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Molecular Dynamics Simulation of Straight-chain Alkanes Adsorption and Diffusion in Zeolite

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ABSTRACT

Molecular dynamics simulations were applied to calculate self-diffusion coefficients ($D_{i,self}$) and heats of adsorption for ethane, propane and n-butane. Simulations were done in temperature range of 300-525 K for various concentrations inside the pores of silicalite type zeolite. Calculated values of self-diffusion coefficients and heats of adsorption resulted from the current work, were in better agreement with experimental estimated values found in literature than those resulted from simulations reported by other authors. For instance, at temperature of 300K and loading of 5 molecules/unit cell, self-diffusion coefficients of 16.56×10^{-5}, 7.62×10^{-5} and 5.81×10^{-5} cm^2/s were calculated for C_2H_6, C_3H_8 and n-C_4H_{10} respectively was compared to experimental reported values of 10×10^{-5}, 9×10^{-5} and 6×10^{-5} cm^2/s. At the same conditions, adsorption energies of 9.2, 11.48, and 13.66 kcal/mol. were calculated for ethane, propane, and n-butane respectively, while the experimental reported values found to be6.93, 9.7 and 12.7 kcal/mol. Simulations showed that the diffusion decreases when loading increases and the heats of adsorptions were increase by molecular weight of hydrocarbons for all adsorbates studied.

1. INTRODUCTION

Zeolites, as well-ordered micro porous structures, represent promising features for various industrial applications such as purification, separation and catalysis. A key parameter which is proven to play an important role in such applications is the diffusion rate of molecules in zeolite pores [1, 2]. Faujasite (FAU) type zeolites are amongst the most studied micro porous materials and well applied in various laboratorial and industrial applications. The FAU frame work consists of sodalite cages connected with hexagonal prisms which in turn create unique pores with perpendicular arrangments. Getting 10 sodalite cages together, an inner cavity of 12 Å diameter is formed with a quite large entrance of 7.4 Å diameter [3]. Promising features of zeolites and especially FAU type zeolites motivate researchers to broadly study zeolite-containing systems. Specifically, effects of molecule(s)-zeolite interactions on the diffusion rate, the ratio of Al/Si in the zeolite structure, the molecular configuration and the influence of Brønsted acid sites were widely investigated in such systems[2].

Evaluating the diffusion rate of different species in zeolites, is of big concerns of researchers and led to arise several experimental methods [3]. Quasi-elastic neutron scattering and pulsed field gradient nuclear magnetic resonance PFG-NMR techniques are widely performed to experimental measure both self (D_S) and transport (D_T) diffusion coefficients as a function of concentration to different gases in silicate and Faujasite systems [4, 5]. It is repeatedly emphasized that diffusions largely depend on the relevant volume of the studied system and also physical conditions under which the measurements were carried out. In addition, thermal effects, pore size of zeolites and the surface properties also have major impacts on validity and precision of diffusion measurements[6, 7].

Many articles have focused on experimental measurement of diffusions in zeolite pores[8, 9]; However, different measurement techniques led to different results. For instance, self-diffusion of methane, ethane and propane in zeolite frame works were measured by the pulsed field gradient NMR (PFG-NMR) technique[10]. Schwarz et al. measured self-diffusions of propane and propylene in NaX zeolite by using the same technique [11]. Brandani et al. measured the diffusion of propane and propylene in 13X and 5A zeolite crystals, and showed that there is no considerable differences between diffusions of propane and propylene, however associated NMR values were much larger than propane diffusion obtained by ZLC method[12]. Two different measurements, PFG-NMR

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and ZLC methods were carried out by Banas et al. in order to highlight the differences among experimental results[13]. Large deviations were also found in estimation of self-diffusions of branched alkanes in MFI-type structures obtained by different experimental and theoretical techniques[14]. The self-diffusion coefficients are considerably dependent on the configuration of gas molecules. For example, quasi-elastic neutron scattering (QENS) showed that self-diffusion coefficient of isobutene in ZSM-5 is much smaller than that of n-butane[15]. Therefore, experimental measurement of diffusion in zeolites can be a controversial issue. Thus, it seems reliable for comparing the experimental data with simulative calculations if possible [6, 7]. In the similar molecular dynamic simulation work the self-diffusion of methane, ethane, propane and i-butane into the zeolite ZSM-5 were estimated 6.02×10^{-5}, 2.71×10^{-5}, 2.53×10^{-5} and 0.06×10^{-5} respectively [16].

The main purpose of this work was to calculate the heats of adsorption and diffusions of ethane, propane, and n-butane in siliceous faujasite zeolite (silicalite) by molecular simulation using an optimized new force field for the adsorbent,which enabled fast molecular dynamics simulations on parallel structures .Molecular dynamics simulations were applied for alkanes in four levels of temperatures (300, 375, 450 and 525 K) and three levels of concentrations (5, 10 and 15 molecules per unit cell). The results of molecular dynamics simulations were then compared with some of the reported experimental measurements and other simulations.

