Construction of a Potential Energy Surface for Molecular Dynamics Studies of Methane Adsorbed in Zeolites

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A potential for the interaction of methane molecules with the framework atoms of siliceous zeolites is developed empirically. The CH_4 molecule is considered in the spherical approximation. The interaction potential includes repulsion, dispersion, and induction energy. It is shown that even if the effective charges on the framework oxygen and silicon atoms are large, the contribution of the induction energy is weak in comparison with those of dispersion and repulsion energies due to compensation effects. The calculated parameters of a Lennard-Jones potential are compared with those used in previous MD calculations. As an application we calculate diffusion coefficients and the heat of adsorption of methane in silicalite which can be compared to available experimental data.

1. Introduction

Zeolites are a class of microporous materials with a framework consisting of SiO_4 and AlO_4^- tetrahedra. The negative charge on the aluminosilicate framework is compensated by extraframework cations or acidic OH groups. The presence of cavities and pores of molecular dimension allows for a number of applications for these materials as adsorbants, catalysts, molecular sieves, etc.[1] Zeolite structures also represent a good model to study molecular and atomic behavior in a confined medium. The siliceous zeolites with a ratio Si/Al tending to infinity are especially well suited for this purpose, because the lack of charge compensating species significantly simplifies the treatement of adsorbed molecules. Silicalite is an aluminium-free ZSM-5 zeolite (structure type MFI), and its framework represents a complex three-dimensional structure with intersecting straight and sinusoidal channels. The adsorption and diffusion of guest molecules in silicalite have been extensively studied both experimentally[2−7] and theoretically.[8−21]

The classical molecular dynamics (MD) method is an effective tool to simulate the dynamics of complex systems and has been widely used for the investigation of molecules adsorbed in zeolites (for a recent review, see ref 21). With the help of MD simulations, one is able to calculate different statistically averaged quantities such as radial distribution functions, transport coefficients, etc. Also, MD calculations allow for the classical evaluation of autocorrelation functions which upon Fourier transformation yield spectra to be compared to experiment.[22] As in any classical or quantum-mechanical simulation of a process involving the dynamics of several atoms the interaction of the particles, i.e., the potential energy surface, is crucial for the calculation of any quantity. Although for smaller molecules the methods of quantum chemistry by now are able to generate such surfaces for several nuclear degrees of freedom, it is far from realistic to obtain a reliable ab initio potential for a guest molecule adsorbed in a zeolite structure. Moreover, even an empirical determination of the atom−atom or molecule−atom interactions is difficult due to the complex chemical nature of the aluminosilicate crystal. Because of the partial covalency of the Si−O and Al−O bonds neither ionic nor atomic parameters for framework atoms are fully appropriate.

As methane is one of the most frequently considered molecules in MD studies of guest molecules in zeolite structures, we will regard it as a prototype system for the construction of a molecule−framework potential in the present work. Diffusion of methane in silicalite structure has been investigated by Demontis *et al*.[8−10] and by Goodbody *et al*.[12] using a spherical approximation for the methane molecule (united atom model). These calculations have been extended to the atom−atom model for methane using either rigid molecules[11,13,19] or allowing them to vibrate.[15,18,20] The influence of the vibrating framework on the motion of adsorbed molecules has also been examined.[8−10,15] Except for the MM2 parametrization,[13,15,20] potentials for MD simulations of methane in zeolites are mostly based on the parameters introduced in the papers published in 1972 by Ruthven *et al*.[23] and in 1978 by Bezus *et al*.[24] Since by now new information is available, we feel a need to reconsider the used parametrizations and possibly adjust them. Furthermore, substantial and not always well-founded changes and approximations to these "basic" potentials led to a variety of different potentials, which are currently used in theoretical studies of methane dynamics in zeolites (for review see e.g. refs 16 and 25).

The only way to check the quality of a potential energy surface is a comparison of calculated and measured quantities. These are, for example, translational and rotational components of the methane density of states by quasi-elastic neutron scattering measurements,[26] the diffusion coefficient[3,5−7] and its anisotropy,[4] or the heat of adsorption.[2] In comparing experimental and theoretical results on guest molecule−framework systems, however, one has to be aware of the errors inherent to both technologies. If MD simulations reproduce correctly reliable experimental data, the potential might be transfered to other systems, and theoretical studies can help in the analysis of new experimental data. Furthermore, microscopic mechanisms of processes taking place in zeolites can be identified (investigation of adsorption sites, for example).

