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A COMPARISON OF POTENTIAL FUNCTIONS FOR MOLECULAR DYNAMIC SIMULATION OF METHANE SORPTION IN THE SILICALITE

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In order to make the best choice, two types of a force field have been studied to access a possibility of application of one of them to simulation of adsorption and transport processes in the silicalite (synthetic zeolite)-methane system. To accomplish this, the molecular dynamic technique implemented in the LAMMPS package was used. Priority criteria of the choice were retention of the structure completeness during long simulation runs, the system's stability, the possibility of simulation of a separate good-sized zeolite cluster without using periodic boundary conditions for multiplying zeolite's lattice in space. For the force-field, which met these requirements, some structural, thermodynamic and transport characteristics of the system were calculated. Radial and angular distribution functions for different atom pairs and triplets were obtained for both the pure zeolite and the silicalite-methane system. A good agreement of all obtained characteristics with literature data of numerical and natural experiments was achieved.

Keywords: silicalite, ZSM-5 zeolite, methane, molecular dynamic, sorption, potential function

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СРАВНЕНИЕ ПОТЕНЦИАЛЬНЫХ ФУНКЦИЙ ДЛЯ МОЛЕКУЛЯРНО-ДИНАМИЧЕСКОГО МОДЕЛИРОВАНИЯ СОРБЦИИ МЕТАНА В СИЛИКАЛИТЕ

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С целью оптимального выбора, в работе исследованы два вида силового поля для оценки возможности их применения к моделированию процессов поглощения и переноса в системе силикалит (синтетический цеолит) – метан; для этого использован метод молекулярной динамики, реализованный в пакете LAMMPS. Приоритетными критериями выбора были сохранение целостности структур при длительных расчетах, стабильность системы, возможность моделирования отдельного кластера цеолита большого размера без использования периодических граничных условий для размножения решетки в пространстве. Для потенциала, удовлетворившего этим требованиям, проведен расчет структурных, термодинамических и транспортных характеристик системы. Рассчитаны радиальная и угловая функции распределения частиц для различных пар и троек атомов для чистого цеолита и для двухкомпонентной системы силикалит – метан. Достигнуто хорошее согласие всех полученных характеристик с литературными данными численных и натуральных экспериментов.

Ключевые слова: силикалит, цеолит ZSM-5, метан, молекулярная динамика, сорбция, потенциальная функция



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Introduction

Zeolite materials are sorbents widely used in the oil, construction, and chemical industries, medicine and agriculture. These aluminosilicates are capable of absorbing various substances due to their specific composition and framework structure. Synthetic substances are of particular interest, because samples with clearly reproducible characteristics can be obtained during their production.

Silicalite is a synthetic zeolite with a ZSM-5 type structure, is capable of absorbing small diameter molecules [1], including hydrocarbons [2]. This feature makes it possible to use silicalite as a material for the gas-sensitive layer in methane sensors [3].

The mechanisms behind absorption, emission and transport of sorbed molecules should be understood to fabricate such devices. Studies of these processes at the microscopic level are especially informative, allowing to study the mechanisms of interparticle interaction and construct mathematical models of similar phenomena based on these mechanisms. Because zeolite structures have a complex geometry, computer simulation has been increasingly used instead of classical theoretical methods [4]. The molecular dynamics (MD) method has proven advantageous for modeling a variety of physical processes; in particular, it can be used to successfully study the behavior of the silicalite – methane system under different conditions [5 – 10].

The main component of the model in the MD method is the function of potential interaction of particles. The specific representation of the potential is chosen depending on a range of phenomena that are supposed to be reproduced in the simulation.

The goal of this study is to find the form of this function that is best suited for analysis of sorption/desorption processes in the silicalite – methane system.

Two force field models were chosen for solving this problem. The criteria selected as the most important were that the structures could preserve integrity during long computations, the system could remain stable, and it would be possible to simulate an individual zeolite cluster consisting of a large number of unit cells, without using periodic boundary conditions for lattice multiplication in space. An additional condition imposed was for the specific force field to reproduce a number of main characteristics of the system and give good agreement with experimental data [11, 12].

