

Diffusion of an alkane molecule in siliceous zeolite beta

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Abstract

A molecular dynamics (MD) simulation was performed to study the diffusion of an alkane molecule in siliceous zeolite beta, as a function of chain length and temperature. The alkane was modeled as a Lennard-Jones chain, and the simulation was carried out in the microcanonical ensemble. The results suggest that it is energetically favorable for the alkane chains to be within close proximity ($\sim 2 \text{ \AA}$) of the zeolite lattice. However, the histogram data also show that shorter alkane chains are more likely to be found at farther distances ($\sim 4.5 \text{ \AA}$) from the lattice atoms in the zeolite voids, compared to longer chains that experience more attractive interactions with the lattice and thus are confined to the small zeolite cages.

Background

Zeolites are crystalline nanoporous aluminosilicates widely used in industry for catalytic and ion exchange applications. One of the material properties that governs the functionality and performance of a zeolite is the framework topology, where the pore size and connectivity have significant effects on surface area and mass transport properties. Zeolite beta, with framework type 'BEA' as designated by the International Zeolite Association (IZA), is the focus of this study. The structure of zeolite beta is characterized by two distinct polymorphs (A and B) with interconnecting three-dimensional 12-ring pores¹. This complex structure gives zeolite Beta unique selectivity in many industrial reactions, which are catalyzed by framework Bronsted and Lewis acid sites^{2,3}. Fundamental to these processes is the diffusion of reactant molecules within the zeolite pores, which ultimately affects macroscopic catalytic properties such as turnover frequency and reaction rates. Thus, the focus of this simulation study is to investigate the diffusion of an alkane molecule in zeolite beta. Specifically, this study will examine the how parameters such as chain length and temperature affect the proximity of the alkane chain to the lattice atoms by constructing a histogram of shortest distances.

Simulation methods

In this work, only polymorph A of zeolite beta is considered, which is modeled as a static lattice of 204 atoms. The lattice atoms are placed in a unit cell according to crystallographic data for the BEA framework type, available from the online IZA database⁴. Periodic boundary conditions are imposed along the x, y, and z axes. It should be noted that the lattice atom positions modeled here are all characteristic of siliceous zeolite beta ($\text{Si/Al} = \infty$). Substitution of framework tetravalent Si atoms by trivalent Al atoms introduces a negative charge on the framework, as well as changes the bonding geometry of the tetrahedrally coordinated lattice.

All lattice atoms were modeled as spheres of the same type interacting through a 12-6 Lennard-Jones potential that is cut and shifted with $r_c = 4.0$. Alkane molecules are

modeled as Lennard-Jones chains of various lengths $M = 4, 6, 8$, characterized by both non-bonded (12-6 Lennard-Jones potential) and bonded (harmonic potential) interactions, as given by the dimensionless potential energy function U^* :

$$U^* = \sum_{i < j, ij \text{ not bonded}} 4 \left(\left(\frac{r_{ij}}{\sigma_{PP}} \right)^{-12} - \left(\frac{r_{ij}}{\sigma_{PP}} \right)^{-6} \right) + \sum_{i < j, ij \text{ bonded}} \frac{k}{2} (r_{ij} - r_0)^2$$

Values for the fundamental length-scales of the polymer-polymer (σ_{PP}) and lattice-polymer (σ_{LP}) Lennard-Jones interactions were chosen to reflect the geometries of the different atoms in the zeolite lattice (Si, O) and the alkane molecule (C, H). Similarly, the equilibrium bond distance, r_0 , for the bonded interactions between alkane chain molecules was assigned based on experimental data for C-C bond distances⁵.

The MD simulation is performed in the microcanonical ensemble (constant NVE) using the velocity Verlet algorithm. A single alkane chain of length M is initially placed in the center of one of the large 12-ring zeolite pores, and the energy of the initial configuration is minimized using a conjugate gradient method with line search. Before the production run with constant NVE dynamics, the system undergoes two equilibration periods, in which the velocities are rescaled to the target temperature T using a Berendsen thermostat. At the end of the second equilibration period, the average total energy is computed and used to rescale the velocities such that the sum of the current kinetic and potential energies is equal to the target average total. The production run is then performed without velocity rescaling for a total of 100,000 integration steps ($dt = 0.001$, $t_{tot} = 100$). During the production run, a histogram is constructed of the shortest distance between the alkane chain center-of-mass and the lattice atoms. Histogram counts are added to bins every 1000 integration steps during the production run.

Results and interpretation

Production runs are carried out for each $M = 4, 6, 8$ and $T = 1.0, 1.5, 2.0, 2.5, 3.0$. Additionally, three simulation trials are performed to give histogram data of high statistical quality. The histograms are constructed to show the how the distance from the center-of-mass of the diffusing alkane chain to closest lattice atom varies throughout the simulation. The results are summarized in Figures 1-3.