The aim of the present paper is to construct a new potential energy surface for methane in silicalite using a general approach to determine the molecule−framework interaction. The estimations based on general physical principles to describe intermo-

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lecular forces are given in section 2. The developed potential is then used in MD calculations of diffusion coefficients and the heat of adsorption for methane adsorbed in silicalite. The calculated values are compared with experimental and other theoretical data (section 3).

2. Potential Energy Surface

2.1. General Parametrization. The potential energy of a methane molecule considered in the spherical approximation being located in the coordinate origin and interacting with the atoms (i) of the zeolite framework at positions $\vec{r}_i$ can be written as a sum of electrostatic, U_E, inductive, U_I, dispersive, U_D, and repulsive, U_R, interactions:

$$U = U_E + U_I + U_D + U_R \tag{1}$$

The electrostatic term is conventionally expressed in a multipole expansion. Because of the approximately spherical symmetry of the CH_4 molecule we set $U_E = 0$ in what follows. The inductive interaction is given by

$$U_I = -{}^1/_2\, \alpha \vec{E}^2 \tag{2}$$

where $\vec{E}$ is the electrostatic field vector at the position of the molecular center of mass and α is the static polarizability of the molecule. The electrical field is the vector sum of fields originating from the ions:

$$\vec{E} = -\sum_i q_i \frac{\vec{r}_i}{r_i^3} \tag{3}$$

Here r_i is the distance between the molecular center of mass (COM) and the ion (i), and q_i is the respective charge.

The dispersion interaction term reads

$$U_D = -\sum_i C_i r_i^{-6} \tag{4}$$

where the van der Waals (vdW) dipole−dipole coefficient C_i is estimated via the Slater−Kirkwood combination rule:[27]

$$C_i = \frac{3}{2} \frac{\alpha\alpha_i}{(\alpha/n)^{1/2} + (\alpha_i/n_i)^{1/2}} \tag{5}$$

Here α_i (α) is the static polarizability of the ion i (molecule), and n_i (n) is the number of valence electrons. Equation 5 can be transformed to the Lennard-Jones expression,[27] if the diamagnetic susceptibility is expressed via α_i and n_i, e.g. in au

$$\chi_i = \sqrt{n_i \alpha_i}/4c^2 \tag{6}$$

where c is velocity of light.

Finally, the repulsion energy is given as

$$U_R = \sum_i B_i r_i^{-12} \tag{7}$$

where the coefficients B_i are calculated at the equilibrium distances between a framework atom (i) and the CH_4 molecule through the derivatives of U with respect to the intermolecular distance r_i:

$$B_i = \frac{1}{2}(R + R_i)^6 C_i - \frac{(R + R_i)^{13}}{12} \alpha \vec{E} \frac{d\vec{E}}{dr_i}\Big|_{r=R+R_i} \tag{8}$$

where $R + R_i$ is the sum of the vdW radii of CH_4 and the ion i. Because of the quadric dependence of the induction energy on the vector sum of the electric fields originating from the framework atoms, this energy term cannot be represented by the sum of pairwise interactions, so that one has to use different approximations. One of them is an isolated ion−molecule model, in which only the electric field from the ion located at the vdW distance is taken into account. However, as will be shown later, this model significantly overestimates the electric field at the vdW distance in zeolites and artificially changes the B_i constants. Neglecting the induction energy is a more justified procedure, if the overall electric field is weak. Neglecting the induction term leads to a simple equation for the repulsion constants:

$$B_i = {}^1/_2 (R + R_i)^6 C_i \tag{9}$$

The above parametrization for the guest−framework interaction requires only a set of four parameters for every kind of interacting particles, i.e., the van der Waals radius, the ionic charge, the polarizability, and the number of valence electrons. The estimation of these crucial numbers will be discussed in detail below.