The main parameters estimated for the system considered in the study were its structural, thermodynamic and transport characteristics.

Parameters of the system

The silicalite – methane system was considered in the study. Two type of zeolite channels are present: sinusoidal and straight; they are located along the [100] and [010] crystallographic directions, respectively. The channels are formed by 10-membered rings, whose diameters are $5.1 \times 5.5 \text{ \AA}$ for sinusoidal types and $5.3 \times 5.6 \text{ \AA}$ for straight types. The channels mutually intersect, allowing for three-dimensional diffusion in the inner space of the silicalite despite the absence of channels along the [001] direction. The maximum diameter of the spheres along which diffusion can occur is 4.70 \AA along the [100] crystallographic direction, 4.46 \AA along the [010] and [001] directions. The critical diameter for methane molecules is 3.8 \AA , making it possible for them to move in all crystallographic directions inside the zeolite interior.

We considered different properties of the system for lattices of different sizes whose parameters are given in Table 1.

Table 1

Structural parameters and composition of ZSM-5 zeolite with different crystal lattice sizes

Zeolite size along the crystal axes, unit cells	Zeolite size along the axis, Å			Number of atoms		
	<i>a</i>	<i>b</i>	<i>c</i>	Total	Si	O
1 × 1 × 1	20.09	19.738	26.284	288	96	192
1 × 1 × 2	20.09	19.738	26.284	576	192	384
2 × 2 × 2	40.18	39.476	65.709	2304	768	1536
5 × 5 × 5	100.45	98.689	26.284	36000	12000	24000

Parameters of computational experiments

The experiments in this study were carried out by means of molecular dynamics (MD) computations. The computations were performed in the free LAMMPS package (Large-scale Atomic/Molecular Massively Parallel Simulator) [13]. Periodic boundary conditions were imposed in all experiments; the potential cutoff radius r_s was 12.5 Å. Either microcanonical (NVE) or canonical (NVT) modeling ensembles were used depending on the problem (N is the amount of substance, V is the volume, E is the energy, T is the temperature). The average temperature of the system corresponded to 298 K. The simulation step was $dt = 1$ fs, the number of steps was from 1 to 2 million. The initial velocities followed a normal distribution for an average temperature of 298 K. Before the main computations were started, the energy minimization procedure was performed using the conjugate gradient method. After the desired accuracy was reached for energy, the system was equilibrated for 100 ps (10^5 simulation steps) in the NVE ensemble using the Langevin thermostat to allow the system to achieve the temperature $T = 298$ K.

Problems of force field model

The processes of absorption and transfer of molecules inside the sorbent substance are often well described by the potential represented as additive functions of the interparticle distance:

$$U(\mathbf{r}) = U_{inter}(\mathbf{r}) + U_{intra}(\mathbf{r}), \quad (1)$$

where $U_{inter}(\mathbf{r})$ and $U_{intra}(\mathbf{r})$ describe inter- and intramolecular interactions, respectively.

Because the methane molecule is nonpolar and there are no cations in the silicalite lattice, the silicalite molecule is generally electrically neutral; therefore, the intermolecular interaction of unbound particles can be described by the Lennard – Jones potential for the interaction of unbound particles without using the Coulomb potential.

We used the Lennard – Jones (12-6) potential:

$$U_{inter}(\mathbf{r}) = \sum 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (2)$$



where r_{ij} , Å, is the distance between the atoms i and j ; ϵ_{ij} , kcal/mol, is the characteristic interaction energy of the i th and j th atoms; σ_{ij} , Å, is the characteristic length of such interaction.

