

Structural changes in nanoporous solids due to fluid adsorption: thermodynamic analysis and Monte Carlo simulations†

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A thermodynamic analysis based on the osmotic ensemble scheme enables the prediction of structural changes occurring in silicalite-1 zeolite upon halocarbon molecule adsorption.

Open framework nanoporous materials are gaining increasing interest on account of their exceptional adsorption properties. Zeolites are now widely used in industry as molecular sieves and catalysts. More recently, metal–organic framework (MOF) materials were shown to be very promising for such applications as carbon dioxide or hydrogen capture and storage.^{1,2} Molecular simulations can help in understanding the adsorption process at the molecular level,³ and contribute to the design of new materials.⁴ There is ample literature on fluid adsorption in zeolites. New Monte Carlo algorithms allow the simulation of systems that a few years ago were considered impossible to study *via* computer simulations (for instance long alkane chains,⁵ halocarbon or aromatic molecules^{6,7} and water⁸). In most cases, a rigid framework was assumed for the zeolitic adsorbent. Framework flexibility is generally assumed to play a role in transport properties,⁹ but not much on thermodynamics. However, a few examples were reported of “stepped” adsorption isotherms, instead of the usual continuous Langmuir (or type I) isotherm. This was the case for nitrogen,¹⁰ benzene¹¹ and *p*-xylene^{12–14} in silicalite-1 for instance, and was attributed to a structural transition of the host framework taking place upon fluid adsorption. With the advent of “soft” hybrid adsorbents such as MOFs, it is likely that framework–adsorbate coupling will become more frequent than in the relatively stiff zeolite solids.¹⁵

The need exists then to devise a method that enables the description and prediction of structural changes in adsorbent upon fluid adsorption.¹⁶ A direct route would of course be to simulate the fully flexible solid in presence of various amounts of fluid adsorbate. Unfortunately the existing forcefields are not always appropriate for such simulations.

On the one hand, the framework potentials were most often designed for lattice dynamics computation, and it is not guaranteed that they will properly address a phase transition phenomenon of the solid originating from a coupling of the host with the adsorbed fluid.

On the other hand, the available adsorbate–framework forcefields were usually developed from a simple extension of effective two-body potentials used for liquid-state simulations. Moreover the latter forcefields were parameterised assuming a rigid adsorbent framework. Developing a general forcefield that reconciles the concepts and methods of mineralogy and liquid state physical chemistry is a difficult task, though some groups have made recent progress in this direction.¹⁷

We propose here a thermodynamic analysis of the framework–adsorbate coupling, based on the so-called “osmotic” statistical ensemble. This method makes use of standard Grand Canonical Monte Carlo simulations only. It allows to compute the thermodynamic potential of the combined host + fluid system, and thus to predict the occurrence of a structural change upon fluid adsorption. The inputs of this method are the crystallographic structures of the host solid phases and their relative lattice energies.

Our case study is silicalite-1 zeolite¹⁸ which has been observed in three different crystalline structures: MONO (the stable monoclinic structure for the bare zeolite at room temperature),¹⁹ ORTHO (observed at high temperature and also when filled by some guest molecules)^{20,21} and PARA (observed at high loading of aromatic molecules).^{12,22} A stepped adsorption isotherm has been recently reported in the case of tetrachloroethene (4CE).^{23,24} Structural changes of the host framework were reported but no conclusion was drawn on which transition was responsible for this step. Interestingly enough, the adsorption isotherm for a similar molecule: 1,1,2-trichloroethene (3CE), was smooth, although zeolite structural changes were also reported.^{23,24} We have thus studied in some detail the 4CE/3CE adsorption process in silicalite-1 in order to test our method and try to shed some light on the experimental findings.

The “osmotic” statistical ensemble initially proposed by Brennan and Madden,²⁵ and further developed by de Pablo and co-workers,²⁶ was designed to describe a physical situation in which a solid system A (for instance a polymer network with N_A atoms) is subject to a mechanical constraint σ and is interacting with a fluid B (an adsorbed gas for instance) in equilibrium with an external reservoir at a given chemical potential μ_B . The constant (N_A, σ, μ_B, T) ensemble transforms, in our case, into an $(N_{\text{host}}, \sigma, \mu_{\text{ads}}, T)$ ensemble, and the constraint σ is simply equal to the external pressure, which is the total pressure of the reservoir in equilibrium with the adsorbed phase.