(a) van der Waals Radii. The vdW radii of the framework atoms are difficult to define since the Si−O bonds in siliceous zeolites are partially covalent. The values of the ionic radii for framework oxygen and silicon have been estimated quantum chemically.[28] Values $R(O) = 1.28$ Å and $R(Si) = 0.36$ Å were found using the minimum in the electron density along the Si−O bond as a measure of atomic size. If, on the other hand, the minimum in the electron density along the O−O distance (anionic contact) is used, an oxygen radius $R(O) = 1.38$ Å is obtained. These values can be compared with values of Pauling's book:[29] the ionic radius of O^{2-} is 1.40 Å and that of Si^{4+} is 0.41 Å. We take Shannon's value of the oxygen radius $R(O^{2-}) = 1.35$ Å for a coordination number CN = 2[30] as a compromise between the data in the region (1.28−1.40 Å). Note that Shannon gives $R(O^{2-}) = 1.40$ Å for a coordination number CN = 6. For the radius of the silicium atom we also take the value from ref 30, i.e. $R(Si^{4+}) = 0.26$ Å for Si^{4+} with coordination number CN = 4.

The vdW radius of methane is taken from crossed molecular beam measurements of the total differential cross sections for methane-methane scattering:[31] $R_{CH_4} = 2.01$ Å. The same value (2.0 Å) one can find in Pauling's book[29] for CH_2 and CH_3 groups, and it is not unrealistic to assume a similar value for the CH_4 molecule.

(b) Ionic Charge. The ionic charge q of oxygen is about −1 e, as follows from recent quantum-chemical calculations. For example, Mulliken analysis of charges in periodic Hartree−Fock calculations of siliceous mordenite and silicalite gives values of $q(O) = -1.04\ e$[32] and $q(O) = -0.74\ e$,[33] respectively. The charges were also obtained from high-quality ab initio calculations of a sufficiently big molecular model ($Si_2O_7H_6$). The procedure of calculating the molecular electrostatic potential at a grid of points from ab initio calculated electronic densities and choosing atomic charges that best reproduce the potential on the grid yields the value of $q(O) = -0.788\ e$.[28] This number is used in our further calculations.

(c) Polarizabilities. The polarizability of CH_4 is 2.593 Å^3.[34] The polarizabilities of the framework atoms can be estimated with the help of the screening constants method as described in detail in ref 27. Briefly, the following equations are used: the polarizability of an atom is calculated using the variational principle to obtain

$$\alpha = \frac{4}{9}\sum_i (\langle r_i^2 \rangle)^2 \tag{10}$$

where summation runs over all electrons i in the atom and

$$\langle r_i^2 \rangle = \left[\frac{n_i^*}{2(Z - S_i)}\right]^2 (2n_i^* + 1)(2n_i^* + 2) \tag{11}$$

Here the effective nuclear charges $(Z - S_i)$ and the effective quantum numbers n_i^* are calculated by empirical rules. Straightforward application of the screening constants method yields the values of the effective nuclear charge for O and Si and their ions (only valence electronic shells are considered):

O: $(Z - S)_{2s,2p} = 4.55$ $(n^* = 2)$

Si: $(Z - S)_{3s,3p} = 4.15$ $(n^* = 3)$

O^{-1}: $(Z - S)_{2s,2p} = 4.20$ $(n^* = 2)$

Si^{2+}: $(Z - S)_{3s,3p} = 4.85$ $(n^* = 3)$

Substituting $\langle r_i^2 \rangle$ from eq 11 into eq 10 and neglecting the small contributions from inner shells, we obtain the following relation between the polarizability of an atom a and its ion i (here only the changes in the number of valence electrons are considered):

$$\alpha_i = \alpha_a \left[\frac{(Z - S)_{va}}{(Z - S)_{vi}}\right]^4 \frac{n_{vi}}{n_{va}} \tag{12}$$

A number of quantum chemical calculations show[28,32,33] that the charge on the oxygen atom in zeolites lies in the range about −1.0 au; thus it is appropriate to use the polarizability of the O^- anion in our calculation. With the formula (12) and the polarizability of the oxygen atom 0.802 Å^3 ± 2%[34] one obtains $\alpha_{O^-} = 1.29$ Å^3. Correspondingly, for Si^{2+} ($\alpha_{Si} = 5.38$ Å^3 ± 2%[34]) one obtains $\alpha_{Si^{2+}} = 1.44$ Å^3.

(d) Valence Electrons. The use of the number of valence electrons in eq 5 in general overestimates the dispersion coefficient, and therefore one should use effective values for this quantity.[35] For methane we use the effective value $n_{CH_4} = 5.797$.[35] For the charged framework atoms we use $n_i = n_{0i} - q_i$, n_{0i} being the number of valence electrons for the neutral atom and q_i the charge on the atom. This gives $n_{O^-} = 7$ and $n_{Si^{2+}} = 6$.

