthalpy of adsorption of 2,4-dimethylpentane at various loadings using the Widom test particle method are presented. In the same way as the method based on the energy difference, the error bars associated with the Widom's test particle method are evidently larger when the loading is higher. This difficulty arises from the fact that even when the structure is empty most of the randomly chosen positions for the test hydrocarbon chain result in an overlap with the host atoms. These positions have very low Rosenbluth weight and consequently very limited contribution to the overall averages in eq 18. This problem becomes more significant as the length of the chain increases and as the loading is increased.

Various methods to compute the heat of adsorption at nonzero loadings have been investigated. Comparison between the results of different approaches coherently showed that the method based on energy/particle fluctuations in the grand-canonical ensemble can provide the best estimate for the heat and entropy of adsorption of C_7 isomers. However, even this approach was not appropriate to compute the aforementioned
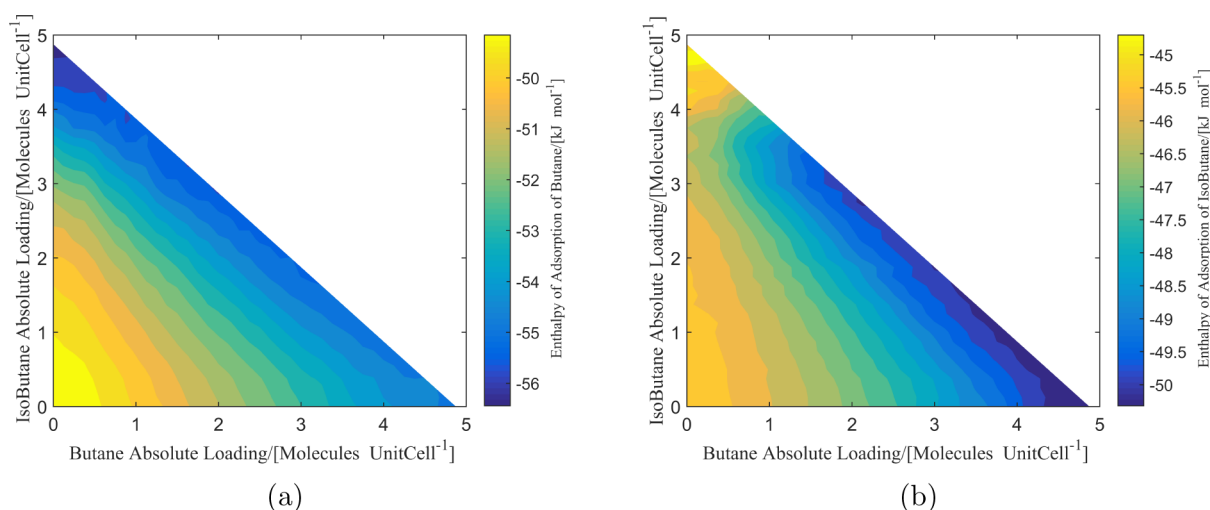
Figure 9. Enthalpy of adsorption of butane (a) and isobutane (b) computed with the energy slope method in the canonical ensemble at 400 K in MFI-type zeolite.

thermodynamic properties at loadings higher than four molecules per unit cell in MFI- and MEL-type zeolites. In this part, the energy slope method is used to enhance our estimation of the heat and entropy of adsorption after the inflection.