Intramolecular interaction is often described by an additive potential consisting of two-, three-, and four-particle terms:

$$U_{intra}(r) = U_{stretch}(r) + U_{bend}(r) + U_{tor}(\varphi), \quad (3)$$

$$U_{stretch}(r) = \sum k_r (r_{ij} - r_0)^2, \quad (4)$$

$$U_{bend}(\theta) = \sum k_\theta (\theta_{ijk} - \theta_0)^2, \quad (5)$$

$$U_{tor}(\varphi) = \sum k_\varphi [1 + d \cos(n\varphi_{ijkl})]. \quad (6)$$

The potentials $U_{stretch}(r)$ and $U_{bend}(\theta)$ are harmonic. They describe the deviation of the bond length r between a pair of atoms relative to the equilibrium value r_0 and the angle θ formed by three atoms from its equilibrium value θ_0 . The term $U_{tor}(\varphi)$ is the torsion potential, which is periodic and simulates the change in the dihedral angle φ formed by four atoms of the same molecular structure. Potential parameters k_r , k_θ , k_φ are the stiffness constants of linear, angular and dihedral bonds, respectively; $d = \pm 1$ (depends on the specific implementation of the potential); n is the symmetry coefficient, represented by an integer.

The first model of the force field is represented by Eqs.(1) – (6) with the coefficients given in Table 2. A factor of 1/2 is already included in the stiffness constants. The coefficients ϵ and σ for atoms of different types were found by the formulas of the geometric and arithmetic mean, respectively (the Lorentz – Berthelot combining rule).

Most studies generally consider zeolite samples consisting of 2 – 8 unit cells [6 – 8]; the authors impose periodic boundary conditions, where the boundaries of the simulation box coincide with the boundaries of the lattice, to provide an infinite extension of the zeolite framework in space.

We considered a system of the following composition and configuration to reproduce the processes of sorption on zeolite from a state of complete freedom from sorbate molecules to maximum occupancy at a given temperature, as well as further desorption to minimum possible occupancy. A ZSM-5 type zeolite was represented by a lattice of $5 \times 5 \times 5$ unit cells, surrounded by 10,000 methane molecules at the initial instant. The total number of particles in such a system is two orders of magnitude greater than the number typically considered.

The first force-field model was used for this system. Experimental computations of the interaction of particles revealed unstable behavior of the zeolite framework, where an excessively large vibrational amplitude of lattice atoms led to its subsequent decay. This behavior was detected over long simulation times of 2 million steps (for an NVT ensemble).

The second potential consists of terms (1) – (5). Its parameters coincide with the values given in Table 2, with the exception of the constants describing the binding potentials of zeolite. The following values were used for them [16]:

$$\begin{aligned} k_r(\text{Si} - \text{O}) &= 298.53 \text{ kcal}/(\text{mol} \cdot \text{Å}^2), \\ r_0(\text{Si} - \text{O}) &= 1.59 \text{ Å}, \\ k_\theta(\text{O} - \text{Si} - \text{O}) &= 69.03 \text{ mol} \cdot \text{rad}^2, \\ \theta_0(\text{O} - \text{Si} - \text{O}) &= 109.5^\circ, \end{aligned}$$

Table 2

Parameters of particle interaction function (1) – (6)

Substance	Atom	σ , Å	ϵ , kcal/mol
ZSM-5	Si	4.009	0.1274
	O	2.890	0.1547
CH ₄	C	3.400	0.05565
	H	2.963	0.06618
–	Bonds	k_r , kcal/(mol·Å ²)	r_0 , Å
ZSM-5	O – Si	298.75	1.649
CH ₄	C – H	170	1.09
–	–	k_θ , kcal/(mol·rad ²)	θ_0 , degrees
ZSM-5	O – Si – O	69.0897	109.47
	Si – O – Si	5.427	141.00
CH ₄	H – C – H	17.5	109.50
–	–	k_ϕ , kcal/mol	$d = +1$
ZSM-5	Si – O – Si – O	–0.35	$n = 3$

Note. All parameters related to the ZSM-5 zeolite were taken from [14], those related to methane (CH₄) from [15].

$$k_\theta (\text{Si} - \text{O} - \text{Si}) = 9.06 \text{ mol} \cdot \text{rad}^2,$$

$$\theta_0 (\text{Si} - \text{O} - \text{Si}) = 149^\circ.$$

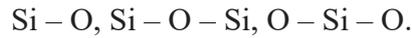
The mutual influence of atoms is reduced in this form of force field due to limited simulated degrees of freedom, namely, by eliminating the four-particle interaction potential. At the same time, the system particles are still described realistically. This potential function is called the simplified general valence force field and was used in [16], analyzing the reproduction of the structural characteristics in several types of zeolites, including silicalite, as well as their infrared and Raman spectra.

