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Adsorption and Diffusion of C₁ to C₄ Alkanes in Dual-Porosity Zeolites by Molecular Simulations

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We employ grand canonical Monte Carlo and molecular dynamics simulations to systematically study adsorption and diffusion of C_1 to C_4 alkanes in hierarchical ZSM-5 zeolite with micro- (~ 1 nm) and mesopores (> 2 nm). The zeolite is characterized by a large surface area of active sites at the microporous scale with high permeability and access to the active sites, which arises from the enhanced transport at the mesoporous scale. We model this zeolite as a microporous Na^+ exchanged alumino-silicate zeolite ZSM-5/35 (Si/Al=35) in which cylindrical mesopores with diameter of 4 nm have been built by deleting atoms accordingly. We use the TraPPE and Vujić-Lyubartsev’s force fields along with the Lorentz-Berthelot mixing rules to describe adsorbate-adsorbate and adsorbate-adsorbent interactions. Performance of the force fields is assessed by comparing against experimental single-component adsorption isotherms of methane and ethane in microporous ZSM-5/35, which we measured as part of this work. We compare adsorption isotherms and diffusivities of the adsorbed alkanes in the dual-porosity zeolite with those in the microporous ZSM-5/35, and discern the specific behavior at each porosity scale on the overall adsorption, self-diffusion and transport behavior in zeolites with dual micro/mesoporosities.

1 Introduction

Zeolites are crystalline microporous materials typically made from the tetrahedral SiO_4 and AlO_4 building blocks being connected by corner-sharing oxygen atoms to form highly-ordered open pores ranging from 0.3 to 1.2 nm in diameter. Due to their large surface areas and tunable pore sizes, they are widely applied in catalysis, adsorption, phase separation, energy storage, and decontamination. At present, there exist more than 60 natural zeolites and about 230 synthetic analogues. They differ in crystal structure, and the size, shape, and connectivity of their pore systems from 8- to 14-rings and one-, two-, or three-dimensional pore arrays with or without intersecting pores. In some zeolites, cages can also be present in the structure, the sizes of which are usually larger than pore entrances [1].

In zeolites, the large Brunauer-Emmett-Teller (BET) surface areas, the small sizes of the pores and the strong interactions of adsorbate molecules with the surface lead to strong confinement effects on the adsorbed phase [2]. Confinement hinders diffusion of the adsorbate molecules inside the micropores, and restricts access to the active sites [3, 4]. An approach used to overcome the very slow diffusion and limited accessibility to these active sites includes connecting the microporous framework to a transport pore network with wider pores. Such hierarchical porous structures enhance the overall diffusivity of the adsorbate molecules along with access to the active sites located in the microporosity, while still retaining the properties of the microporous materials such as a large surface area. A first class of hierarchical porous solids includes microporous materials (~ 1 nm pores), in which mesopores (> 2 nm pores) are introduced. Typically, zeolites or metal-organic frameworks (MOFs) [5, 6, 7, 8, 9] are used as the microporous component. A second class of hierarchical porous solids can be obtained by incorporating guest microporous particles into a mesoporous network of a host material, e.g., zeolite or MOF nanocrystals incorporated in mesoporous silica [9, 10, 11, 12].

Due to the ability to prepare different zeolites with “almost continuously”

increasing pore sizes, as well as zeolites with dual micro/mesoporosities [13, 14], we have recently proposed to use microporous and dual-porosity zeolites as engineered (model) materials for development, testing and improvement of analytical models [15, 16], used to describe the transport of fluids in the clay and kerogen micro- and mesopores of shale rocks [17, 18, 19]. Using both experimental approaches and molecular simulation in a complimentary manner, the idea is to systematically change the pore sizes, pore shapes, and pore chemistry so as to reproduce some of the features of shale rocks, and then study adsorption and transport of natural gas, water, and other substances in the engineered model materials at thermodynamic conditions of hydraulic fracturing (temperatures up to 100°C and pressures from a few up to hundred bar). Although shale and zeolites pores are very different (e.g., shale pores are amorphous [20], while zeolites are crystalline), the analytical models such as ROXOL [21, 22] that are capable of describing the simultaneous formation of fractures in rocks and the transport of fluids through these fractures, are robust enough to handle these differences. In addition, the dual-porosity zeolites allow us to discern the roles played by each porosity scale and the underlying links between the two porosity networks on the structure and dynamics of adsorbed, confined fluids.