As in other related work,[21] we neglect the dispersion interaction with Si because the electronic density of the large oxygen anions screens effectively the electric field on Si from the methane molecule which enters into the matrix elements describing this interaction. Although this effect is difficult to estimate, a calculation of the heat of adsorption, which is related to the total potential energy, can confirm the validity of this approximation (see below). The repulsion interaction with Si is also neglected since due to the large repulsion from the oxygens methane is sufficiently far away from Si. In a calculation of the electrostatic and induction contributions to the molecule−framework potential, the charges on Si should be considered since both the charges on Si and O were used to reproduce the ab initio electrostatic energy maps.[28]

2.2. Lennard-Jones Parametrization. A Lennard-Jones (LJ) parametrization of a many-body potential energy surface is computationally advantageous and has been used in many studies. Nevertheless, one should check the approximations leading to this functional form for the interaction potential. The Lennard-Jones 6−12 form of the potential can be related to the general potential form (1) by neglecting the induction term. Therefore, we calculated separately the $U_R + U_D$ and U_I contributions to the total energy. Figure 1 shows contours of the potential energy for a single methane molecule in the plane $x-z$ through the center of a sinusoidal channel. The contour plot for the straight channel along the y axis is shown in Figure 2. As can be seen in the figures, the induction energy (shown in panel b) is 1 order of magnitude smaller than the dispersion energy (shown in panel a), except in regions where straight and sinusoidal channels intersect. Here, contributions from the induction energy become important but still are much smaller than those of the dispersion energy.[36] In contrast to this observation, an estimate of the interaction of methane with a single oxygen ion at the vdW distance leads to $U_I = -35.5$ kJ/mol in comparison with $U_D = -3.25$ kJ/mol. It is clear that the large dispersion energy in the channels of the silicalite originates from its additive nature so that a large number of relatively small individual contributions lead to the large molecule−framework dispersion interaction. In contrast, the opposite signs of charges on Si and O result in the compensation of different contributions to the total electric field thus reducing the induction energy. Taking these results into account, we neglect the induction term in our calculation of the total energy U leading to a Lennard-Jones parametrization, where the repulsion constant B_i is calculated according to eq 9.

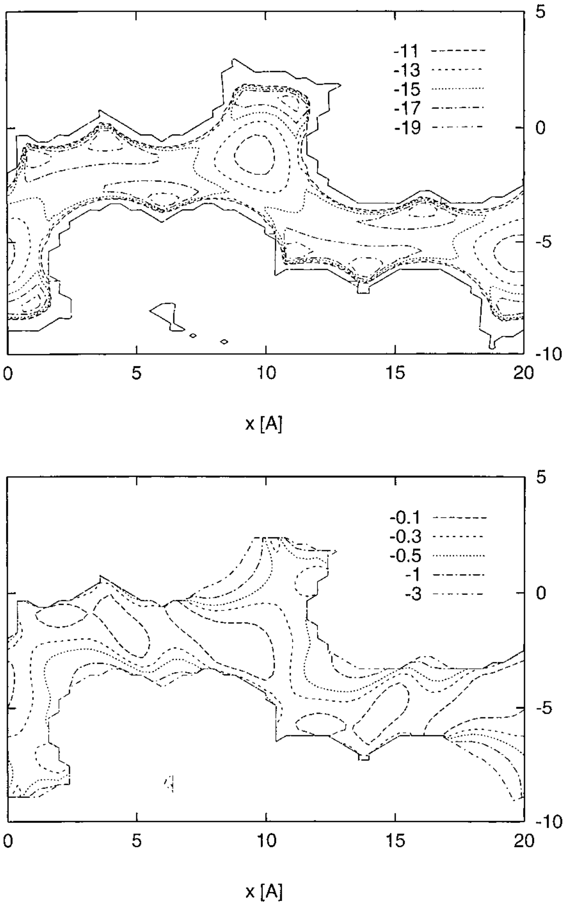

Figure 1. Contours of the potential energy surface for a single methane molecule in the plane $x-z$ through the center of a sinusoidal channel at $y = 0.25b$. The sum of dispersion and repulsion energies is shown in panel a (top), the induction energy in panel b (bottom) (in kJ/mol).