No problems with maintaining the system integrity were uncovered in computations using the second potential [17]. Since it is sorption/desorption and transport processes in a multicomponent system that interest us in this study, we had to ascertain not only that the structure of the lattice was preserved, but also whether the dynamics of interaction between sorbate and sorbent particles within the sorbent lattice was described realistically, and the processes of substance transfer were reproduced. For this reason, we carried out comprehensive analysis of this potential to assess whether it could be applied to the silicalite – methane system, including computations of its structural, thermodynamic and transport characteristics.

Computation of structural characteristics of pure silicalite

The radial (RDF) and angular (ADF) functions characterizing the distributions of particles in the system were chosen as the estimated structural characteristic of the particle system. These parameters were estimated both for a pure silicalite lattice and for a two-component silicalite – methane system.

RDF and ADF were computed separately for a silicalite lattice of different sizes (in unit cells): $1 \times 1 \times 2$, $2 \times 2 \times 2$, and $5 \times 5 \times 5$. The compositions of these silicalite samples are given in Table 1. Since the topology of silicalite is represented by the junction of tetrahedral complexes of oxygen and silicon, the following pairs and triplets of atoms acted as arguments for the distribution functions:



Only the sizes of the ZSM-5 zeolite sample differed in this series of computations: it was placed in a simulation box with the boundaries corresponding to the boundaries of the zeolite. The microcanonical NVE simulation ensemble was used.

The radial particle distribution function was plotted for a cutoff radius of 10 Å with an accuracy of 0.01 Å. The function $g(r)$ for Si and O atoms was computed assuming silicon to be the central atom. The angular distribution functions for the combinations of Si – O – Si and O – Si – O atoms were plotted with an accuracy of 1°.

The plots obtained as a result of the computations have characteristic peaks corresponding to the most probable mutual arrangement of atoms in the structure. The peak on the RDF curve for Si – O pairs of particles is sharp and narrow, which corresponds to a highly ordered system. Its maximum falls on the distance between the particles equal to 1.59 Å (Fig. 1). This value is consistent with the structural data presented in the database of zeolite materials [18].

The peaks on the ADF curve for Si – O – Si and O – Si – O atom triplets correspond to the angles $\theta = 145.1^\circ$ and $\theta = 109.5^\circ$, respectively. The values of the O – Si – O angle forming a tetrahedral complex were obtained in [19, 20] and lie in the ranges of $107.9 - 110.9^\circ$ and $107.1 - 111.5^\circ$, respectively. The location of the first peak on the distribution of Si – O – Si triplets coincides with the position of the peak in the range from 145.7 to 177.7° , obtained experimentally in [20], while the values from [19], where the distribution functions were computed theoretically, have a much larger scatter: from 140 to 180° . We can conclude then that the stability and integrity of the lattice is preserved for different sizes of silicalite samples.

We performed several numerical experiments to assess the influence of the simulation boundaries on the relative position of the lattice. Namely, the boundaries were either set according to the dimensions of the simulation box, or were taken so as to exceed its dimensions by 3, 5, and 7 times, respectively. Since it was established that the sizes of the silicate lattice do not affect the reproduction of its structural characteristics, we considered the ZSM-5 sample only with a lattice consisting of $2 \times 2 \times 2$ unit cells.