2. METHODOLOGy

2.1. Zeolite framework The structure of zeolite was taken from the work of Zhu and Seff [17]. The faujasite unit cell is cubic and belongs to the space group Fd3m. Each unit cell has an edge length of 24.4 Å, and a composition of $Si_{192}O_{384}$. However, our simulation included 16 connected cells for higher accuracy.

2.2. Potential parameters A new force field for silicalite structure was proposed, by which fast molecular dynamics simulations were possible[18]. In this investigation, the potential energy of the zeolite included energies of O–Si–O and Si–O–Si angle bends, Si–O bond stretches, and bond torsions which are expressed as simple harmonic potentials. In addition Si–O–Si–O dihedral interactions were approximately estimated with acosine potential model. Table 1 lists all mentioned potential formulas in this work. The summation of Lennard-Jones (LJ 12-6) and Coulomb terms were used to present the inter molecular interactions (i.e. guest-guest, guest-zeolite). A very common method was applied to approximate the values of LJ parameters for C–O, C–Si, H–O and H–Si; in which the values of σ_{ij} and ε_{ij} were presented as a function of characteristics of O–O, Si–Si, H–H and C–Cbonds based on Lorentz–Berthelot combination rules theory:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (1)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (2)$$

TABLE 1. Terms in the analytical intra molecular potential for siliceous faujasite zeolite and alkanes.

Type of term	Equation
Bond	$U(r_{ij}) = K(r_{ij} - r_0)^2$
Angle	$U(\theta_{ijk}) = K(\theta_{ijk} - \theta_0)^2$
Dihedral angle	$U(\emptyset) = A[1 + \cos(m\emptyset - \alpha)]$
Lennard-Jones	$U(r_{ij}) = 4\varepsilon[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}]$
Coulomb	$U_{coul} = k\frac{q_i q_j}{r_{ij}}$

Where ε_{ij} and σ_{ij} are constants of i-j interaction. Required potential parameters derived by this method are presented in Table 2[18, 19]. The molecular orbital calculations were done by using density functional theory (DFT) methods in which all computations were carried out using Gaussian 98 program[20]. The geometry was established by the B3LYP method with 6-31++G** basis set and NBO populations were taken for the atomic partial charges of the alkanes (Table 3).

TABLE 2. Inter molecular harmonic force field parameters for zeolite and alkanes[18, 30].

Bond	K (kcal/mol. A2)			R_0 (A^2)		
	Ethane	Propane	Butane	Ethane	Propane	Butane
C-H	338.47	331.059	338.47	1.093	1.13	1.093
C-C	341.49	316.66	341.49	1.543	1.523	1.543
Si-O	300	300	300	1.61	1.61	1.61

Angle	K (kcal/mol. rad2)			θ_0 (0)		
	Ethane	Propane	Butane	Ethane	Propane	Butane
H-C-H	43.61	23.03	35.69	109.47	109.40	109.47
H-C-C	38.93	25.90	47.64	109.47	109.39	109.47
C-C-C	-	32.38	82.33	-	111.70	109.5

Angle	K(kcal/mol. rad2)	$\theta_0(0)$	Ku(kcal/mol. A2)	$u_0(0)$
si-o-si	300.0	1.61	30.0	3.12

Lennard Jones	ε (kcal/mol.)	σ(Å)
Lennard Jones	ε (kcal/mol.)	σ(Å)
Si-Si	0.6	3.92
O-O	0.152	3.15
C-C	0.0514	3.344
H-H	0.055	2.64

TABLE 3. Calculated atomic partial charges of zeolite and alkanes.

	Atom	Partial charge
Zeolite	Si	+2.00000
	O	-1.00000
Ethane	C1, C2	-0.66600
	H1, H2	+0.22200
Propane	C1, C3	-0.66100
	C2	-0.46000
	H1, H2, H3	0.22275
Butane	C1, C4	-0.65800
	C2, C3	-0.45500
	H1, H2, H3, H4	0.22260

2.3. Molecular dynamics simulations The Lammps program package [21]was used for MD simulations on windows work stations. Since the simulation needs infinite frame work, cubic periodic boundary conditions were defined in each simulation box direction. Four temperature levels of 300, 375, 450 and 525K and three levels of loadings (5, 10 and 15 molecules/unit cell) were applied in simulation. The pppm summation method was performed for coulomb ic and the van der Waals interactions calculations within a cut off length fixed at 12 Å. Equations of motion were modeled by obtaining the velocity form of the Verlet algorithm with a time step of 1 fs. Prior to the simulation, the structure of the frame work was optimized for a while by using the NPT ensemble. During optimization step, total energies were monitored and investigated in order to find out if the system reached the equilibration. Finally, the optimized frame work configuration was employed as the input for the main simulation run in a 10000 fs period at different temperatures.