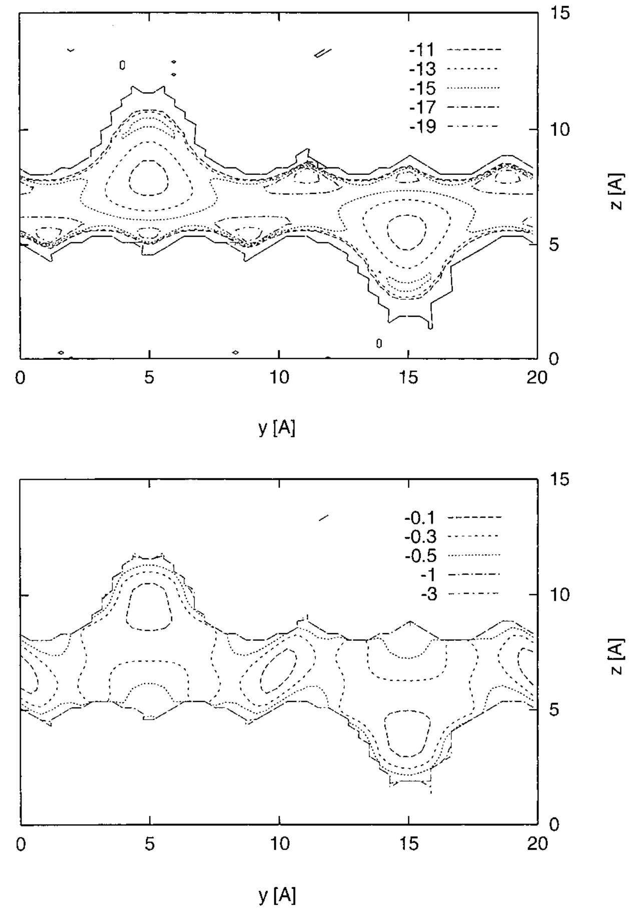

Figure 2. Same as Figure 1, but in the plane $y-z$ through the center of a straight channel at $x = 0$. The sum of dispersion and repulsion energies is shown in panel a (top), the induction energy in panel b (bottom) (in kJ/mol).

TABLE 1: Lennard-Jones Parameters for the Methane–Oxygen Potential

O-CH_4	σ, Å	ϵ, kJ/mol
this work	2.985	1.62
ref 12	3.214	1.108
ref 8	3.885	0.811
ref 16	3.694	0.755

The dispersion coefficient for the CH_4–O interaction is calculated as $C_{O-CH_4} = 80.1$ au using eq 5. Finally, the Lennard-Jones potential is given by

$$U = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]; \qquad \sigma = \frac{R}{2^{1/6}}; \qquad \epsilon = \frac{C}{2R^6} \qquad (13)$$

where R is the sum of the vdW radii of interacting atoms $R = R_O + R_{CH_4}$. The values of our Lennard-Jones parameters are given in Table 1 together with data from other papers. Apparent differences occur in the parameters used in this and other work. In order to understand their origin, we list in Table 2 the atomic parameters used in the construction of our potential together with those given in refs 23 and 24. The method used to obtain the potential in the latter work has been essentially the same as ours with one exception: in the calculation of the repulsion constant for the methane–oxygen interaction the authors of refs 23 and 24 added the contribution of the induction energy (eq 8) between the two isolated particles.

Let us first discuss the atomic parameters for oxygen. The value of the oxygen radius used by Bezus *et al.*[24] (R(O) = 1.52 Å) has been taken from the paper by Bondi.[38] This value corresponds to the upper limit of the oxygen contact radius for polyether molecules obtained by the few X-ray data available at that time and cannot be considered to be sufficiently accurate.

TABLE 2: Molecular and Atomic Parameters for the Interaction of Framework Oxygen and CH_4 Molecules Used in Host–Guest Potentials in MD Studies

ion/mol	r_i, Å	α, Å^3	q, e^-	χ, 10^{-6} Å^3
O^{2-} (ref 23)	1.4	1.47	−0.25	17.7
O^{2-} (ref 24)	1.52	1.4	−0.2	10.0
O^{2-} (this work)	1.35	1.29	−0.788	15.4[a]
CH_4 (ref 23)	2.34	2.6		20.2
CH_4 (ref 24)	2.0	2.6		16.0
CH_4 (this work)	2.0	2.593		19.9[a]

[a] Formula 6 was used for the calculation of the atomic hyperpolarizability.