The computed results for the RDF and ADF functions in the cases of all possible two- and three-particle interactions have shown that the position of the simulation boundaries relative to the given structure does not affect the positions of the peaks. The only changes observed were in the height of the peaks on the function plots, which is explained by the peculiarities of RDF and ADF computa-

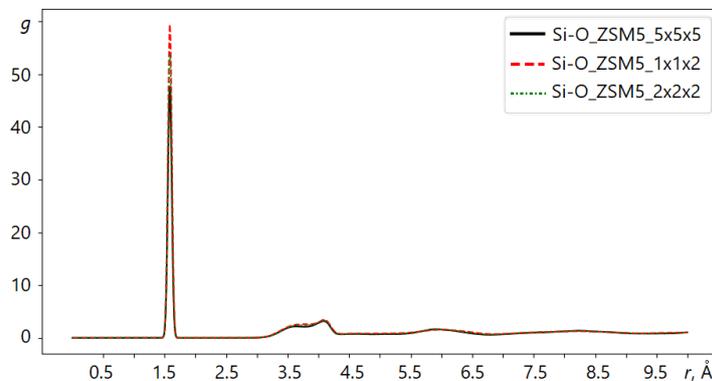


Fig. 1. Radial distribution function (RDF) for pairs of Si – O particles for ZSM-5 zeolite with crystalline lattices with $1 \times 1 \times 2$, $2 \times 2 \times 2$ and $5 \times 5 \times 5$ unit cells

tions, namely, their dependence on the total volume of the system. Therefore, it is possible to simulate a zeolite cluster located far from the boundary of the simulation box without structural distortions of the lattice.

Computation of structural characteristics of the silicalite – methane system

The following systems were prepared to test the interaction potential of the silicalite lattice with absorbed methane molecules:

silicalite with a size of $1 \times 1 \times 2$ unit cells with a different number of methane molecules inside: 8, 16, 24 and 32, which corresponds to 1, 2, 3 and 4 molecules per channel intersection in silicalite. These sizes were chosen for comparison with the literature data [6 – 8].

In each case, a ZSM-5 zeolite was placed in the center of the simulation box. Methane molecules were randomly distributed inside the zeolite using the Packmol package. The microcanonical NVE simulation ensemble was used. Similar to the case of pure silicalite, the cutoff radius and the accuracy with which the RDF of the particles was computed were 10 and 0.01 \AA , respectively.

The distribution of methane molecules in zeolite was estimated by computing the radial distribution function RDF for pairs of O – C atoms, since carbon and oxygen atoms are central for the methane molecule and the tetrahedral complex of the zeolite lattice, respectively.

The resulting graph has three peaks. The first one corresponds to the range of distances between molecules from 3.9 to 4.1 \AA , the second one to the range from 5.7 to 5.9 \AA , and the third lies in the range from 8.1 to 8.3 \AA . These values are close to those of the radii of silicalite channels, which indicates the preferred arrangement of the molecules in the center of the channels. A slight difference in the positions of the peaks for different degrees of zeolite loading is fairly characteristic and is explained by the shift in the energy minimum with a change in the number of absorbed molecules. The shift in the peaks towards decreasing distance is the most pronounced at loading close to the limit. The shape of the curves is consistent with the data obtained earlier by computer simulation [6 – 8].

The RDF for a pair of C – C atoms (Fig. 2) was computed to assess the peculiarities of mutual arrangement of methane molecules in the interior of the zeolite. It is evident from Fig. 2 that the main peak lies in the range from 4.1 to 4.4 \AA . Its position shifts towards smaller distances with increased zeolite loading with adsorbate molecules. Our result is consistent with the data obtained by the molecular dynamics method in [7]. The location of the first peak strongly depends on the concentration