3. RESULT AND DISCUSSION

3.1. Self-diffusion coefficients Sample MD geometry is depicted in Figure 1. which shows 5 molecules of studied alkanes loaded in one cage of silicalite in the simulation cell defined for this work. Figure 2. demonstrates the mean-square displacements (MSDs) of ethane, propane and n-butane molecules at different loadings and temperatures for 3000s of simulation. At low loading, MSD changes seem to rapidly stabilize to establish a linear relationship with time (Figure 2.) while for high loadings, more time was required for stabilization of simulation results.

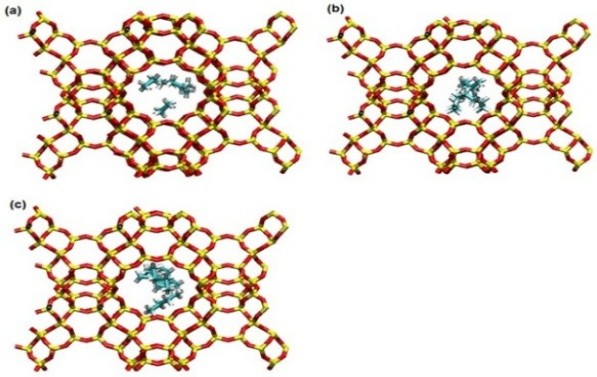


Figure 1. Loading of a unit cell for ethane (a), propane (b) and butane (c) with5 molecules per cell.

According to Einstein equation, self-diffusion coefficients can be easily calculated by applying a relatively constant slope from MSD curve sat elevated time scales.

$$D_s = \lim_{t\to\infty} \frac{1}{6Nt} \sum_{i=1}^{N} \Delta r(t)_i^2 \quad (3)$$

Where $\Delta r(t)_i^2$ is the mean-square displacement of particle i at time t, N is the number of particles and$D_s$is the self-diffusion coefficient. So self-diffusion coefficients were easily calculated by fitting a linear regression on calculated data at specific periods of time and are presented in Figure 3. Experimental determined values of self-diffusion coefficients for studied alkanes were inferred from the work of Ka¨rger et al. in which the pulsed field gradient (PFG)-NMR technique was used[22]. At the temperature of 300 K and almost the same concentration of 5 molecules/cell these values were reported 10×10^{-5}, 9×10^{-5}, and 6×10^{-5} cm^2/s for ethane, propane, and n-butane, respectively, which are in a good agreement with calculated values of our work. Comparing Figures 3a, 3b and 3c showed self-diffusions were decrease by increasing the chain length of the molecules. At low loadings, molecules have very high mobility and are free to move in all directions inside the structure of zeolite through the super cages and inter cages. At high loadings, the overall mobility is significantly decreased due to reduced volume for an individual molecule. The mobility of molecules like ethane is moderately higher than those of other alkanes because of their small sizes. Therefore, differences between self-diffusions at low and high loadings are the most for n-butane and the least for ethane, as seen in Figure 3.