In Figures 7a and 7b, the total internal energies of MFI- and MEL-type zeolite systems as a function of the loading of 2,4-dimethylpentane are plotted (results for other C_7 isomers are shown in the Supporting Information). The plot of the total internal energy of the structure and the guest molecules as a function of the loading is divided into a number of blocks (Figures 7a and 7b). Since the MEL-type zeolite consists of three different adsorption sites, three blocks are considered in Figure 7a. The first block includes the total internal energy of the MEL-type zeolite with 0−2 molecules per unit cell. The second block contains the data for loadings between 2 and 4 molecules per unit cell, and the last one presents the data for loadings higher than four molecules per unit cell. In the same way, two blocks are considered in Figure 7b, the first one considering the data for the loadings below four molecules per unit cell and the second one including the data for the loadings larger than four molecules per unit cell. As shown in Figures 7a and 7b, in each block, the total internal energy of the structures and guest molecules varies approximately linearly with the loading. More interestingly, there is a clear difference between the slope of the lines fitted to the data in the different blocks. All above can confirm the theory that the enthalpy of adsorption of 2,4-dimethylpentane is roughly constant at each block. As a result, noticeable variations in the value of the enthalpy of adsorption occur only when the more energetically favorable adsorption sites are filled and additional molecules start to fill the less energetically favorable adsorption site. This is along the same line with what was expected from the enthalpy of adsorption data computed from the energy/particle fluctuations. Below the loading of four molecules per unit cell, two plateaus for the enthalpy of adsorption of 2,4-dimethylpentane in MEL-type zeolite and only one for the enthalpy of adsorption of 2,4-dimethylpentane in MFI-type zeolite have been perceived.

In the energy slope method, the zeolite contribution to the enthalpy of adsorption is computed from the slope of the best line fitted to the series of data points describing the variation of total internal energy of structure and guest molecules as a function of loading at each block. In Figures 8a and 8b, the results obtained from the energy slope method are compared with the ones computed from the method based on the energy/particle fluctuations (results for other C_7 isomers are shown in the Supporting Information). The values computed with the energy slope method are in good agreement with the results obtained from the energy/particle fluctuation method. The main advantage of the energy slope method over the energy/particle fluctuation method appears at loading near and above the inflection point where the method based on energy/particle fluctuations performs poorly. As discussed in previous sections, the performance of the energy/particle fluctuation method is directly related to the acceptance rate of the insertion/removal move. Significantly low acceptance rate of the insertion/removal move results in an inadequate performance of the energy/particle fluctuation method at loading near and above the inflection point. Using the energy slope method, all simulations are performed in a canonical ensemble where the number of adsorbate molecules is fixed (no insertion/removal move). Moreover, in the energy slope method, the main disadvantage of the energy difference method which is the difference in scales of either of the two averages in eq 16 and their difference is eliminated. In the energy slope method, instead of using the difference between the two average internal energies in eq 16 (which is highly vulnerable to even limited errors in computation of the average internal energies), the slope of the best fitted line to the set of data points corresponding to each block is used to compute the partial derivative in eq 10. The slope of this line is much less affected by the computational error in calculation of any of the average internal energies. Therefore, even at loadings higher than the inflection point, where the computational error in the calculation of average energies in the canonical ensemble is considerably high (Figures 7a and 7b), the energy slope method is still capable of providing an accurate estimation of the enthalpy of adsorption.