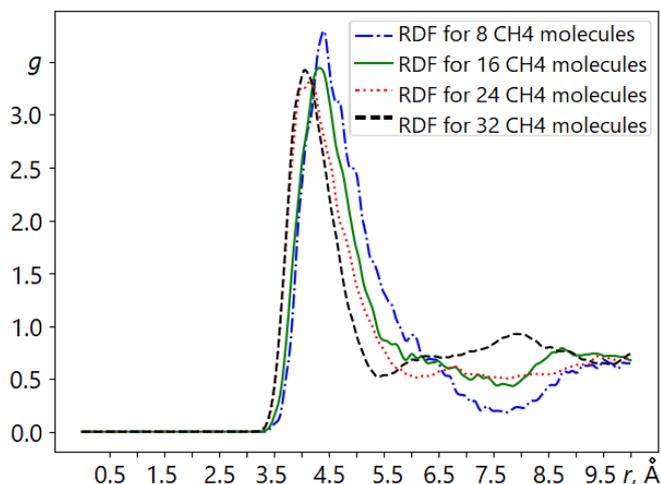


Fig. 2. Radial distribution function for pairs of C – C atoms for different numbers of methane molecules inside the crystal lattice of ZSM-5 zeolite with $1 \times 1 \times 2$ unit cells

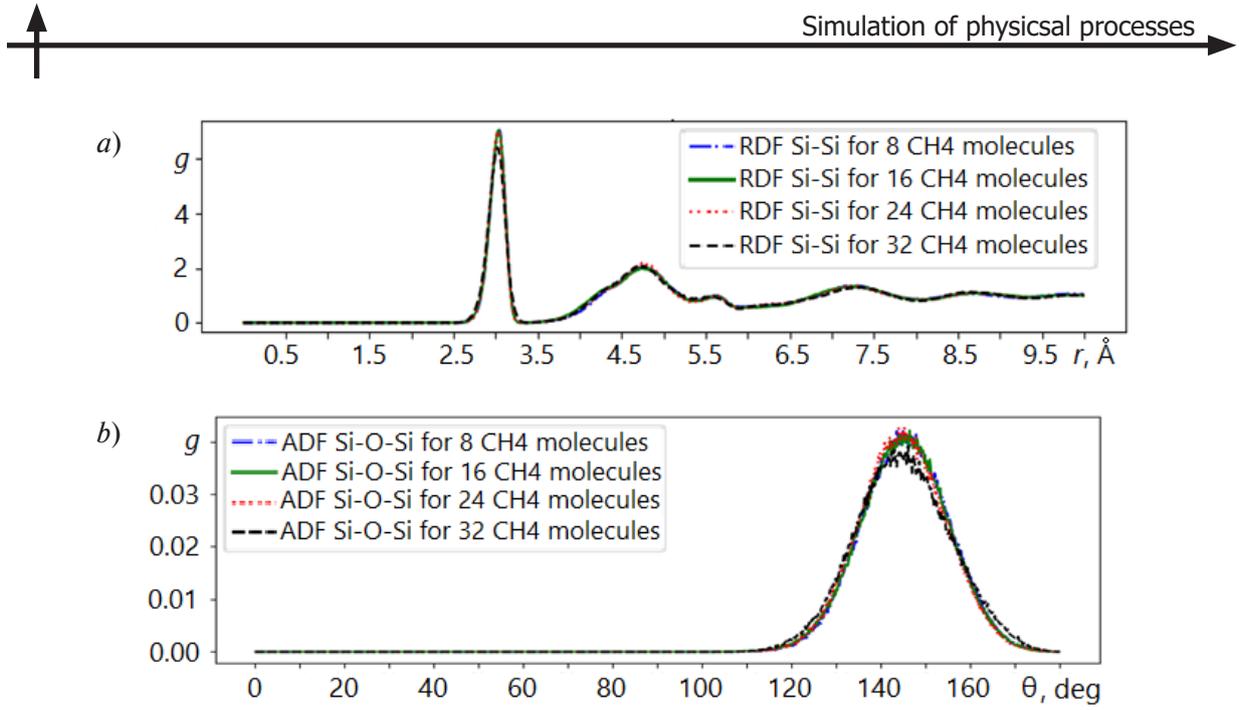


Fig. 3. The RDF of a pair of Si – Si atoms (a) and the ADF of a triplet of Si – O – Si atoms (b) with different numbers of methane molecules inside the crystal lattice of ZSM-5 zeolite with $1 \times 1 \times 2$ unit cells

of methane (CH₄) molecules, since the RDF value, according to [7], essentially depends on the Lennard – Johnson interaction between its molecules.