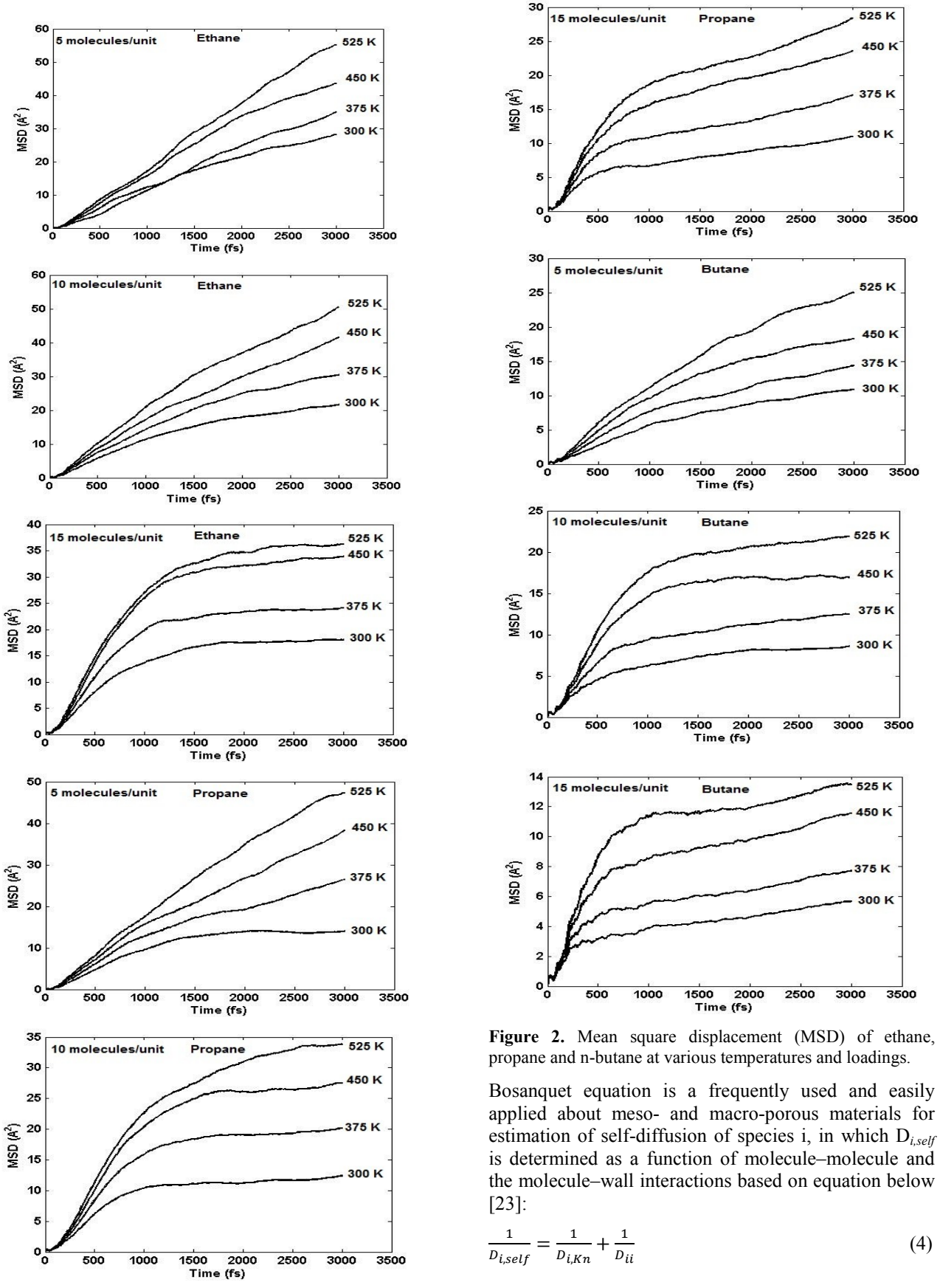


Figure 2. Mean square displacement (MSD) of ethane, propane and n-butane at various temperatures and loadings.

Bosanquet equation is a frequently used and easily applied about meso- and macro-porous materials for estimation of self-diffusion of species i, in which $D_{i,self}$ is determined as a function of molecule–molecule and the molecule–wall interactions based on equation below [23]:

$$\frac{1}{D_{i,self}} = \frac{1}{D_{i,Kn}} + \frac{1}{D_{ii}} \quad (4)$$

The quantities of the molecule–wall interactions are expressed byKnudsen equation:

$$D_{i,Kn} = \frac{d_p}{3}\sqrt{\frac{8RT}{\pi M_i}} \quad (5)$$

And the term D_{ii} which stems from molecule–molecule interactions, is estimated by several approximations of fluids [24]. In this studyD_{ii} was calculated by using Chapman and Hirsch felder equation for binary mixtures[25].

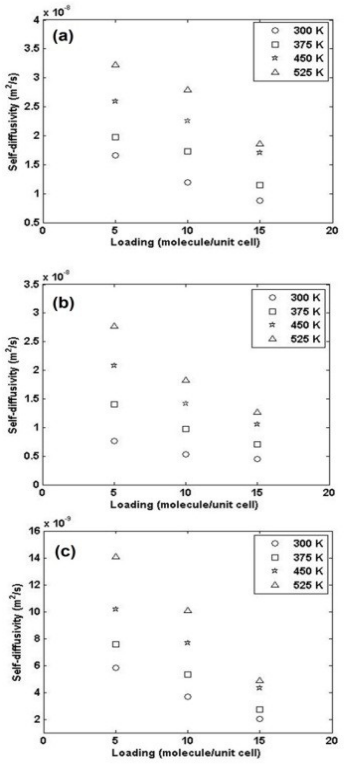


Figure 3. Simulated self-diffusions of(a) ethane, (b) propane and(c) n-butane in zeolite as a function of loading at various temperatures.

