Supporting Information

Unraveling Argon Adsorption Processes in MFI-type Zeolite

E. García-Pérez¹, J. B. Parra², C. O. Ania², D. Dubbeldam³, T. J. H. Vlugt⁴, J. M. Castillo¹,⁵, P. J. Merkling¹, and S. Calero¹∗

¹ Department of Physical, Chemical, and Natural Systems, University Pablo de Olavide, Ctra. Utrera km. 1. 41013 Seville, Spain.
² Energy and Environment Department, Instituto Nacional del Carbón, CSIC, P.O. 73, 33080 Oviedo, Spain.
³ Chemical & Biological Engineering Department, Northwestern University Evanston, IL 60208 USA
⁴ Delft University of Technology, Process & Energy Laboratory, Leeghwaterstraat 44, 2628CA Delft The Netherlands
⁵ Centre Européen de Calcul Atomique et Moléculaire (CECAM), Ecole Normale Supérieure, 46 allée d’Italie, 69007 Lyon, France
Functional form of the force field for flexible MFI-type zeolite$^1$. 

- $U^\text{total} = U^\text{bonded} + U^\text{nonbonded}$

- $U^\text{bonded} = U^\text{bond} + U^\text{bend} + U^\text{Urey-Bradley} + U^\text{torsion}$

- $U^\text{bond} (r_{ij}) = \frac{k}{2} (r_{ij} - r_0)^2$ ; $k/k_B = 300724.77 \text{ K } \text{Å}^{-2}$ and $r_0 = 1.61 \text{ Å}$

- $U^\text{bend}_\text{O-Si-O} (\theta_{\text{O-Si-O}}) = \frac{k}{2} (\theta_{\text{O-Si-O}} - \theta_0)^2$ ; $k/k_B = 69537.44 \text{ K } \text{deg}^{-2}$ and $\theta_0 = 109.5 \text{ deg}$

- $U^\text{bend}_\text{Si-O-Si} (\theta_{\text{Si-O-Si}}) = \frac{k_1}{2} (\theta_{\text{Si-O-Si}} - \theta_0)^2 + \frac{k_2}{3} (\theta_{\text{Si-O-Si}} - \theta_0)^3 + \frac{k_3}{4} (\theta_{\text{Si-O-Si}} - \theta_0)^4$ ; $k_1/k_B = 5462.51 \text{ K } \text{deg}^{-2}$, $k_2/k_B = -17157.81 \text{ K } \text{deg}^{-4}$, $k_3/k_B = 13351.67 \text{ K } \text{deg}^{-6}$, and $\theta_0 = 149.5 \text{ deg}$

- $U^\text{Urey-Bradley}_\text{Si-Si} (r_{\text{Si-Si}}) = \frac{k}{2} (r_{\text{Si-Si}} - r_0)^2$ ; $k/k_B = 27488.74 \text{ K } \text{Å}^{-2}$ and $r_0 = 3.1261 \text{ Å}$

- $U^\text{torsion} (\phi_{ijkl}) = k \left[ 1 + \cos(3\phi_{ijkl}) \right]$ ; $k/k_B = -176.21 \text{ K}$

- $U^\text{nonbonded} = U^{\text{VDW}} + U^{\text{Ewald}}$

- $U^{\text{VDW}} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$
• Silicon-silicon Lennard-Jones interaction parameters:
  \( \epsilon_{\text{Si-Si}}/k_B = 29.43 \text{ K} \) and \( \sigma_{\text{Si-Si}} = 29.43 \text{ Å} \)

• Oxygen-oxygen Lennard-Jones interaction parameters:
  \( \epsilon_{\text{O-O}}/k_B = 29.43 \text{ K} \) and \( \sigma_{\text{O-O}} = 3.06 \text{ Å} \)

Lorentz Berthelot mixing rules were applied for the Si-O Lennard Jones interaction parameters.

• Electrostatic interactions (\( U^{\text{Ewald}} \)) were calculated with Ewald summations.

**Functional form of the force field for argon in MFI-type zeolite**

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U = U_{\text{Ar-Ar}}^{\text{VDW}} + U_{\text{Ar-Zeo}}^{\text{VDW}}
\]

Argon-argon Lennard-Jones interaction parameters were obtained by fitting the force field to the experimental vapor-liquid equilibrium curve using a potential truncated and shifted at 12 Å. Argon-oxygen Lennard-Jones parameters were obtained by calibrating the force field through explicitly fitting three points of the experimental isotherm at 77 K. Simulations were performed at \( 2.0 \times 10^{-3} \) kPa, \( 9.0 \times 10^{-2} \) kPa, and \( 9.0 \times 10^{-1} \) kPa using the rigid, monoclinic structure at 77 K. The interactions of the adsorbed molecules with the zeolite are dominated by the dispersive forces between the guests atoms and the oxygen atoms of the zeolite\(^2\), meaning that the silicon van der Waals interactions are taken into account through an effective potential with only the oxygen atoms.

• Argon-argon Lennard-Jones interaction parameters:
  \( \epsilon_{\text{Ar-Ar}}/k_B = 124.07 \text{ K} \) and \( \sigma_{\text{Ar-Ar}} = 3.38 \text{ Å} \)

• Argon-oxygen Lennard-Jones parameters:
  \( \epsilon_{\text{O-Ar}}/k_B = 107.69 \text{ K} \) and \( \sigma_{\text{O-Ar}} = 3.15 \text{ Å} \)
**Figure 1.** Vapor-Liquid Equilibrium curve of Ar showing experimental\(^4\) and simulated data. Red crosses, values obtained with a previous forcefield\(^5\); blue asterisks, forcefield used in this article.

![Graph showing Vapor-Liquid Equilibrium curve of Ar with different data points and labels.](image-url)
Figure 2. Energy profiles obtained directly from our simulations during argon adsorption at 77 K and 5 $10^{-3}$ kPa. On average, 23 molecules of argon per unit cell are adsorbed at these conditions, corresponding to the loop in the adsorption isotherm. The orthorhombic structure is drawn in yellow (always rigid) and the monoclinic in green, being rigid in (a) and flexible in (b).
**Movie 1.** Changes observed in the monoclinic, flexible structure of MFI with increasing loading of Ar. The movie is taken directly from our simulations at 77 K and spans from a loading of 2 molecules per unit cell (0.000117 kPa) up to 30 molecules per unit cell (0.0904 kPa). The monoclinic starting framework (shown in the first frame of the movie) is drawn in grey to compare with the changing structure in green.
REFERENCES