In this work, we report molecular simulations of the adsorption and dynamics of a series of short alkanes (from methane to *n*-butane) in a model hierarchical porous solid with interconnected microporosity (~ 1 nm) and mesoporosity (> 2 nm). The short alkanes, methane, ethane, propane and *n*-butane are abundant components of shale gas [23]. The porous model consists of an MFI zeolite in which hydroxylated silica mesopores are introduced. The MFI zeolite structure consists of zigzag and straight intersecting channels along the *x*- and *y*-directions, respectively, with average diameter of 0.54 nm. Diffusion along the *z*-direction is only possible by following a tortuous path through zigzag-straight channel intersections [24]. In this work, we consider mesopores oriented in the direction of the straight channels. Our model is analogous to models of hierarchical faujasite zeolite [25] or hierarchical Cu-

BTC MOF [26], proposed by Coasne’s group and used to study adsorption and transport of nitrogen. The molecular simulations for the dual-porosity MFI zeolite are compared with those for microporous MFI zeolites. While enormous numbers of molecular simulations have been reported on the adsorption, self-diffusion and transport in zeolites and mesoporous silica, e.g., Refs. [27, 28, 29, 30, 31], there exist only a few molecular-level simulation studies for hierarchical porous materials [25, 26, 32, 33, 34].

The remainder of the paper is organised as follows. Experimental details about the zeolite synthesis and adsorption measurements are outlined in Section 2. Section 3 provides the computational details of the zeolite models, the intermolecular interactions, and the simulation of adsorption, self- and transport diffusion. In Section 4, we compare the experimental and simulation adsorption isotherms for methane and ethane in the microporous zeolite, which are used to validate the molecular model. This is followed by a discussion of our simulation results for adsorption isotherms, and self-, collective and transport diffusivity of short alkanes in both zeolites. Finally, we present our conclusions in Section 5.

2 Experimental Details

2.1 Zeolite Synthesis

We synthesized 10-ring zeolite ZSM-5 (IZA structure code MFI [24]) with a Si/Al ratio of 35, denoted by ZSM-5/35. First, we mixed together 36 g of TEOS (Aldrich 131903) and 7.2 g of ethyl alcohol, absolute. Then, the solution was mixed with 1.8 g of $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (Lachner, p.a.) dissolved in 14.5 ml of H_2O , and stirred at room temperature for 90 minutes. Second, 64.8 g of tetrapropyl ammonium hydroxide solution (20 % in H_2O , Fluka 88111) was dissolved in 63 ml of H_2O , and the stirred solution was added to the first mixture. The final mixture was then stirred for 3 hours at room temperature. After that, the mixture was poured into a PTFE lined stainless steel autoclave and was kept at 170°C for 5 days without agitation until the solidified sample settled on the bottom.

We determined the structure and crystallinity of the zeolite by X-ray powder diffraction using a Bruker AXS D8 Advance diffractometer equipped with a graphite monochromator and a position sensitive detector Vântec-1 using $\text{CuK}\alpha$ radiation in the Bragg-Brentano geometry. We also measured nitrogen adsorption/desorption isotherms using a Micromeritics GEMINI II 2370 volumetric Surface Area Analyzer at 77 K to determine the surface area, pore volume and pore size distribution (PSD). Prior to the sorption measurements, all samples were degassed in a Micromeritics FlowPrep 060 instrument under helium at 300°C (heating rate of 10 K/min) for 4 hours. We evaluated the specific surface area, S_{BET} , by the BET method using adsorption data in the relative pressure range from 0.05 to 0.25. We applied the t -plot method to determine the volume of micropores, V_{micro} . The adsorbed amount at relative pressure 0.98 reflects the total adsorption capacity, V_{tot} . As a result, we obtained $S_{\text{BET}} = 429 \text{ m}^2/\text{g}$, $V_{\text{micro}} = 0.17 \text{ cm}^3/\text{g}$, $V_{\text{tot}} = 0.23 \text{ cm}^3/\text{g}$, and the average pore diameter, $D_{\text{micro}} = 0.54 \text{ nm}$.