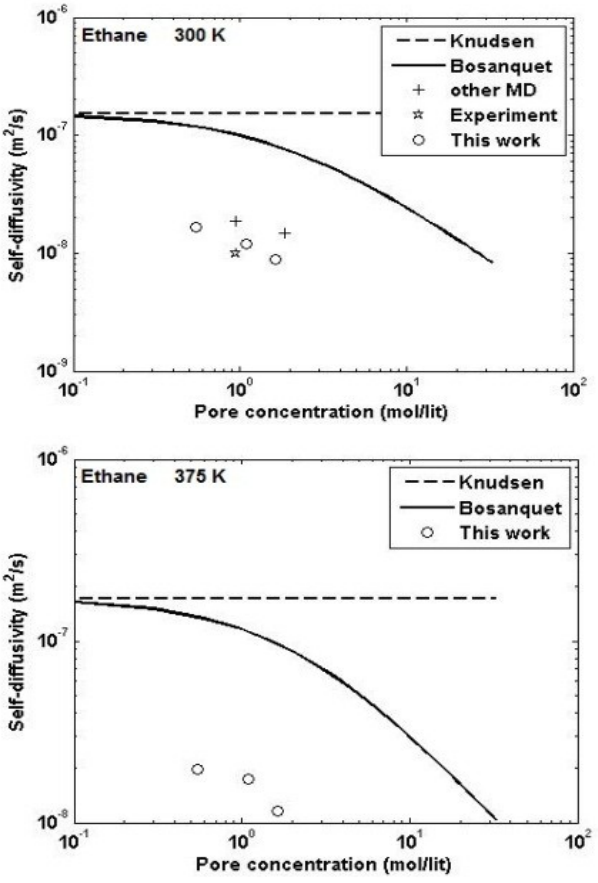
We also compared self-diffusion coefficients obtained by Molecular Dynamics (MD) simulations with those estimated by Bosanquet equation for the studied molecules in the afore mentioned ranges of molar concentration (C_i) and temperature (Figure 4). It was supposed that over-estimation in self-diffusion coefficients would be occurred by using Bosanquet formula when the molecules had relatively strong adsorption on the zeolite, in other words when the molecule-wall interaction is considerable. In all studied molecules, an inverse relationship between $D_{i,self}$ and concentration is obvious, which is contributed to less free volume available for molecule to move when concentration increases. The values of $D_{i,self}$ obtained by MD simulation are significantly lower than those calculated by Eq.4 whether the adsorption is considerable or not. In other words, when interactions between alkanes and zeolite are significant, self-diffusions are quite over-estimated by the Bosanquet formula. However, the differences become less for low pore concentrations. This deviation seems to be the result of the error of Knudsen formula for molecules with strong molecules-zeolite interaction, a failure marked in many articles[26].

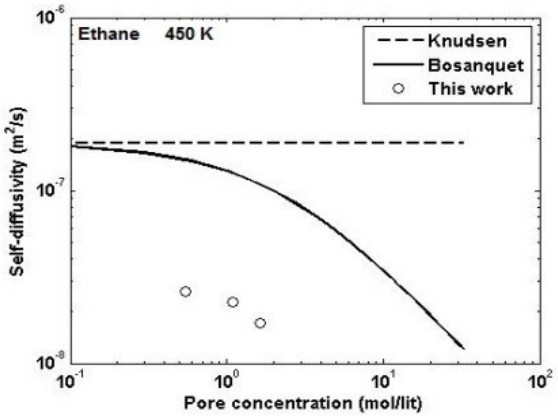
Figure 4. also compares the simulation results of present work with both the experimental data[22] and the simulation results reported by other authors[27] under identical conditions; which hints better agreement between our simulation results and the experimental data than those of the previous simulations.

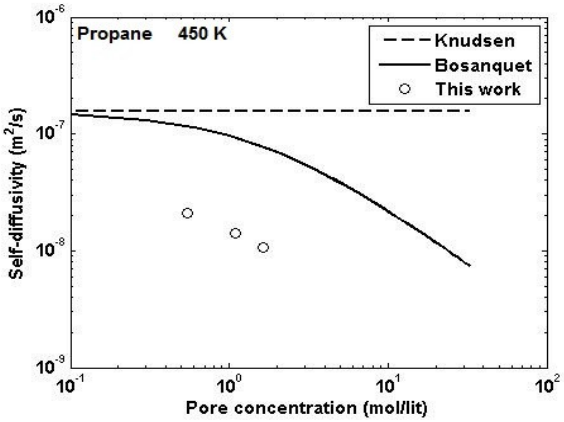
Quantitatively the relationship between the self-diffusion coefficient and the temperature is expressed by the Arrhenius Equation:

$$D_s = D_0 \exp(\frac{-E_{act}}{RT}) \quad (6)$$

Where E_{act} represents the activation energy, D_0 is the self-diffusion coefficient at a specified temperature, T is the absolute temperature and R is the ideal gas constant. Plottingln D_s versus $\frac{1}{T}$ gives a straight line which slope is $\frac{E_{act}}{R}$ and can be well interpreted by our simulation results (Figure 5). The values of E_{act} and D_0 estimated in this manner are listed in Table 4.




