

Adsorption Isotherm and Other Properties of Methane in Zeolite A from an Intermolecular Potential Derived from *ab Initio* Calculations

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Zeolites are porous aluminosilicates well known for their catalytic and molecular sieve properties.¹ An understanding of the properties of hydrocarbons in zeolites is indispensable for developing zeolitic materials with superior catalytic and separation characteristics.² Interesting insights into chemical aspects of cracking of hydrocarbons or rearrangement reactions or hydrocarbon separation taking place within zeolites have been obtained by computer simulation methods such as molecular dynamics³ as well as with the help of quantum chemical calculations.⁴ The potential for interaction between the hydrocarbon and the zeolite plays a crucial role in these studies. While molecular simulation is extensively employed in studies involving biomolecules such as proteins, carbohydrates, and DNA as well as organic molecules, similar application to this more complex organic–inorganic system consisting of hydrocarbons and zeolites has not been possible due to the nonavailability of more accurate intermolecular potential functions.

Further, hydrocarbons in zeolites are of particular interest to the petrochemical industries, and this has been an active area of research.⁵ Recently, there have been several computational studies on different guests (including hydrocarbons) adsorbed in zeolites reported in the literature.⁶ However, the proposed potentials have not been tested to see whether they reproduce accurately both equilibrium and dynamical properties. Here we develop accurate methane–zeolite potentials from *ab initio* calculations. These are then shown to reproduce not only equilibrium properties such as adsorption isotherms but also dynamical properties such as diffusivities. Methane, the simplest member of the alkane family, may be considered to be a prototypical member of the alkane family, and the potentials may be transferable to higher alkanes. The intermolecular potentials are derived from a fit to *ab initio* energies obtained for methane in various locations inside zeolite A. Grand canonical Monte Carlo (GCMC) simulations have been performed to get the adsorption isotherms. Comparison with results for the potential reported by Murad and Gubbins⁷ (MG) shows that it is possible to develop accurate potentials for the guest–zeolite A interactions from purely *ab initio* calculations in the absence of experimental data. Classical molecular dynamics (MD) simulations have also been carried out to compute the self-diffusivity of methane.

The structure of zeolite A was taken from the work of Pluth and Smith.⁸ Zeolite A is a cubic microporous crystal (space group *Fm3c*) with a lattice parameter of 24.555 Å. The structure consists of an extended void network with α -cages of diameter ~ 11.4 Å, interconnected through narrower eight-ring windows of (free) diameter ~ 4.5 Å. The diagonal distance between the centers of the oxygen that form part of the eight-ring window is 6.77 Å. Extraframework sodium cations are known to occupy three distinct locations. In the present simulations, we have used a model of NaA zeolite with a Si/Al ratio of 2.0. The unit cell formula is Na₆₄Si₁₂₈Al₆₄O₃₈₄.

We have simplified the *ab initio* calculations by including only

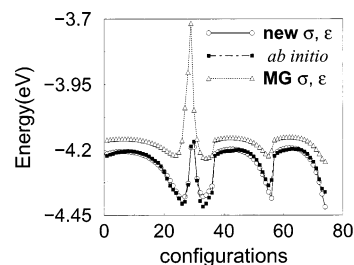


Figure 1. *Ab initio* methane–zeolite interaction energies for different configurations, along with the energies obtained from the fitted LJ potential. Also shown are the predictions by the MG potential.

Table 1. Interaction Parameters for MG and Proposed Potential

	type	σ (Å)	ϵ (kJ/mol)
(a) CH ₄ –CH ₄ and CH ₄ –Zeolite A Interaction Parameters			
CH ₄ –CH ₄ ^a	C–C	3.350	0.405
	C–H	2.813	0.068
CH ₄ –zeolite	C–O	2.950	0.723
	H–O	2.682	0.297
(b) Proposed CH ₄ –Zeolite Interaction Parameters			
CH ₄ –zeolite	C–O	3.042	0.975
	H–O	1.900	1.456

^a Reference 7.

the framework Si and O (no Na atoms) atoms. Thus, through the present study we obtain the interaction potential parameters for C and H with the O of the framework. However, in the classical GCMC and MD simulations, Na atoms have been included. The potential parameters for interaction between the Na and CH₄ have been taken from the study of Kiselev and Du.⁹ This enables us to compare the results of the classical GCMC and NVE-MD calculations with experimentally derived data.

Ab initio calculations were carried out using an all-electron full-potential mixed-basis approach within the local density approximation.¹⁰ Details of *ab initio* calculations are given in the Supporting Information. Density functional calculations of the energy landscape are possible because the methane molecule charge overlaps considerably with that of the zeolite rings during passage through the eight-ring window. The local density approximation was chosen because, for such rather weak bonding cases, it performs generally better than the generalized gradient approximation.¹¹

In the classical calculations, the interaction between the atoms of the methane molecule as well as atoms with the zeolite have been modeled by (6-12) Lennard-Jones (LJ) form, given by $\phi(r_{ij}) = 4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6]$, where ϵ_{ij} is the well depth, σ_{ij} is the diameter, and r_{ij} is the distance between the interacting atoms i and j . The methane–methane interaction parameters have been taken from the work of MG,⁷ and the cross-interaction parameters between methane and zeolite have been obtained from the use of Lorentz–Berthelot combination rules. They are listed in Table 1a. The short-range LJ interactions of the methane atoms with only the oxygens are included, and those with the Si and Al atoms of the framework are negligible and are not included. Interaction