The charge on oxygen was calculated by Bezus *et al.*[24] from arbitrarily prescribing the zero charge to Si and Al atoms for zeolites containing extraframework cations. The value q(O) = −0.2 e is very underestimated in comparison with results of recent quantum-chemical calculations.[28,32,33] However, even with the latter values the induction term makes comparably small contribution to the total energy and can be neglected.

The set of parameters proposed by Ruthven *et al.*[23] includes the parameters for oxygen (charge, polarizability, hyperpolarizability) from older work of Kiselev;[39] the radius of oxygen was taken to be R(O) = 1.4 Å. For methane, the authors of ref 23 used a very different vdW radius of 2.34 Å from what is commonly used (2.0 Å). This originates from the following procedure for the calculation of this quantity: the vdW radius of hydrogen (1.20–1.29 Å) was added to the C–H bond length (1.09 Å). This calculation overestimates the vdW radius of methane significantly, since the electronic shells of hydrogen atoms in CH_4 are more contracted in the outward direction due to the covalency of the C–H bond, so that the simple additive procedure fails in this case.

Based on the two sets of parameters as listed in Table 2, a number of MD studies were performed using different LJ potentials. Demontis *et al.*[8–10] took Ruthven's parameters, neglecting the induction term. Note that the necessary redefinition of the repulsion constant (eq 9) was not carried through. Some attempts were made to fit the LJ potential to experimental data. Goodbody *et al.*[12] used Bezus's vdW radius of oxygen and a value of 2.088 Å for the vdW radius of methane. The ϵ parameter was selected to fit the experimental Henry constant for methane adsorbed in silicalite. With help of Monte Carlo calculations, Smit[16] fitted the LJ parameters to reproduce the experimental adsorption isoterms. Some compilations of potentials used in the literature can be found in refs 16 and 25. As our LJ potential differs from the ones used in previous studies, we performed MD calculations of different quantities in order to compare them with results of available experiments. The construction of a potential is the aim of this work, so the full aspects of the methane dynamics such as the dependence on loading or temperature are out of the scope of the present paper. The results are described in the following section.

3. Results of MD Calculations and Discussion

We investigate the motion of methane molecules in two models of the rigid (RF) and flexible (FF) framework. The influence of framework vibrations on the calculated quantities is investigated using the ab initio generalized valence force field (GVFF) model of the framework potential.[40] We used a MD box consisting of 3456 framework atoms arranged in the MFI structure (2 × 2 × 3 unit cells). An unit cell has an orthorhombic

TABLE 3: Diffusion Coefficient, Its Anisotropy, and the Heat of Adsorption of Methane Adsorbed in Silicalite Calculated in the Rigid Framework Model (RF) and the Flexible Framework Model (FF). Experimental Data Are Given for Comparison

	RF	FF	exp
D, Å^2/ps	1.0 ± 0.2	1.4 ± 0.25	1.3 ± 0.55[a]
D_x, Å^2/ps	1.0	1.6	
D_y, Å^2/ps	1.8	2.3	
D_z, Å^2/ps	0.23	0.37	
$^1/_2(D_x + D_y)/D_z$	6.1	5.3	4.5[b]
H, kcal/mol	−4.69	−4.76	−4.8[c]

[a] Extrapolation to zero loading of mean diffusion coefficient obtained by pulsed-gradient spin-echo NMR method.[3] [b] Reference 4. [c] Reference 2.

Pnma space group with $a = 20.07$ Å, $b = 19.92$ Å, and $c = 13.42$ Å. Atomic coordinates were taken from ref 41. Periodic boundary conditions were applied to the system in order to simulate the infinite zeolite structure. The cutoff distance for the shifted potentials[42] was taken as $R_{\mathrm{cut}} = 19$ Å. 48 methane molecules were initially distributed in the intersections of straight and sinusoidal channels of the MFI zeolite. Newton's equations of motion are integrated with the velocity form of the Verlet algorithm[42] with a time step of 2 fs. The initial velocities of the methane molecules were taken from the Maxwell−Boltzmann distribution at $T = 300$ K. During the first 20 ps the system was equilibrated at 300 K by scaling the velocities with a relaxation constant of 0.4 ps.[43] The positions of the methane molecules were stored every fifth step during the 50 ps propagation, and the final positions and velocities were taken as initial conditions for a new run. We used an average of 16 statistically uncorrelated runs in the calculation of the diffusion coefficient.