Ethane 450 K
Knudsen
Bosanquet
This work
Self-diffusivity (m²/s)
Pore concentration (mol/lit)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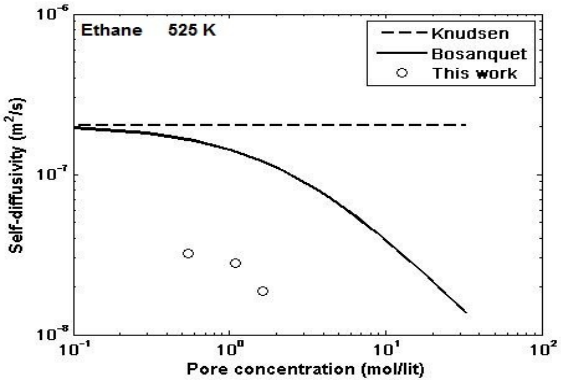
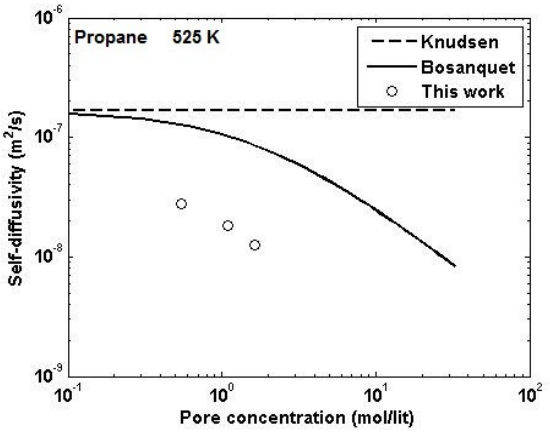
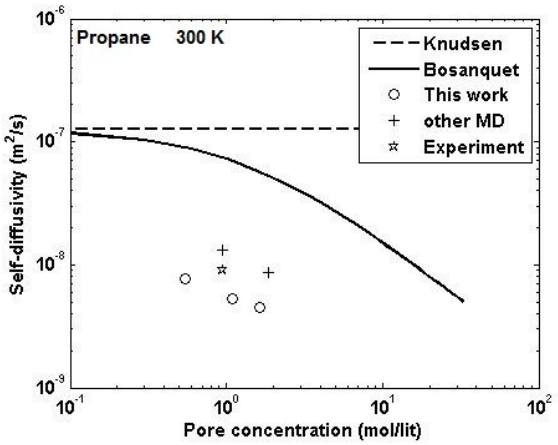
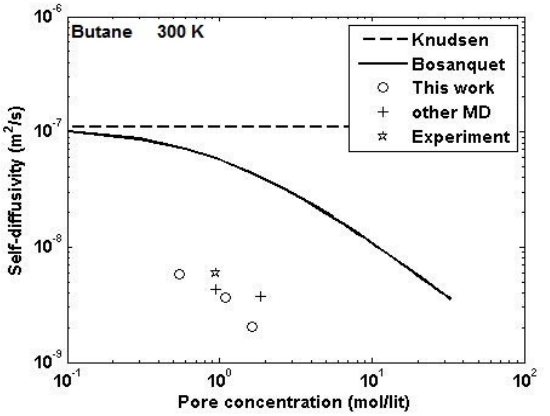
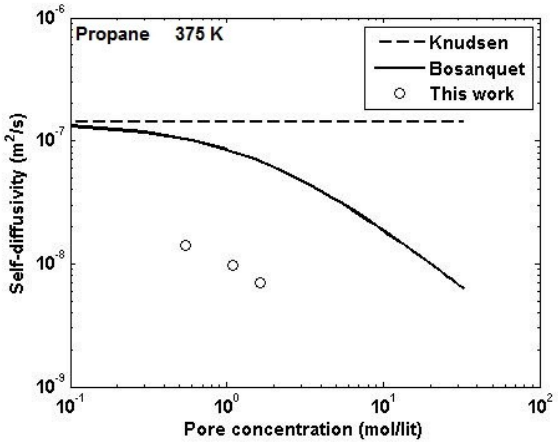
Knudsen
Bosanquet
This work
Self-diffusivity (m²/s)
Pore concentration (mol/lit)

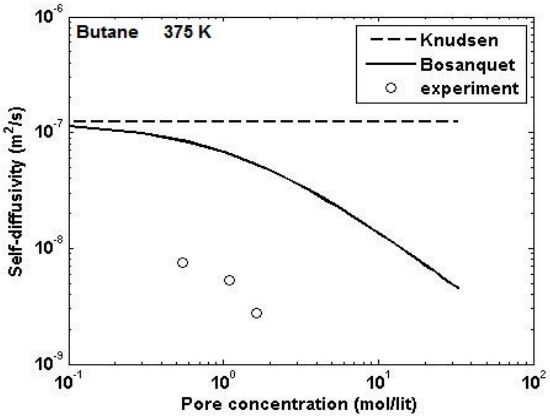

Ethane 525 K
Knudsen
Bosanquet
This work
Self-diffusivity (m²/s)
Pore concentration (mol/lit)

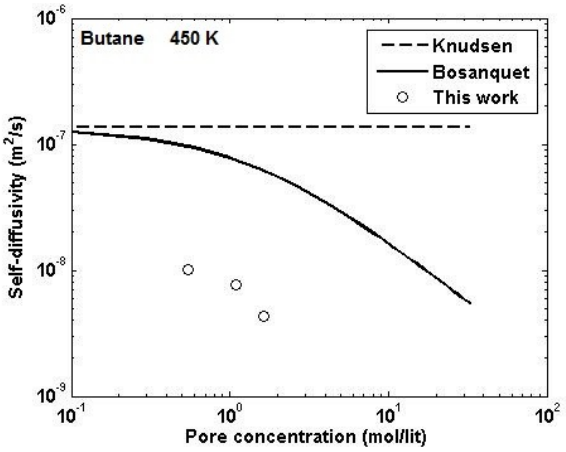

Propane 525 K
Knudsen
Bosanquet
This work
Self-diffusivity (m²/s)
Pore concentration (mol/lit)