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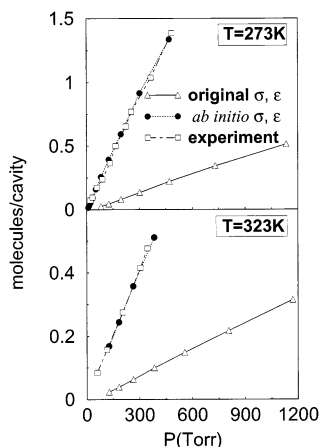


Figure 2. Adsorption isotherms at two different temperatures for the MG, the proposed potential derived from ab initio calculations, and experiment.

between the Na and (C,H) of CH_4 are⁹ $\epsilon_{\text{Na-C}} = 0.1261$ kJ/mol, $\sigma_{\text{Na-C}} = 3.36$ Å, $\epsilon_{\text{Na-H}} = 0.0517$ kJ/mol, and $\sigma_{\text{Na-H}} = 3.092$ Å.

Classical MD simulations of methane within the α -cages of zeolite A have been simulated in the microcanonical ensemble using the velocity Verlet algorithm. GCMC simulations have been carried out to compute the adsorption isotherm.¹² For more details on the MD and GCMC simulations, see the Supporting Information.

The fit to the ab initio energies E_{ab} was carried out with starting values in the neighborhood of the potential parameters of MG listed in Table 1a. The fit is to the 74 different configurations simultaneously by minimizing the function using a Monte Carlo algorithm,

$$f = \sqrt{\sum_{i=1}^{74} (E_{\text{cl}} - E_{\text{ab}})^2}$$

where E_{cl} is the classical interaction energy between CH_4 and zeolite host. Details of the fitting procedure adopted by us are described in the Supporting Information.

Figure 1 shows a plot of the ab initio energy differences between an arbitrary reference configuration and the configuration under consideration for 74 configurations. The values obtained from the fit to the LJ potential are listed (see Table 1b). It is seen that the fit reproduces quite accurately the energies from the ab initio calculations for most configurations. Larger deviations are seen whenever the interactions between the methane and zeolite are most favorable. This suggests that the predictive capability at rather low temperatures of the proposed potential may be poorer than at room temperature. Fortunately, since the range of temperatures in which we are interested is closer to room temperature, this may not pose a serious problem. The values of energy for the 74 configurations for the MG potential are seen to be shifted to higher values. Larger deviations occur near the potential minima and the maxima.

The pressure dependence of loading obtained using the original parametrization of MG and the proposed potential are shown in Figure 2. The variation is linear throughout. The results of experimental uptake measurements of methane in zeolite A, that is, of pressure variation with loading by Yucel and Ruthven, are also shown.¹³ The proposed potential reproduces *accurately* the adsorption isotherm at the two temperatures. The agreement is excellent, suggesting that the parametrization is good. The heat of adsorption ΔH_{ads} at 300 K for the proposed potential (20.16 kJ/mol) is closer to the experimental value than that predicted by MG (see Table 2).

A more crucial test of the intermolecular potential is when it can reproduce the dynamical properties. We have therefore carried out MD simulations at 1 methane/cage at 150 K. The value obtained

Table 2. Comparison of Self-Diffusivity and Heat of Adsorption for Various Potential Models.

	$D \times 10^{-9}$ (m ² /s)	ΔH_{ads} (kJ/mol)
MG ^a	4.62	14.70
this model	2.60	20.16
experiment	0.75 ^b	18.06 ^c 21.0–16.8 ^d

^a Reference 7. ^b For NaCaA zeolite with lower Si/Al ratio. ^c Reference 13. ^d Reference 14.

for the MG potential is higher than that predicted by the present potential (see Table 2). Pulsed-field-gradient NMR measurements by Karger et al.¹⁵ in NaCaA zeolite gave a value of 0.75×10^{-9} m²/s. The Si/Al ratio of the zeolite A sample used by Karger et al. is not mentioned, but the presence of Ca^{2+} certainly will lead to a decrease in the mobility of methane due to the interaction of the octupolar moment with the Ca^{2+} . In view of this, the agreement between the MD simulation and the experiment is good.

In conclusion, the results of the present study suggest that it is possible to derive accurate potentials on the basis of ab initio calculations. This augurs well for development of hydrocarbon–zeolite interaction potentials that will be of considerable use in modeling separation and other processes of importance to petrochemical industries. Development of such potentials when combined with multiple length and time scale simulations might aid or even obviate the need for expensive, time-consuming laboratory experiments. Previously Jorgensen¹⁶ and Kollman¹⁷ and others have developed accurate force fields for organic and biomolecules, respectively. As a result, studies on organic liquids and biologically important molecules are being carried out routinely. The present results suggest that it is possible to carry out similar studies on systems consisting of organic as well as inorganic elements.

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Supporting Information Available: Details of ab initio calculations, computational details of molecular dynamics simulations, computational details of grand canonical Monte Carlo (GCMC) simulations, and details of fitting procedure for the derivation of potential parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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