For all alkane chain lengths, the histograms exhibit a skewed bimodal probability distribution, which suggest that it is energetically favorable for the alkane chains to be within close proximity ($\sim 2 \text{ \AA}$) of the zeolite lattice. However, the distribution of shortest alkane chain ($M = 4$) is the least positively skewed, as shown in Figure 1(a). This result indicates that it is statistically more likely for this polymer chain to diffuse throughout the zeolite lattice in the larger pore voids, compared to the longer alkanes. As the chain length is increased to $M = 6$ and $M = 8$, the probability of finding the alkane at farther distances ($\sim 4.5 \text{ \AA}$) from the lattice decreases. In other words, the longer alkane chains are more likely to diffuse from their initial positions in the large zeolite pore into smaller

cages, where the attractions to the zeolite lattice atoms are energetically favorable. This trend is shown in Figures 2(a) and 3(a), respectively. Within the simulation error, there is no statistically discernible relationship between temperature and minimum chain-lattice distance. However, it is expected that simulations with higher concentrations of alkane chains would show such a trend.

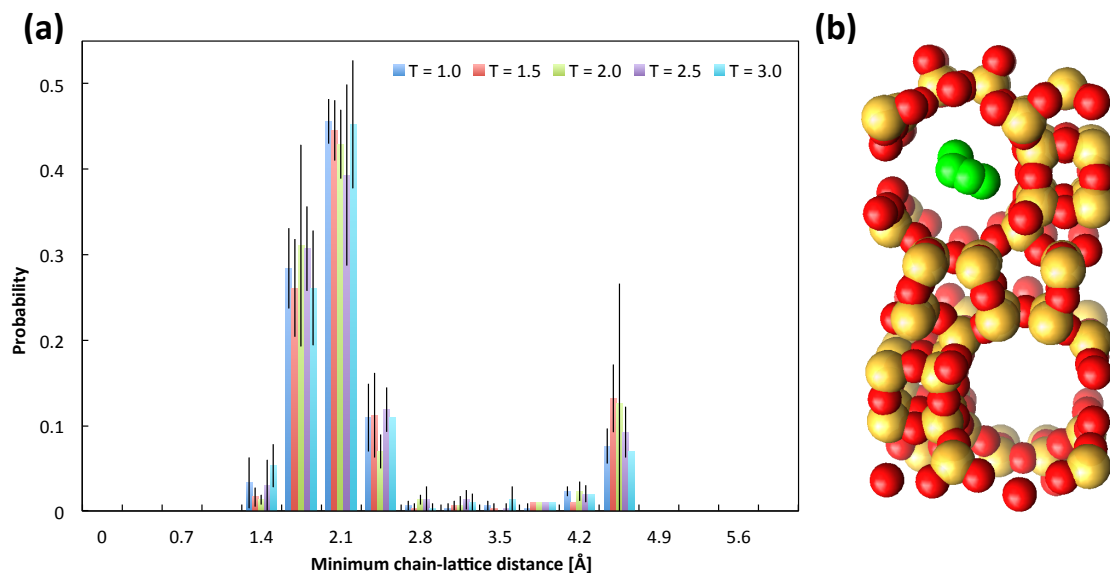


Figure 1: (a) Histogram for alkane chain of length $M = 4$, plotted for each $T = 1.0, 1.5, 2.0, 2.5, 3.0$. Results are averaged for three simulation runs, where the error bars reflect the standard deviation of the separate trials. (b) Chimera screenshot of MD simulation with $M = 4$ and $T = 2.5$, showing the alkane chain (green) diffusing within the large zeolite pore. Si and O lattice atoms are colored yellow and red, respectively.