2.2 Adsorption Measurement

We determined adsorption isotherms of methane and ethane at room temperature in ZSM-5/35 using an ASAP 2020 (Micromeritics) volumetric instrument. The instrument was equipped with three pressure transducers covering the ranges up to 0.133, 1.33 and 133 kPa, respectively. The ZSM-5/35 was outgassed before the adsorption measurement using a procedure starting from room temperature and ending at 383 K (heating rate of 0.5 K/min) until the residual pressure of 1 Pa was reached. After a 1 hour delay at 383 K, the temperature was further increased (heating rate of 1 K/min) to 573 K. The sample was outgassed at this temperature under a turbomolecular pump vacuum for 8 hours. The temperature of the sample was maintained with accuracy of ± 0.01 K using the thermostat Iso-Therm (e-Lab Services, Czech Republic).

3 Computational Details

3.1 Zeolite Models

We built models for microporous (all-silica) ZSM-5 and (alumino-silicate) ZSM-5/35 zeolites, and dual-porosity ZSM-5/35 zeolite by taking the initial MFI framework from the IZA database [24]. The unit cell was periodically duplicated in the x -, y - and z -directions, and zeolite supercells were treated as rigid structures. Since the positions of Al^{3+} ions in a zeolite framework are generally unknown, we used a random distribution of Al^{3+} ions under the constraint given by the Löwenstein rule: avoid the formation of Al-O-Al linkages, which are energetically highly unfavorable [35]. Each time an Si^{4+} ion is replaced by an Al^{3+} ion, the zeolite framework becomes negatively charged. To balance the overall framework charge, Na^+ ions were randomly placed in the supercells near the Al substituents to avoid an overlap with neighboring atoms.

For the microporous zeolites, we used $2 \times 2 \times 3$ ($4.0180 \text{ nm} \times 3.9476 \text{ nm} \times 3.9426 \text{ nm}$; 3456 zeolite atoms, 33 Na^+ ions) and $2 \times 4 \times 3$ ($4.0180 \text{ nm} \times 7.8952 \text{ nm} \times 3.9426 \text{ nm}$; 6912 zeolite atoms, 66 Na^+ ions) supercells in the Monte Carlo (MC) and molecular dynamics (MD) simulations, respectively. For the dual-porosity zeolite, we first built $4 \times 4 \times 6$ ($8.0360 \text{ nm} \times 7.8952 \text{ nm} \times 7.8852 \text{ nm}$) and $4 \times 8 \times 6$ ($8.0360 \text{ nm} \times 15.7904 \text{ nm} \times 7.8852 \text{ nm}$) ZSM-5/35 crystals, for the MC and MD simulations, respectively. A cylindrical mesopore with a 4 nm diameter was then carved from the center of the zeolite crystals in the y -direction, i.e., along the zeolite straight channels. This was achieved by deleting all of the atoms within the 2 nm pore radius, i.e., sodium cations, and silicon or aluminium atoms with incomplete valency, as well as any oxygens bonded only to these silicons or aluminiums. To ensure the electroneutrality of the supercell, the dangling bonds of the oxygen atoms at the mesopore surface were saturated by hydrogen atoms. A hydrogen atom was placed perpendicular to the surface at a distance of 0.1 nm from an unsaturated oxygen atom [25]. The resulting $4 \times 4 \times 6$ and $4 \times 8 \times 6$

supercells consisted of 22512 and 45024 zeolite atoms, respectively, and 205 and 410 Na^+ ions, respectively. Fig. 1 shows the simulation supercells for both microporous and dual-porosity zeolites.