Propane 300 K
Knudsen
Bosanquet
This work
other MD
Experiment
Self-diffusivity (m²/s)
Pore concentration (mol/lit)


Butane 300 K
Knudsen
Bosanquet
This work
other MD
Experiment
Self-diffusivity (m²/s)
Pore concentration (mol/lit)


Propane 375 K
Knudsen
Bosanquet
This work
Self-diffusivity (m²/s)
Pore concentration (mol/lit)


Butane 375 K
Knudsen
Bosanquet
experiment
Self-diffusivity (m²/s)
Pore concentration (mol/lit)



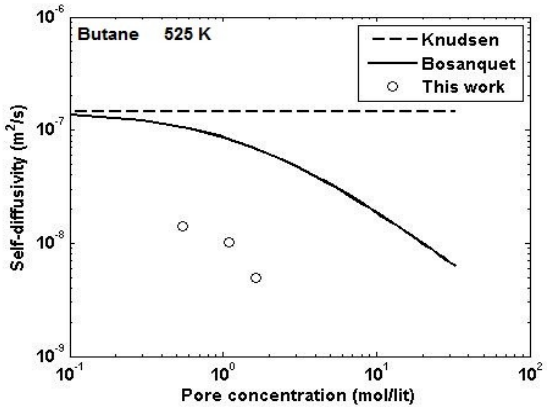


Figure 4. MD simulation of self-diffusions of ethane, propane and butane at four different temperatures 300, 375, 450 and 525 K are compared to estimations using the Bosanquet and Knudsen formula.

TABLE 4. Arrhenius coefficients for alkanes in zeolite.

Molecule	Loading (molecules/unit cell)	E_{act} (kj/mol)	D_0 (m^2/s)
Ethane	5	3.85	7.39×10^{-8}
Ethane	10	4.93	8.50×10^{-8}
Ethane	15	4.59	5.42×10^{-8}
Propane	5	7.51	15.49×10^{-8}
Propane	10	7.17	9.58×10^{-8}
Propane	15	6.18	5.32×10^{-8}
n-Butane	5	5.00	4.09×10^{-8}
n-Butane	10	5.85	3.71×10^{-8}
n-Butane	15	5.33	1.68×10^{-8}

TABLE 5. Adsorption energies in silicalite from molecular dynamics (MD), molecular mechanics (MM) and experiment values.

Adsorbate	Our MD (kcal/mol)	Other MM (kcal/mol) [31]	Experiment (kcal/mol) [28]
Ethane	9.2	8.7	6.93
Propane	11.48	12.1	9.7
Butane	13.66	15.1	12.7

3.2. Adsorption of alkanes The molecules-wall interaction energies were exploited to calculate the heats of adsorption for the corresponding molecules. In Table 5 the heats of adsorption at low coverage of linear alkanes in siliceous faujasite resulted from our MD simulations were compared with the experimental data reported by Titiloye et al.[28] and molecular mechanics data reported by Stach et al.[29] measured at 300 K.

The heats of adsorption of alkanes on zeolite consist of both terms of van der Waals and the Coulombic interactions. In fact, the values of 9.2, 11.48, and 13.66 kcal/mol. for ethane, propane, and n-butane respectively resulted from our work are in a better agreement with the experimental values[28] of 6.93, 9.7 and 12.7 kcal/mol. compared to those reported by the others[23]. It should be noted that the heat of adsorption does not change noticeably by increasing adsorbate loading (Figure 6). Since alkanes are non-polar molecules and columbic attractions are negligible, the heat of adsorption is in a direct relationship with the molecular mass of gases, i.e. based on the van't H off equation [30] the calculated energy increasesas the chain length in alkanes rises. The increase of adsorption energies with number of carbons showed in this study, are in quite agreement with the conclusion made in section 3.1 in explanation of the increase in the error of Bosanquet formula with molecular weights of alkanes. In addition, the thermodynamic data of adsorption of alkanes onto the zeolitepores are summarized in Table 5 and Table 6.