The anisotropy of the silicalite framework leads to the anisotropy of diffusion in different spatial directions in dependence on the direction of the concentration gradient. One has to consider this case in the terms of the diffusion tensor. Different components of the latter can be calculated in an MD simulation by monitoring the mean-square Cartesian displacements of the molecules

$$D_{ss} = \frac{1}{2t}\langle[s(t) - s(0)]^2\rangle \tag{14}$$

where $s = x, y, z$.

The spatially averaged mean diffusion coefficient is calculated using the formula[5]

$$D = {}^1/_3\,(D_{xx} + D_{yy} + D_{zz}) \tag{15}$$

The heat of adsorption $\langle H\rangle$ was calculated as

$$\langle H\rangle = \langle U\rangle - RT \tag{16}$$

where $RT = 0.596$ kcal/mol for $T = 300$ K, and $\langle U\rangle$ is an ensemble-averaged potential energy of the methane−framework interaction.

The numerical results are listed in Table 3. One finds a good agreement between calculated and experimental values taking into account that no adjustment of the potential parameters was performed. A good agreement with experiment validates the proposed parametrization. Taking into account the framework vibration in ref 8 augmented the diffusion coefficient by 20%. The same tendency is seen in our results. It has been recently shown that differences between the results of calculations with rigid (RF) and flexible (FF) frameworks originate from using different lattice structures.[46] One usually calculates diffusion in the rigid zeolite structure using the coordinates of the framework atoms taken from the crystallographic data. In simulations with a flexible framework, the mean coordinates of the framework atoms are determined by the equilibrium parameters of the potential function describing the vibration of the lattice. In order to check this issue, we carried out an additional calculation in the RF model, in which the atomic coordinates of the framework atoms were obtained from a run with a vibrating lattice by cooling the system down to the zero temperature. The then calculated diffusion coefficient of 1.2 Å^2/ps lies between the values 1.0 Å^2/ps in the RF model and 1.4 Å^2/ps in the FF model, confirming the importance of the equilibrium zeolite structure in the determination of the molecular diffusion properties.

The analysis of the data obtained for the heat of adsorption has shown[16] that the value $\langle H\rangle = 4.8$ kcal/mol is reproduced by many measurements on different silicalite samples. On the other hand, the diffusion coefficient is much more difficult to obtain. A comparison of experimental results for methane in ZSM-5 shows significant differences depending on the technique chosen. As a rule, macroscopic measurements give lower values of the diffusion constant. This can be explained by the presence of the intercrystalline diffusion. The results obtained by microscopic technique of pulsed field-gradient spin-echo NMR experiments are in good agreement with the results of quasi-elastic neutron scattering[5] and of the modeling.[8,12,13] The error in the experiment reported in ref 3 is 50%. In addition, a recent measurement of the mean diffusion coefficient[17] has given the value $D = 0.5$ Å^2/ps at $T = 300$ K and loading of 8 mol/uc which can be compared with the value $D = 0.9$ Å^2/ps obtained by Caro *et al*.[3] for the same conditions.

Let us now turn to the discussion of statistical details entering into the simulation of molecular diffusion in a zeolite framework. In averaging the diffusion coefficients over 16 independent runs we found a large mean-square deviation for the diffusion coefficients despite of the large number ($N = 768$) of single molecule trajectories. The calculation with 64 runs gave the same error, and the test calculation with 16 runs for trajectories of 200 ps showed that this error does not depend on the length of the trajectory. It is noteworthy that the transport in pores of zeolites is a different phenomenon in comparison with "classical" diffusion in liquids, described by the Einstein relation. Looking at Figures 1 and 2 one can think about the motion of a molecule in a complex potential. A very slow convergence of the mean-square displacement is observed even in the trivial case of diffusion on a lattice. Moreover, peculiarities of the channel system of silicalite could introduce deviations from predictions of the random-walk model and additional correlations between the elements of the diffusion tensor.[44]

Although the influence of the two LJ parameters on the thermodynamic and mobility properties cannot be considered separately since they both define paths and barriers for the moving molecule, one can generally suppose that the heat of adsorption is related to the average potential energy which could mainly be defined by the LJ parameter ϵ. The diffusion coefficient D depends on the diameter of the channels which in turn depends on the LJ parameter σ. An agreement of calculated and measured values for these two quantities would be a good test for any form of parametrization.