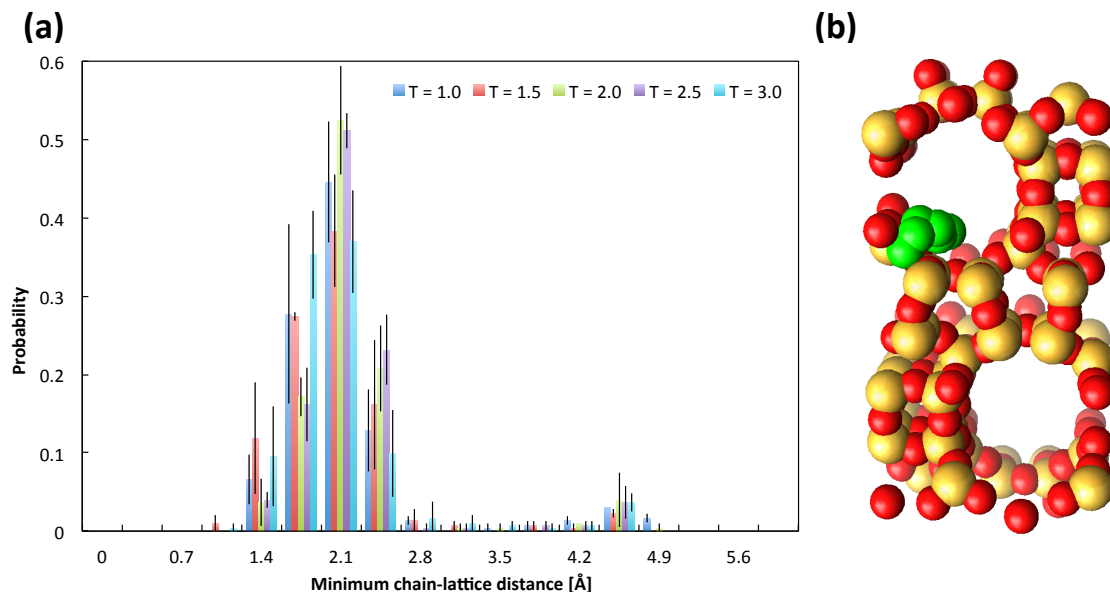


Figure 2: (a) Histogram for alkane chain of length $M = 6$, plotted for each $T = 1.0, 1.5, 2.0, 2.5, 3.0$. Results are averaged for three simulation runs, where the error bars reflect the standard deviation of the separate trials. (b) Chimera screenshot of MD simulation with $M = 6$ and $T = 2.5$, showing the alkane chain (green) entering one of the small zeolite cages. Si and O lattice atoms are colored yellow and red, respectively.

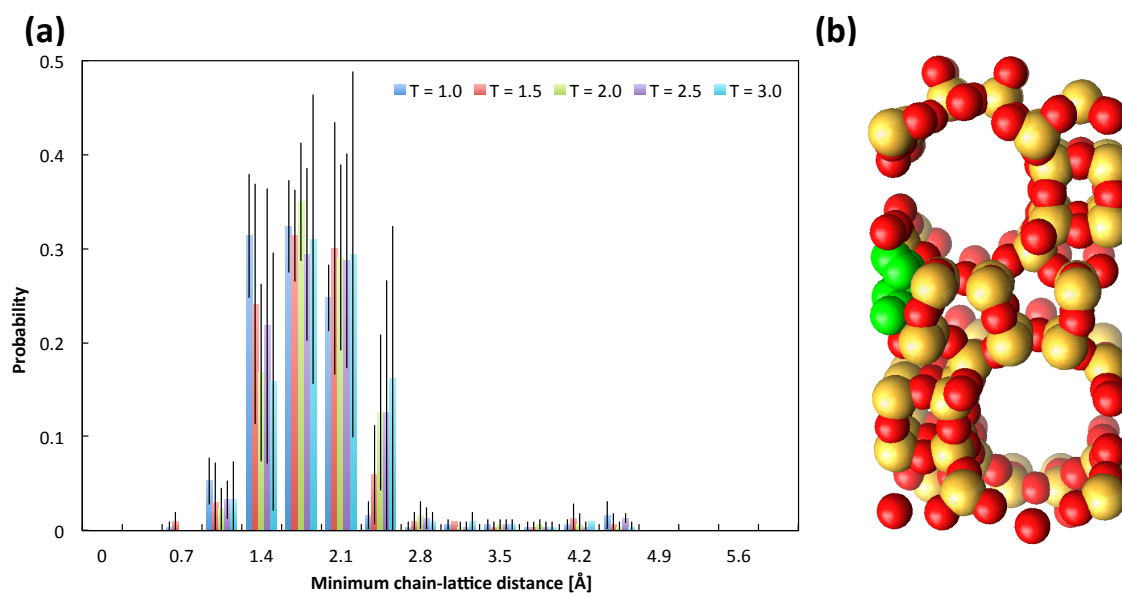


Figure 3: (a) Histogram for alkane chain of length $M = 8$, plotted for each $T = 1.0, 1.5, 2.0, 2.5, 3.0$. Results are averaged for three simulation runs, where the error bars reflect the standard deviation of the separate trials. (b) Chimera screenshot of MD simulation with $M = 8$ and $T = 2.5$, showing the alkane chain (green) within one of the small zeolite cages. Si and O lattice atoms are colored yellow and red, respectively.

Improvements to this model can be made in regards to robustness, system size, and energetics. The initial placement of the alkane chain in the large zeolite void was based on trial-and-error inspection. Instead, it would be desirable to randomly place the chain in the lattice, such that the simulation methods could be applied to other zeolite framework topologies. Furthermore, this modification to the current code architecture would allow for the simulation of multiple polymer chains in the zeolite lattice. In this way, the self-diffusion coefficient could be estimated from mean-squared-displacement data as a function of concentration. Finally, the energetics of the chain-lattice interactions could be improved upon by accounting for binding energies, as well as the electrostatic effects of the zeolite cages.

Movie

Diffusion of a single alkane chain of length $M = 4$ with temperature $T = 2.5$ in siliceous zeolite beta. Si and O lattice atoms are colored yellow and red, respectively.

References

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