■ MIXTURES

The adsorption of the equimolar mixture of butane and isobutane at 400 K by MFI-type zeolite is considered to compare the different methods. While using the energy slope
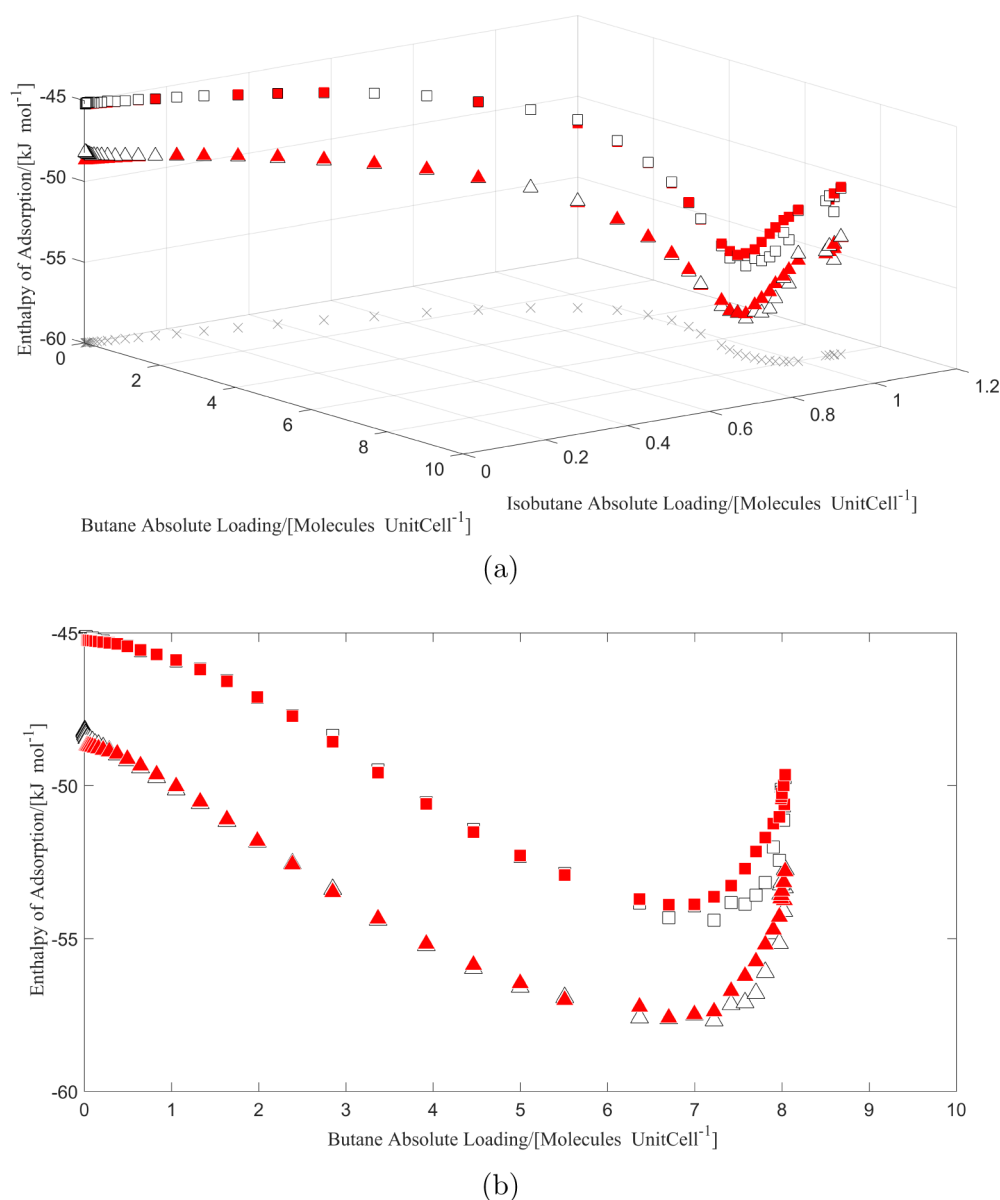
(a)

(b)

Figure 10. (a) Comparison between the enthalpy of adsorption of butane (△) and isobutane (□) computed with energy/particle fluctuations in the grand-canonical ensemble (open symbols) and using the energy slope in the canonical ensemble (closed symbols) at 400 K in MFI-type zeolite. Data points correspond to adsorption of an equimolar gas mixture of butane and isobutane at various pressures of the gas phase. The symbol (×) shows the loading of the components at each point. (b) 2D representation of Figure (a).

method, it is necessary to consider the total internal energy of the zeolite at a series of points, where the loadings of all of the components are constant except the one that its heat/entropy of adsorption should be computed. Therefore, a two-dimensional grid of data points is required to compute the heat/entropy of adsorption of each component in a binary mixture at different loadings. In the same way, if one is interested in computing the heat/entropy of adsorption at various loading of either of components in a binary mixture, using the method based on the energy/particle fluctuations, a two-dimensional grid including different partial pressures of each component is needed.

In contrast to the pure heptane isomers, by increasing the pressure of the gas phase the variations in the heat of adsorption of each component in the binary mixture of butane and isobutane occur gradually. The reason is that these molecules are much smaller than heptane isomers. Therefore,

they are not as tightly fitted within the different adsorption sites as the heptane isomers are. As a result, the difference between the heats of adsorption corresponding to different adsorption sites is less significant in this case. Moreover, in the case of the binary mixture, at low loadings, there are enough adsorption sites for both components to sit freely at their favorable adsorption sites. There is no competition between the different molecules to occupy an adsorption site. Consequently, their heats of adsorption in the mixture are almost equal to their heats of adsorption in the case of pure gas. As the total loading increases, molecules start to compete over the available adsorption sites. The molecule that fits better within the zeolite and has the higher stacking efficiency will occupy more adsorption sites. This component gradually takes over the adsorption sites that were occupied by the other component at lower loadings. This results in a gradual change in the heat of adsorption of both components. Considering all the above, to

compute the enthalpy of adsorption at each grid point with the energy slope method, the slope of the best fitted straight line passing through the grid point in question and its neighbors in the corresponding direction is used.