In addition to the above data, RDF and ADF were computed for groups of C – H and H – C – H methane atoms, as well as for combinations of Si – O, O – O, Si – Si, O – Si – O, Si – O – Si silicalite atoms. The single peaks on the function plots for methane atoms have a sharp shape, and their position coincides with the equilibrium value of the bond length of 1.09 Å and the angle of 109.5°. This allows us to conclude that the harmonic potential with the parameters used satisfactorily reproduces the structure of the methane molecule.

The curves of $g(r)$ and $g(\theta)$ dependences for zeolite atoms, whose examples are shown in Fig. 3, indicate that no structural changes occur in the zeolite framework at the given values of silicalite loading with methane molecules, and the actual presence of adsorbate molecules does not distort the lattice topology. Thus, the simulation potentials used ensure the stability of the zeolite lattice structure during sorption processes.

Computation of adsorption heat

The adsorption heat was computed to assess whether the thermodynamic properties of the silicalite – methane system were reproduced correctly. We used a method based on computing the energy difference between the (sorbert + single sorbed molecule) system and the pure sorbert system in the canonical ensemble (NVT) [21]. Adsorption heat ΔH was computed by the following formula:

$$-q = \Delta H = \langle U_1 \rangle - \langle U_0 \rangle - \langle U_g \rangle - \frac{1}{\beta}, \quad (7)$$

where $\beta = 1/(k_B T)$ (k_B is the Boltzmann constant); U_0 , kcal/mol, is the sorbert energy in the absence of a guest molecule; U_1 , kcal/mol, is the total energy of the sorbert with one guest molecule; U_g , kcal/mol, is the energy of an isolated guest molecule in the absence of sorbert; the notation $\langle \dots \rangle$ corresponds to averaging over the ensemble at constant temperature and volume.

The quantity U_g depends only on the temperature T and can be computed once. Eq. (7) is applied in the zero-occupancy approximation, which implies ideal gas behavior.

This method requires simulation of different systems to obtain the energies used in Eq. (7). Therefore, the following systems were used for the computations:

- silicalite with $1 \times 1 \times 2$ unit cells with one methane molecule inside;
- silicalite of the same size in the absence of other molecules;
- one methane molecule placed in a simulation box corresponding in size to the silicalite sample used.

The minimum number of methane molecules meets the requirement for low zeolite loading (zero-occupancy approximation). The boundaries of the simulation box correspond to the boundaries of a cell in the ZSM-5 zeolite of the given size (they remain unchanged for an individual methane molecule). The methane molecule was placed in the center of the simulation box, which coincided (with an accuracy of 2 Å) with the location of the straight channel of the zeolite and the large cavity. According to [7, 9, 22], this position is energetically favorable for the methane – silicalite system. Configurations were created using the Packmol utility. The simulation was conducted in the canonical NVT ensemble. A series of statistical simulations was carried out to minimize the possible computational inaccuracies: 5 experiments for each system, differing in initial conditions (velocities).

The computed value of adsorption heat was -6.7 kcal/mol. A computational method similar to that in our study was used in [7, 9]. The values obtained by the authors were -4.2 and -5.8 kcal/mol, respectively. Values of -5.0 , -6.1 and -6.7 kcal/mol were obtained by experimental procedures such as the calorimetric method [22, 23] and the vacuum microbalance method combined with the Clausius – Clapeyron equation [23]. The reason for such a wide value range is that techniques yielding different accuracies were used, with several aspects affecting the results. Thus, the value of adsorption heat computed in this paper is consistent with the literature data and is closer to the threshold values obtained in the full-scale experiment. Consequently, the given force field potential correctly reproduces the thermodynamic characteristics of the silicalite – methane system.

