Force Field Parametrization through Fitting on Inflection Points in Isotherms

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We present a method to determine potential parameters in molecular simulations of confined systems through fitting on experimental isotherms with inflection points. The procedure uniquely determines the adsorbent-adsorbate interaction parameters and is very sensitive to the size parameter. The inflection points in the isotherms are often related to a subtle interplay between different adsorption sites. If a force field can predict this interplay, it also reproduces the remaining part of the isotherm correctly, i.e., the Henry coefficients and saturation loadings.

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The effect of confinement on adsorption and diffusion is still poorly understood despite its importance for practical applications. The performance of molecular sieves in separation and catalytic processes depends critically on the match between sieve topology and the shape and size of the adsorbate [1]. It is therefore of considerable industrial importance to explore the adsorption and diffusion of linear and branched alkanes in different topologies using realistic simulations at the microscopic level [2]. Different parameter sets yield values of diffusivities that differ not only quantitatively but also show a different qualitative dependence on the molecular loading [3]. The critical unresolved question follows: Which of these parameter sets is the most physically realistic one? Here, we hope to remedy this situation.

Potential parameter sets can be checked only via comparison with experiment. For diffusion the comparison is complicated by large discrepancies between microscopic and macroscopic experimental measurement methods, and even within the same measurement technique there are many disagreements between various studies. However, adsorption results seem to be well established and provide a more solid basis for a detailed comparison between experiment and simulation. Moreover, a large amount of data exists on adsorption of hydrocarbons in siliceous zeolites.

Silicalite-1 (Fig. 1) consists of a three-dimensional pore system with straight parallel channels, intersected by zigzag channels [4]. The channels of approximately 6 Å in diameter lead to shape selectivity, especially for the isomers of hexane, which have dimensions close to the silicalite-1 pores. The linear channels intersect with the zigzag channels 4 times per unit cell. Interestingly, for *n*-heptane and for the branched alkanes in silicalite-1 a kink in the isotherm is observed [5]. This inflection is directly related to the number of intersections in the structure and occurs at *exactly* four molecules per unit cell. As these inflections are caused by a subtle interplay between the size and configuration of the molecule and two different adsorption sites, it becomes clear that the adsorbent-adsorbate potential size parameter σ is the most sensitive parameter in the force field.

In general, adsorption in any periodic structure has steps or kinks. The reason is that steps and kinks signal transitions between different types of packing and are similar to adsorption on substrates; at low loadings the packing of molecules is often imposed by the sieve while at higher loading such packing is only by exception commensurate with the packing of the adsorbed molecules. This change in packing is reflected in a kink or plateau in an adsorption isotherm. To illustrate our method we exploit the close physical connection between potential parameters and inflection points in isotherms to

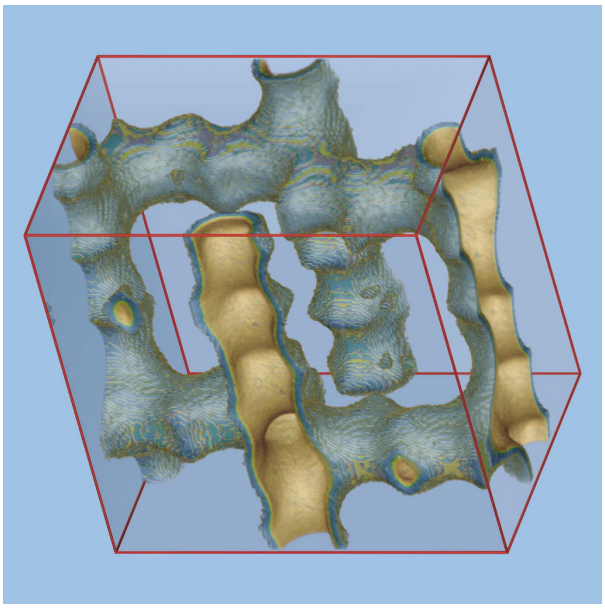

FIG. 1 (color online). Silicalite-1 has linear channels intersected with zigzag channels 4 times per periodic unit cell.

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optimize a force field for adsorption and diffusion of alkanes in siliceous zeolites.

We use the united-atom model [6] and consider the CH_x groups as single interaction centers with their own effective potentials. The beads in the chain are connected by harmonic bonding potentials. A harmonic cosine bending potential models the bond bending between three neighboring beads, a Ryckaert-Bellemans potential controls the torsional angle. The beads in a chain separated by more than three bonds interact with each other through a Lennard-Jones potential. The Lennard-Jones potentials are shifted and cut at 12 Å. The interactions between the rigid framework and the guest molecules are assumed to be dominated by the oxygen atoms [7]. Some of the alkane-alkane interactions are taken from Ref. [8].