In Figures 9a and 9b, the heat of adsorption of butane and isobutane at various loadings of each component is presented. The enthalpy of adsorption of butane is always lower (more negative) than isobutane, implying that butane molecules fit better within the confinements provided by MFI-type zeolite and that they have more favorable stacking efficiency. Consequently, it can be concluded that MFI-type zeolite prefers the adsorption of butane over isobutane (Figures 10a and 10b). There is an agreement between the values for the heat of adsorption of both components computed with the energy slope method and the ones calculated from the method based on the energy/particle fluctuations (Figures 10a and 10b). For each data point, the discrepancy between the values computed with the two methods is less than each of their uncertainties (not shown here). The data presented in Figures 10a and 10b show that the applications of the energy slope method are not limited to the adsorption of pure gases. This method can also be used for the computation of the heat/entropy of mixtures. However, since an N dimensional grid of data points is needed to compute the heat/entropy of adsorption of all N components in a mixture, the computational effort associated with this method increases sharply with the number of components. Therefore, it might not be the most computationally efficient method while the heat of adsorption of all the components in a multicomponent mixture with a single set of partial pressures is of interest. In this case, if the acceptance rate for the insertion/removal move is high enough, the method based on energy/particle fluctuations would be more computationally efficient.

CONCLUSIONS

We systematically compared the effectiveness of various methods to compute the heat and entropy of adsorption at different loadings. We showed that at low loadings the method based on the energy/particle fluctuations in the grand-canonical ensemble is the most efficient method to compute the equilibrium enthalpy of adsorption of relatively large molecules such as C_7 isomers. However, none of the conventional methods discussed in the first part of this paper exhibited a satisfactory performance around the inflection point. We showed that the enthalpy of adsorption of C_7 isomers is a weak function of the loading, and the value of the enthalpy of the adsorption of C_7 isomers is mainly determined by the host–adsorbate interactions at the adsorption site which is being filled at the particular loading. Therefore, large changes in the value of the enthalpy of adsorption occur only when a more favorable adsorption site is completely filled and additional molecules are forced to fill the less favorable adsorption site. On the basis of this observation, we introduced the "Energy Slope" method to compute the enthalpy of adsorption. In this method, the variations in the total internal energy of zeolite with respect to the hydrocarbon loading are divided into different blocks. Each of these blocks corresponds to the adsorption of hydrocarbon chains in a particular adsorption site. Then, at each block the enthalpy of adsorption is computed using the slope of the best fitted straight line describing the variations in the total internal energy of zeolite as a function of the loading. Compared to commonly used energy difference method, the energy slope method is far less sensitive

to the computational error in calculation of the average energies. We showed that this method has the best performance among the currently available methods for the computation of the enthalpy of adsorption near the inflection point. We also investigated the application of the energy slope method for the calculation of the enthalpy of adsorption of mixtures. We showed that the use of either the energy slope method or the method based on the energy/particle fluctuations leads to identical results for the enthalpy of adsorption of a binary mixture of butane and isobutane. From the computational point of view, the energy/particle fluctuation method appears to be more efficient, when the acceptance rate for insertion/removal move is sufficiently high (loadings lower than the inflection point). This is due to the fact that, using the energy slope method, the number of simulations to compute the enthalpy of adsorption of all components in a mixture increases significantly as the number of mixture components increases.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b11606.

> The comparison between the heats of adsorption computed from the energy slope method and the ones computed with the method based on the energy/particle fluctuations for C_7 isomers (linear (heptane), mono-branched (2-methylhexane), and geminal dibranched (2,2-dimethylpentane)) in MFI- and MEL-type zeolites (PDF)

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Notes
The authors declare no competing financial interest.

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