Computation of self-diffusion coefficient

The standard parameter characterizing transport phenomena in sorbent – sorbate systems is the self-diffusion coefficient of the sorbate in sorbent pores. Unlike ordinary diffusion, self-diffusion occurs under equilibrium conditions in the system, in particular, without a concentration gradient of the diffusing substance. We found the self-diffusion coefficient D_s of methane in silicalite using a method based on the relationship between diffusion and standard deviation:

$$D_s = \frac{1}{2dN} \lim_{\Delta t \rightarrow \infty} \frac{d}{dt} \left\langle \left(\sum_{i=1}^N r_i(t + \Delta t) - r_i(t) \right)^2 \right\rangle, \quad (8)$$

where r_i , Å, is the position of the particle i at a certain instant; t , s, is the time; N is the number of molecules; d is the dimension of the system.

This method is widely accepted and provides good agreement between the results and experimental data.

The experiment involved a system consisting of silicalite with $1 \times 1 \times 2$ unit cells with 8 methane molecules inside, which corresponds to one molecule per intersection. Methane molecules were randomly positioned inside the zeolite using the Packmol package. The boundaries of the simulation box coincided with the boundaries of the silicalite lattice. Energy conservation in the system was ensured by using the microcanonical NVE ensemble.

The self-diffusion coefficient of methane in silicalite was determined for the given parameters of the system over a time interval from $2 \cdot 10^5$ to 10^6 steps to ensure stable diffusion flow in the system.



The obtained value of the coefficient D_s was $1.1 \cdot 10^{-10}$ m²/s. Experimental techniques were used for computing D_s in [24 – 26], yielding values of $1.1 \cdot 10^{-8}$, $1.1 \cdot 10^{-10}$ and $1.3 \cdot 10^{-10}$ m²/s, using pulsed field gradient NMR, membrane technique and pulsed gas chromatography, respectively. Computer simulations by the MD method in [5, 27] yielded the range from $9.0 \cdot 10^{-10}$ to $1.1 \cdot 10^{-8}$ m²/s. Consequently, the value of the self-diffusion coefficient of methane in silicalite that we have found is in agreement with the literature data obtained both in a full-scale experiment and as a result of computer simulation. Such a small value of the self-diffusion coefficient indicates that the configurational mechanism of substance transfer is predominant under equilibrium conditions, which is typical for porous substances where the channel sizes are comparable to the sizes of absorbed molecules.

Conclusions

The most probable mutual positions of the given pairs and triplets of atoms, computed through their radial and angular distribution functions, respectively, agree with the theoretical and experimental values (within the error). This applies both to the structure of the silicalite lattice and to the methane molecule. Furthermore, we have established that the position of the modeling boundaries relative to the zeolite lattice does not affect the integrity of the structures, and the presence of methane molecules in the interior of the crystal lattice introduces only slight distortions if limiting values of sorbent occupancy are taken. This confirms that the potential function is suitable for modeling the interaction between the lattice atoms of silicalite and methane. In addition, reproducing the position of the peaks on the curves of the RDF and ADF functions eliminates the influence from the size of the computational cell and confirms the stability of the selected simulation potential with the parameters used.

We have established for the given force field that it is possible to simulate a sufficiently large silicalite sample adopting the position of the simulation boundaries significantly exceeding the boundaries of the zeolite.

The adsorption heat of methane on silicalite, computed in the study, was equal to -6.7 kcal/mol, which is close to the known experimentally obtained value and is in agreement with the computational data. Thus, the potential used for the force field satisfactorily reproduces the thermodynamic properties of the given system.

We have computed a crucial characteristic of transport processes, which is the self-diffusion coefficient D_s of the absorbed substance for the silicalite – methane system. The obtained value of $1.1 \cdot 10^{-10}$ m²/s does not contradict the data found in the literature, allowing us to conclude that transport processes proceed mainly along the configuration mechanism for normal conditions and zeolite occupancy, equal to 4 molecules per unit cell.

To summarize, the computed structural, thermodynamic, and transport characteristics of the silicalite – methane system using the potential of a simplified general valence force field are consistent with the data presented in literature, giving reason to believe that it is correct to use the potential function we have chosen to simulate the sorption/desorption processes.

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