In adsorption studies, the natural ensemble to use is the grand-canonical ensemble (or μ, V, T ensemble). The adsorbed phase is simulated by specifying the temperature T, the volume V, and the chemical potential μ. At these conditions the number of adsorbed molecules is computed. We convert the imposed chemical potential to the corresponding pressure using the Peng-Robinson equation of state. To successfully insert and remove molecules we use the configurational-bias Monte Carlo technique [9], in which chains are grown bead by bead biasing the growth process towards energetically favorable configurations. This bias is exactly removed by adjusting the acceptance rules. Further details are given in Ref. [5].

In Fig. 2 we show the influence of the size parameter $\sigma_{O_x\text{-}CH}$ on the inflection of 2-methylpropane (CH_3-CH[-CH_3]-CH_3) in silicalite-1. The experimental data are taken from Ref. [10] and simulation data from Refs. [5,11–14]. The models of Smit *et al.* and Vlugt *et al.* exaggerated the inflections because their size parameters were too large. The models of Pascual *et al.,* June *et al.,* and the all-atom consistent valence force field did not show a clear inflection at all because their size parameters were too small. Although the size parameters differ by less than 10%, the shape of the isotherms is dramatically different. The model of June *et al.* uses a small value of $\sigma = 3.364$ Å, the anisotropic united atom model uses $\sigma_{O\text{-}CH_3} = 3.30$ Å, $\sigma_{O\text{-}CH_2} = 3.23$ Å, and $\sigma_{O\text{-}CH} = 3.18$ Å. The models of Vlugt *et al.* and Smit *et al.* use a fixed σ; $\sigma_{O\text{-}CH_3} = \sigma_{O\text{-}CH_2} = \sigma_{O\text{-}CH} = 3.60$ Å for the Vlugt model, and $\sigma_{O\text{-}CH_3} = \sigma_{O\text{-}CH_2} = \sigma_{O\text{-}CH} = 3.64$ Å for the Smit model. The model proposed in this work uses $\sigma_{O\text{-}CH_3} = 3.48$ Å, $\sigma_{O\text{-}CH_2} = 3.58$ Å, and $\sigma_{O\text{-}CH} = 3.92$ Å Å. It yields exact overlap with experimental data and the inflection is reproduced faithfully. We stress that only a single strength or size parameter pair is able to describe the inflection and the entire isotherm properly. This is in contrast with the common belief that for each value of σ there is a corresponding ϵ that can describe the isotherm correctly [8,15].

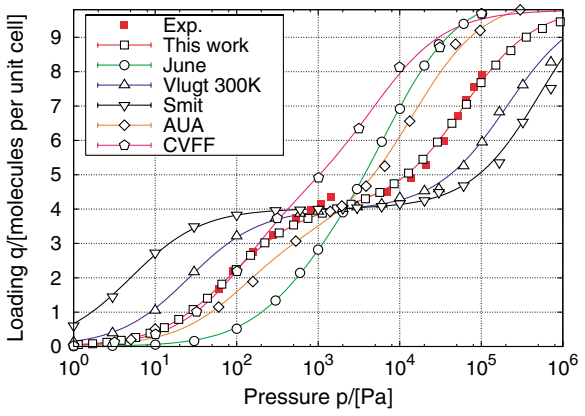

FIG. 2 (color online). Isotherms of 2-methylpropane at 308 K in silicalite-1 compared to various computational models.

In practice we proceed as follows. A reasonable starting size parameter is chosen. For this parameter we iteratively search for the corresponding strength parameter ϵ that matches the experimental data at a pressure significantly below the inflection. The entire isotherm is then followed for increasing pressure until a deviation from the experimental data is observed. The "updated" size parameter is then found by choosing a higher value for a deviation to the left of the experimental data, and by choosing a lower value for the size parameter for a deviation to the right of the experimental data. This scheme proceeds iteratively until the entire experimental isotherm is accounted for. The adsorbent-adsorbate parameters obtained from fitting to inflections are listed in Table I and the errors in the size and strength- parameters are limited to no more than 0.01 Å and 5 K, respectively.

Ethane, *n*-heptane, and 2-methylpropane exhibit isotherms of the Brunauer type-VI in silicalite-1. Experimental data are taken from Sun *et al.* [10,16], Choudhary *et al.* [17], and Zhu *et al.* [18,19]. Ethane

TABLE I. Force field guest-host and guest-guest interactions of hydrocarbons in charge neutral nanoporous materials. Lennard-Jones parameters, ϵ/k_B [K] in top row, σ [Å] in bottom row of each field. Some of the alkane-alkane interactions are taken from Ref. [8] and optimized to reproduce vapor-liquid coexistence curves of the phase diagrams. The parameters may be combined with any reasonable internal interaction model.