The corresponding thermodynamic potential, associated with the osmotic ensemble, is:²⁷

$$\Omega_{\text{OS}} = U - TS - \mu_{\text{ads}}N_{\text{ads}} + \sigma V \quad (1)$$

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where N_{ads} is the number of adsorbed molecules. U is the sum of two contributions: the lattice framework energy (hereafter named U_{host}) and the adsorbate–adsorbate and adsorbate–zeolite interaction energy: U_{fluid} . This latter energy corresponds to the energy calculated in GCMC simulation. Ω_{OS} can thus be related to the Grand Canonical potential Ω in the following way:

$$\Omega = U_{\text{fluid}} - TS - \mu_{\text{ads}}N_{\text{ads}} \quad (2a)$$

$$\Omega_{\text{OS}} = \Omega + \sigma V + U_{\text{host}} \quad (2b)$$

The GC potential Ω can be computed from its derivatives, following Peterson and Gubbins.²⁸

The method proposed here consists of calculating the fluid adsorption isotherms in the different *rigid* host structures in the Grand Canonical ensemble, and to extract the corresponding *osmotic grand potential*, using eqn (2b). This allows the prediction of the relative stability of each structure whatever the pressure.

As stated above, we need as an input the lattice energy of the host framework in its different crystallographic states. The MONO structure of silicalite-1 is the most stable one and was chosen as the energy reference. The lattice energy difference between MONO and ORTHO structures has been determined experimentally to be $\sim 3.7 \text{ kJ mol}^{-1}$.²¹ To our knowledge, such data does not exist for the ORTHO–PARA transition. We assumed here that the difference of energy between ORTHO and PARA was the same as that between MONO and ORTHO.

We then performed Grand Canonical Monte Carlo simulations in each zeolite structure. To ensure convergence, pre-insertion²⁹ and rotational^{7,30} bias were used. All the intermolecular interactions (adsorbate–adsorbate and adsorbent–adsorbate) were modeled by the sum of an electrostatic term and dispersion–repulsion potential. Ewald summation technique has been applied. Parameter values can be found in the ESI.† Unspecified parameters can be obtained with the Lorentz–Bertholot mixing rule. As stated above, zeolitic frameworks are considered rigid. Zeolitic structures were taken from experimental diffraction results obtained by Van Koningsveld *et al.*^{19,20,22} The simulation box consists of eight unit cells of silicalite-1 with periodic boundary conditions. Each run lasted for 150 million steps.

The adsorption isotherms calculated by GCMC simulation in each of the three structures are presented in Fig. 1 and 2 for 4CE and 3CE, respectively. In the case of 4CE adsorption, isotherms calculated in MONO and ORTHO structures are very similar: both show an inflection point around four molecules per unit cell. In the PARA structure the isotherm is of type I. At very high pressure, all structures lead to a maximum of loadings of eight molecules per unit cell. None of the isotherms reproduce the step observed experimentally. In the case of 3CE adsorption, the isotherms are very similar for the three structures; the MONO structure leading to lower adsorption quantities.

Fig. 1 and 2 show the computed Ω_{OS} of the system in the three structures of the zeolite in the full pressure range. For both 4CE and 3CE adsorption, the MONO structure appears to be the most stable state at low loadings. An initial structural

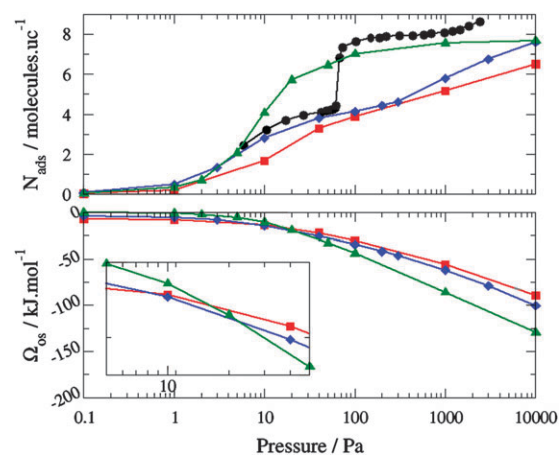


Fig. 1 Tetrachloroethene adsorption isotherms calculated in the grand ensemble (upper panel) at 300 K in the three known silicalite-1 structures: MONO (red squares), ORTHO (blue diamonds) and PARA (green triangles), compared to experiments (black circles).^{23,24} The corresponding grand potential is represented in the lower panel for the three structures.

transition is observed for 4CE at $P = 8 \text{ Pa}$ followed by a second at 22 Pa. Since the adsorbed amount at 22 Pa is higher in PARA than in ORTHO (7 molecules uc^{-1} compared to 4), this second structural change induces a jump in the adsorption isotherm. Two transitions are also found during the adsorption of 3CE: the first occurs at 2.3 Pa and the second at 150 Pa. By comparing the loadings in the different structures at the transition pressures, our model predicts a clear jump in the adsorption isotherm of 4CE at 22 Pa and a simple type I isotherm for 3CE, in very good agreement with the experimental findings.