We systematically characterized the zeolite structures by calculating the geometric PSD, accessible surface area, S_A , and pore volume, V_{pore} [36]. The PSD was determined by a geometric approach that probed the zeolite pore space to find the largest spheres that contained test points and did not overlap with the atoms of the zeolite structure [37]. The accessible surface area corresponds to the positions of the center of a probe particle rolling over the zeolite atoms. It is thus defined as a locus of the points that represents the location of the probe particle at a distance of the collision diameter σ from a zeolite atom and at least a distance σ from all other atoms in the zeolite structure. As a probe particle for the PSD and S_A calculations, we used a nitrogen atom with $\sigma_N = 0.3314$ nm. An analogous geometric approach was used for calculating the pore volume, where a He size probe with $\sigma_{\text{He}} = 0.258$ nm was employed to provide values of the V_{pore} consistent with that determined experimentally by helium pycnometry. For the microporous zeolite, the calculation leads to the average pore diameter, $D_{\text{micro}} = 0.54$ nm, $V_{\text{pore}} \equiv V_{\text{micro}} = 0.172$ cm³/g, and $S_A = 257$ m²/g. The values of D_{micro} and V_{micro} agree with the experimental values, while S_A is smaller than S_{BET} since S_A and S_{BET} have somewhat different physical interpretations [36]. For the dual-porosity zeolite, we obtained $V_{\text{pore}} = 0.308$ cm³/g and $S_A = 440$ m²/g. For comparison with the microporous zeolite, the micropore volume in the dual-porosity zeolite can be determined as the following. If the volume of the mesopores is estimated as $V_{\text{meso}} \simeq \pi (D - \sigma_N)^2 L_y / m_{\text{adsorbent}} = 0.115$ cm³/g, then $V_{\text{micro}} = V_{\text{pore}} - V_{\text{meso}} = 0.193$ cm³/g; where D is the diameter of mesopores, L_y is the box length in the y -direction, and $m_{\text{adsorbent}}$ is the mass of the adsorbent.

3.2 Intermolecular Interactions

The zeolite silicon, alumina, oxygen and hydrogen atoms, and sodium balancing cations were treated as charged Lennard-Jones (LJ) spheres with LJ parameters ε_{aa} and σ_{aa} , and partial charges q_a given by Vujić-Lyubartsev’s force field [38]. The zeolite framework atoms are denoted by Si_*z*, Al_*z*, O_*z*, O_*z*2, and H_*z*, where O_*z* corresponds to oxygen atoms in -Si-O-Si-, while O_*z*2 corresponds to oxygen atoms in -Si-O-Al-. Note that the electroneutrality constraint requires: $q(\text{Si}_z) = -4q(\text{O}_z)$ in all-silica structures and $q(\text{Al}_z) + q(\text{Na}^+) + 4q(\text{O}_{z2}) = q(\text{Si}_z) + 4q(\text{O}_z)$ when an Al atom substitutes a Si atom, and Na^+ is inserted in aluminosilicate structures. The LJ parameters and partial charges of the zeolite atoms are listed in Table 1.

Adsorbate molecules (methane, ethane, propane, and *n*-butane) were described using the united-atom TraPPE force field [39]. The TraPPE force field treats CH_4 as a LJ sphere, C_2H_6 as a rigid two-site LJ molecule with a $\text{CH}_3\text{-CH}_3$ bond of 0.154 nm, C_3H_8 as a rigid three-site LJ molecule with a $\text{CH}_2\text{-CH}_3$ bond of 0.154 nm and a $\text{CH}_3\text{-CH}_2\text{-CH}_3$ angle of 114° , and C_4H_{10} as a semi-rigid four-site molecule with both $\text{CH}_2\text{-CH}_3$ and $\text{CH}_2\text{-CH}_2$ bonds of 0.154 nm and a $\text{CH}_3\text{-CH}_2\text{-CH}_2$ angle of 114° . In the *n*-butane molecule, the internal rotation along the $\text{CH}_2\text{-CH}_2$ bond is described by the OPLS united-atom torsional potential, u_{tors} ; see Table 1. The LJ parameters for the adsorbate pseudo-atoms are summarised in Table 1. The cross LJ parameters were given by the Lorentz-Berthelot combining rules [40]: $\varepsilon_{ab} = \sqrt{\varepsilon_{aa}\varepsilon_{bb}}$ and $\sigma_{ab} = (\sigma_{aa} + \sigma_{bb})/2$.