	O	CH_4	CH_3	CH_2	CH	C
CH_4	115.00	158.50	130.84	94.21	51.91	11.26
	3.47	3.72	3.74	3.84	4.17	4.87
CH_3	93.00	130.84	108.00	77.77	42.85	9.30
	3.48	3.74	3.76	3.86	4.19	4.90
CH_2	60.50	94.21	77.77	56.00	30.85	6.69
	3.58	3.84	3.86	3.96	4.30	5.03
CH	40.00	51.91	42.85	30.85	17.00	3.69
	3.92	4.17	4.19	4.30	4.67	5.46
C	10.00	11.26	9.30	6.69	3.69	0.80
	4.56	4.87	4.90	5.03	5.46	6.38

(CH_3-CH_3) shows a small inflection point in the adsorption isotherm at high loading [20]. The $\epsilon_{O\text{-}CH_3}$ and $\sigma_{O\text{-}CH_3}$ are uniquely obtainable from the ethane isotherm (Fig. 3, top). When the channel interiors are occupied, the probability distribution shows a remarkable order: a repeating pattern of ethane molecules "locked" in the zigzag channels between two intersections. The $\epsilon_{O\text{-}CH_2}$ and $\sigma_{O\text{-}CH_2}$ are obtained from *n*-heptane. The inflection behavior of *n*-heptane (CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3) is well established [9,16]. Smit and Maesen explained this effect in terms of *commensurate freezing: n*-heptane has a size commensurate with the size of the zigzag channel. At high pressures the molecules shift from a random distribution to a distribution where the molecules are localized exclusively in the channels and not at the intersections. Various branched molecules show inflections for another reason [5]. The 2-methylpropane preferentially adsorbs at the intersections. At a loading of four molecules per unit cell the intersections are fully occupied and additional molecules have to be pushed into the channels requiring a significantly higher driving force [21]. The $\epsilon_{O\text{-}CH}$ and $\sigma_{O\text{-}CH}$ are uniquely obtainable from the isotherm of 2-methylpropane (Fig. 3, bottom).

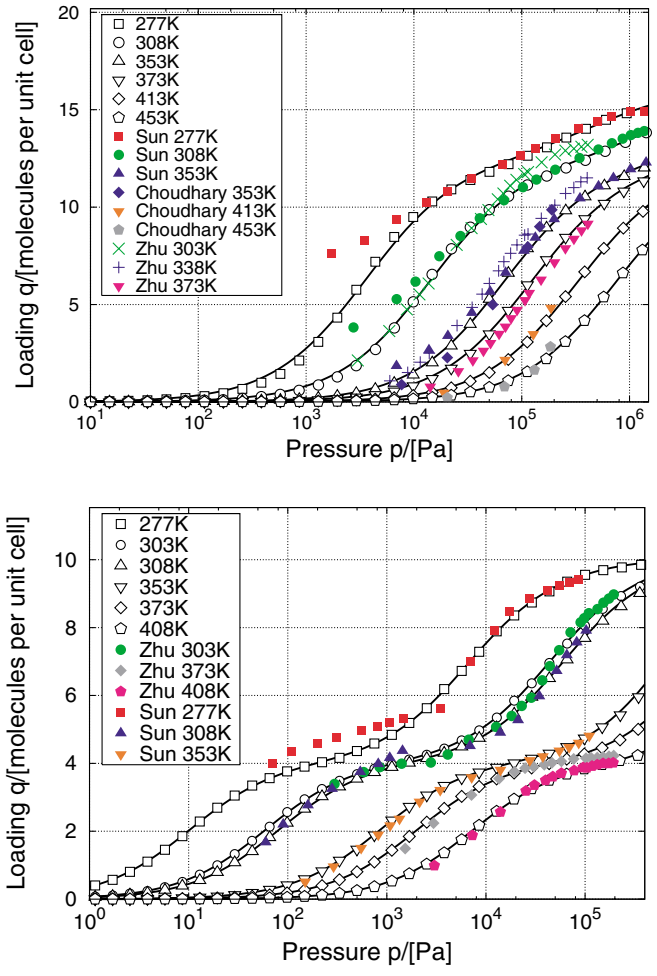

FIG. 3 (color online). Fitting to the isotherms of ethane (top), and 2-methylpropane (bottom) in silicalite-1 at various temperatures.

For 3-methylpentane (CH_3-CH_2-CH[-CH_2]-CH_2-CH_3) in silicalite-1 (Fig. 4) the prediction of our isotherms obtained from simulation is in excellent agreement with Zhu *et al.* [22] and Jolimaitre *et al.* [23]. Thus, the agreement between simulated and experimental data on the adsorption of molecules that are not part of the calibration set is remarkably good. The accuracy of the model and the successful extension to other sorbates, mixtures, and topologies will be published elsewhere.