Next, we propose another strategy which consists of directly simulating structural changes during the simulation run. In such a simulation the number of degrees of freedom of the host material is limited to a set of rigid structures. This corresponds to a sub-ensemble of the osmotic ensemble. A new Monte Carlo step was implemented: it consists of a random swap

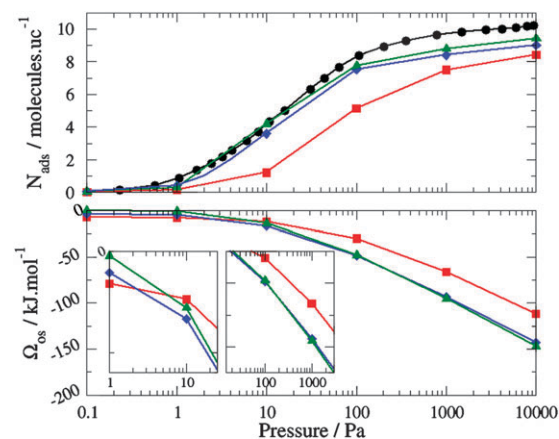


Fig. 2 Trichloroethene adsorption isotherms calculated in the grand ensemble (upper panel) at 300 K in the three silicalite-1 known structures: MONO (red squares), ORTHO (blue diamonds) and PARA (green triangles), compared to experiments (black circles).^{23,24} The corresponding grand potential is represented in the lower panel for the three structures.

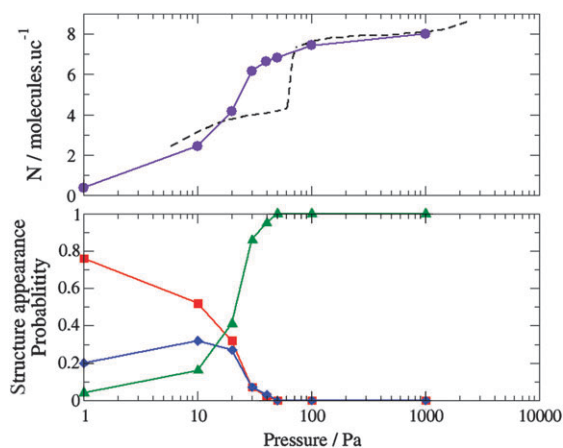


Fig. 3 Tetrachloroethene adsorption isotherm calculated in the osmotic sub-ensemble (see text) using the three silicalite-1 known structures (MONO, ORTHO and PARA) at 300 K (solid line) compared to experiments^{23,24} (dashed line). The probability of occurrence of each structure (MONO (red squares), ORTHO (blue diamonds) and PARA (green triangles)) is given in the lower panel.

between two of the three rigid structures at fixed guest molecules relative positions. The system is then allowed to switch between the three rigid experimental structures of silicalite-1. The simulation box is now limited to one unit cell. The adsorption isotherm obtained in this ‘osmotic sub-ensemble’ is plotted in Fig. 3 and compared to experiments. Even though the agreement with experiment is not perfect, a clear jump in the isotherm is again obtained.

To characterize the structure of the adsorbent, the proportion of steps spent in each structure is also represented in Fig. 3. At low pressure silicalite-1 is mainly in the monoclinic phase (80%). The proportion of MONO decreases slowly in favour of ORTHO and PARA. Around 40 Pa a sharp transition towards the PARA structure is observed. This transition is clearly correlated with the jump in the adsorption isotherm. These results are in perfect agreement with the grand potential calculation.

To our knowledge this is the first time that an adsorption isotherm has been computed, taking into account a structural change effect of the adsorbent material. Our approach can be used with a lattice energy calculation (that is easy to achieve) without the need of a forcefield parametrisation for the porous material. Even if this approach is limited to known structures of the material, we believe it is an interesting alternative to predict phase transition during adsorption process.

The osmotic ensemble provides a framework for modelling adsorption properties of flexible porous media. Simulations with fully flexible materials are now in progress. However the parametrisation of the forcefield appears to be a difficult task, for reasons stated above. Starting from the potential model of Demontis *et al.*³¹ we have performed a systematic search in the potential parameter space to find a set that could describe the relative stability of the three structures. No satisfactory parameters set have been obtained yet. Work is still in progress in this direction. The method proposed here allows the calculation of adsorption properties without such parametrisation, in the limit of a finite number of adsorbent structures. Applied to

silicalite-1, it appears to be able to predict structural changes, and to reproduce the jump resulting from one of these transitions.

The proposed methodology is very general and can be applied to any type of guest/host systems.

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