It has been discussed above that a comparison of calculated and measured diffusion coefficients is rather difficult because of the errors adherent to both, experiment and theory. The results of refs 7−21 show that the value of the diffusion constant varies between 0.5 and 1.6 (in Å^2/ps) using different potentials. The experimental value has a large estimated error as well. On the other hand, the heat of adsorption is defined by the molecular dynamics with a statistical deviation of about 0.1 kcal/mol. We have checked that this quantity is sensitive to the variation of both the molecule−framework parameters ϵ and σ. For example, a change of the σ parameter from 2.985 to 3.25 Å (9%) leads to the change of $\langle H \rangle$ from −4.69 kcal/mol to −6.41 kcal/mol (37%). A similar tendency is observed for the ϵ parameter. On the other hand, comparison of different experimental values for the heat of adsorption for methane/silicalite[16] shows only small deviations. Therefore, we conclude that the heat of adsorption provides a more sensitive measure for the quality of molecule−zeolite potentials than the diffusion coefficient. The use of our potential results in a good agreement between the calculated and experimentally determined heat of adsorption. Other potentials used in the literature give rather deviating values like −4.4 kcal/mol in Demontis's calculations,[9] −4.3 kcal/mol in Goodbody's paper,[12] and −5.8 kcal/mol for the MM2 potential.[13]

Of course, a calculation of the adsorption energy and the diffusion coefficients is necessary but not sufficient for the estimate of the quality of a potential. Supplementary information can be obtained by regarding the vibrational dynamics.[22] Low-frequency vibrations of molecules trapped in potential wells of the molecule−framework PES, as well as rotations and translations, are difficult to measure.[26] For methane adsorbed in silicalite, the calculation of spectra of intramolecular vibrations[15,47] and comparison with experimental infrared, Raman, or inelastic neutron scattering spectra give an opportunity to see the changes in the vibrational dynamics due to the interaction with the framework. Such a theoretical work requires the application of the flexible atom−atom model for methane. The atom−atom interaction parameters for hydrogen, carbon, and framework oxygen can be defined empirically as is done in the well-known MM2[48] or UFF[49] force fields. Using empirical force fields one should take care about the transferability of the intermolecular parameters from the reference system to others. In our case the framework oxygen could have a different electronic structure from that in organic molecules. An alternative procedure for the derivation of parameters of molecule−zeolite interactions is proposed in refs 23 and 24 and in the present paper. A calculation based on the atomic properties explicitly reflects the electronic structure of interacting atoms. However, prior to the application of the Slater−Kirkwood formula one has to calculate atomic parameters as polarizabilities and effective numbers of electrons for the interacting atoms. The atomic parameters are well-defined for the rare gas atoms, which are frequently used in zeolite studies (see e.g. ref 17 for a recent work). For many-atom molecules, the transferability of the present method is limited by the necessity of determining the atomic parameters for atoms in molecules. Here, one can use different approximations, for example, for I atoms in the iodine molecule the parameters of the closest rare gas atom Xe have been used.[50]

The basic parameters for oxygen proposed in the present work can be applied to the calculation of the potential for methane studied in the five-center LJ molecule model[11] or in the flexible model,[13,15,45] as well as for other guest atoms and molecules. The uncertainty in the molecular parameters of oxygen, especially in the vdW radius, leaves place for further improvement of the potential. A possible *ab initio* way to tackle this problem is to perform quantum-chemical calculations of the interaction energy between a molecule and a sufficiently big cluster representing the zeolite framework. A more precise analysis requires calculations with different temperatures and loadings and comparison with available experimental data. In this way it is possible to adjust the molecular parameters of oxygen, varying them in reasonable limits. A good test can also be a comparison of simulations and experiments on binary mixtures of gases in zeolites.[17]

In conclusion, a potential for the interaction of methane molecules with the framework atoms of siliceous zeolites is developed empirically on the basis of general physical principles to describe intermolecular forces. As an application we calculate diffusion coefficients and the heat of adsorption of methane in silicalite. A good agreement with available experimental data indicates the validity of the new potential. Since the proposed determination of the potential is based on atomic and molecular properties of interacting particles, it gives an explicit way to construct molecule−framework potentials for other molecule−zeolite systems.

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