In Table II we compare our simulation results on low-coverage adsorption properties with the experimental results on silicalite-1 from Arik *et al.* [24]. It is also noteworthy that Arik's data set was not part of the set used as a basis for our force field. The quantitative agreement and consistency on low-coverage properties of simulated and experimental data are therefore truly remarkable. The value of $\sigma_{O\text{-}CH_x}$ also has an effect on the maximum loading and packing efficiency. De Meyer *et al.* [25] performed experiments of long chain *n*-alkanes in silicalite. Experiments show that the maximum packing is approximately 53.2 carbon atoms per unit cell for *n*-C_{14}, while the current model yields 52.5 carbon atoms per unit cell in excellent agreement with experiment.

Although the fitting procedure is applied to hydrocarbons, it is by no means restricted to alkanes. In the literature many isotherms with inflections can be found and these molecules are easily included. Examples include adsorbates in clays [26], aromatic molecules in silicalite, gases, alkanes, and cyclo-alkane isomers in $AlPO_4-5$, adsorbates in silica gels, water, and methanol in ferrierite, and benzene, acetonitrile, water in mesoporous materials like MCM-41 silica. For systems that lack inflection data, the strategy is to use an initial set of parameters to identify for which type of sieve an inflection can be expected. Experiments can then focus on accurately determining the location of such an inflection

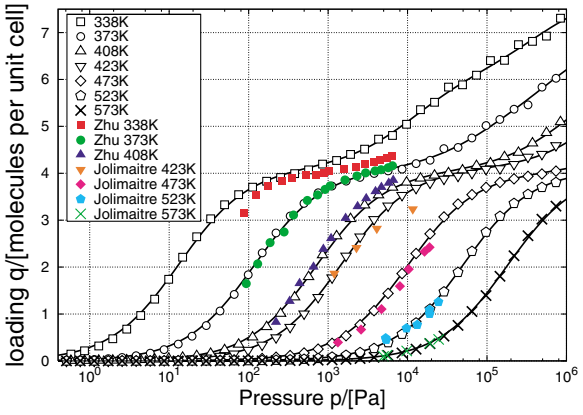

FIG. 4 (color online). Prediction of the isotherm of 3-methylpentane in silicalite-1 at various temperatures.

TABLE II. Comparison of our simulation results of low-coverage properties in silicalite-1 with the experimental results of Arik *et al.* [24]. Both the Arik and the simulation Henry coefficients K_H of the linear alkanes have been fitted to $K_H = K_\infty e^{-\Delta H/RT}$ in the temperature range $T = 473$–673 K. Here, K_∞ denotes the preexponential Henry coefficient, ΔH the enthalpy of adsorption, and $R = 8.314\,51$ J/mol/K the gas constant. The entropy ΔS per carbon number is related to the slope of $\ln(K_\infty)$ plotted as a function of carbon number (CN) [24].

CN	K_H 573 K [mol/kg/Pa]		K_∞ [mol/kg/Pa]		$-\Delta H$ [kJ/mol]	
	Sim.	Expt.	Sim.	Expt.	Sim.	Expt.
5	3.04×10^{-6}	2.99×10^{-6}	2.33×10^{-11}	2.64×10^{-11}	56.13	55.7
6	6.10×10^{-6}	5.93×10^{-6}	6.07×10^{-11}	6.07×10^{-11}	65.87	66.0
7	1.23×10^{-5}	1.22×10^{-5}	1.53×10^{-12}	1.29×10^{-12}	75.77	76.7
8	2.43×10^{-5}	2.49×10^{-5}	3.67×10^{-13}	3.25×10^{-13}	85.82	86.6
9	4.61×10^{-5}	4.73×10^{-5}	8.59×10^{-14}	8.41×10^{-14}	95.81	96.1

Relation	Sim.	Expt.
$-\Delta H = \alpha \mathrm{CN} + \beta$	$\alpha = 9.93$	$\alpha = 10.1$
$-\Delta S = \gamma \mathrm{CN} + \delta$	$\gamma = 11.65$	$\gamma = 11.99$
$-\ln(K_\infty) = -A\Delta H + B$	$A = 0.141, B = 16.54$	$A = 0.143, B = 16.4$

rather then determining "at random" entire isotherms for many different systems.

The fitting to well-established inflection points in the isotherms has many advantages and overcomes problems that have so far impeded the development of more accurate force fields. We obtain a unique set of parameters that all directly relate to a well-defined physical property. Therefore, the parameters are much better transferable to other systems than parameters from previous attempts. By explicitly fitting to entire adsorption isotherms we guarantee the proper reproduction of properties such as Henry coefficients, heats of adsorption, adsorption entropies, and saturation loadings.

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