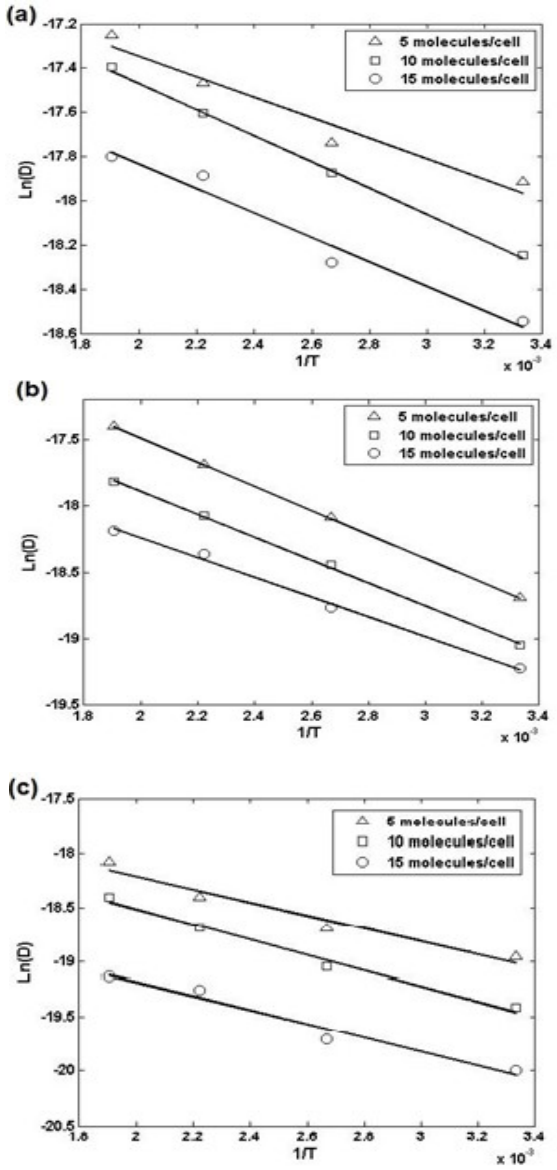


Figure 5. Arrhenius plots of the self-diffusion coefficients of (a): ethane, (b): propane and (c): butane in silicalite obtained for different loading bars.

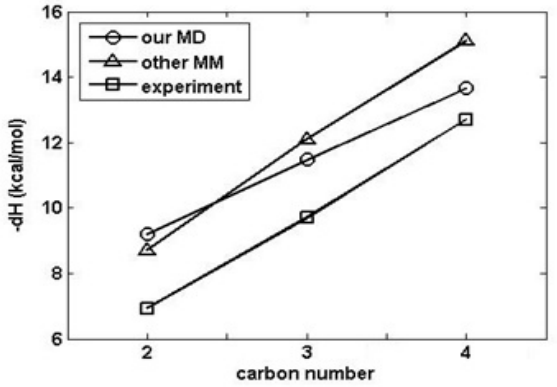


Figure 6. Heats of adsorption at low coverage (kcal/mol.) of linear alkanes.

TABLE 6. The relationship between heats of adsorption at low coverage obtained with our MD and other MM, and the carbon number of linear alkanes on zeolite compared to the experimental data.

$-\Delta H_0\left(\frac{kcal}{mol}\right) = aCN + b$		
Method	A	b
Our MD	2.23	4.757
Other MM [31]	3.2	2.367
Experiment [28]	2.885	1.122

4. CONCLUSION

A developed and new force field facilitating fast and efficient molecular dynamics simulations, was performed to calculate self-Diffusion coefficients and physical adsorption energies of C_2H_6, C_3H_8 and n-C_4H_{10} in to the pores of siliceous faujasite (silicalite) for a range of temperatures and pore concentrations. A comparison was made between the values of self-diffusion coefficients calculated by our simulations and the experimental data which confirmed the validity of simulations. For instance, the values of self-diffusion coefficients at 300 K were calculated 16.56×10^{-5}, 7.62×10^{-5}, and 5.81×10^{-5} cm^2/s for C_2H_6, C_3H_8 and n-C_4H_{10}, respectively, which better mimic the experimental values of 10×10^{-5}, 9×10^{-5}, and 6×10^{-5} cm^2/s than those obtained by similar simulations. Self-diffusion coefficients were also calculated using well known Bosanquet formula, However, significant differences were then seen between these results and experimental data which are mainly attributed to the error of Knudson formula when adsorption of molecules in zeolite pores is significant i.e. when the molecule–wall interactions are dominant. This conclusion was also confirmed by the results of adsorption energies which showed increasing the molecular weights of alkanes leads to increasing both heat of adsorption and error of Bosanquet formula. We calculated the self-diffusions and activation energies for some of the straight-chain alkanes by considering the Arrhenius equation. Their heats of adsorption in siliceous faujasite were also calculated and compared to those determined by the molecular mechanics approach, which in a better agreement with corresponding experimental results was shown by our results.

5. ACKNOWLEDGMENTS

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6. NOTATION

$D_{i,self}$	self-diffusion coefficient [m^2/s]
$D_{i,Kn}$	Knudsen diffusion coefficient [m^2/s]
D_{ii}	molecule–molecule diffusion coefficient [m^2/s]
D_0	pre-exponential factors [m^2/s]
d_p	Pore diameter[Å]
E_{act}	activation energy for diffusion[kj/mol.]
R	Ideal gas constant, 8.314 j/K
T	Absolute Temperature [K]
M_i	Molecular mass [g/mol.]
ΔH_0	Heat of adsorption[kcal/mol.]
Δr	Displacement [m^2]
t	Time [s]
N	Number of atoms or molecules

Greek letters

ε characteristic energy in Lennard–Jones potential, [K]

σ characteristic distance in Lennard–Jones potential, [Å]

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