3.3 Adsorption

We simulated adsorption of alkanes in zeolites using the grand canonical MC (GCMC) technique [41]. In GCMC simulations, we consider a system at constant volume V (zeolite supercell in our case) in equilibrium with a gas reservoir (bulk alkane phase in our case) at temperature T and pressure

P. The reservoir imposes the chemical potential, μ , and its value is an input to the GCMC simulation. We determined the value of μ by the Widom’s insertion method [42] using isothermal-isobaric MC (NPT MC) simulations of the bulk alkane phase. For a given μ and T , the amount adsorbed is then given by the ensemble average of the number of adsorbed molecules in the zeolite supercell. The adsorption isotherm was traced by increasing the pressure, where the corresponding μ (determined from the NPT MC simulations) was imposed in the GCMC simulations. GCMC steps consisted of translation, rotation, insertion/deletion of alkane molecules, and partial regrowth for *n*-butane. We employed a biased procedure for regrowth, and insertion/deletion of *n*-butane molecules to enhance the probability of finding energetically favorable configurations. Additional simulation details regarding the GCMC and NPT MC simulations are given in the Supporting Information.

3.4 Self-Diffusion

The equilibrium amount of adsorbed alkane molecules determined from the GCMC simulations was subsequently used in canonical MD simulations to evaluate the diffusion of the adsorbed alkanes in the *x*-, *y*- and *z*-directions. The MD simulations employed the Nose-Hoover thermostat [43, 44]. Additional simulation details regarding the MD simulations are provided in the Supporting Information.

The diffusion of the alkane molecules in the α -direction ($\alpha \equiv x, y, z$) was described by the self-diffusion coefficient, D_α^s , calculated from the mean-square displacement (MSD) via the Einstein equation [40]

$$\text{MSD}_\alpha(t) = 2D_\alpha^s t \quad (1)$$

In Eq. (1), $\text{MSD}_\alpha(t)$ denotes the MSD in the α -direction at time t . The determination of the MSD included averaging over different time origins [45].

3.5 Transport Diffusion

The equilibrium amount of adsorbed alkane molecules determined from the GCMC simulations was also used in non-equilibrium MD (NEMD) simulations, again using the Nose-Hoover thermostat [43, 44] to study the transport diffusion of the adsorbed molecules in the direction of the zeolite straight channels and the mesopore (in the y -direction) [46, 47, 48, 49]. In our case, the transport diffusion can be described by Fick's law

$$J_y = -D_y^t \frac{dc}{dy} \quad (2)$$

where J_y is the molecular diffusive flux, D_y^t is the transport diffusion coefficient, and dc/dy is the concentration gradient, presumed to drive diffusion [50].

While experimentally it is convenient to impose a concentration gradient, the fundamental thermodynamic driving force for diffusion is given by the gradient in the chemical potential, $d\mu/dy$ in our case, so we can write

$$J_y = -\frac{L_y}{kT} \frac{d\mu}{dy} \quad (3)$$

where L_y is the Onsager coefficient and k is the Boltzmann constant. The two transport coefficients, D_y^t and L_y , can be related via the adsorption isotherm as

$$D_y^t = \frac{L_y}{kT} \frac{d\mu}{dc} \quad (4)$$

where $d\mu/dc$ is determined from the adsorption isotherm data [46, 48].

In the NEMD simulations, we applied an external force in the y -direction on each alkane molecule, f_y^e , which is equivalent to imposing a chemical potential gradient in the system. This leads to a working expression for determining D_y^t in the NEMD simulations

$$\begin{aligned} D_y^t &= \frac{J_y V k T}{N f_y^e} \Gamma \\ &= D_y^c \Gamma \end{aligned} \quad (5)$$

where D_y^c is the collective (corrected, Maxwell-Stefan) diffusion coefficient, N is the number of the adsorbed molecules and

$$\Gamma = \left(\frac{d \ln f}{d \ln N} \right)_T \quad (6)$$

is the thermodynamic correction factor, evaluated from the adsorption isotherm data, where $f = f_0 \exp \left(\frac{\mu - \mu_0}{kT} \right)$ is the fugacity of the adsorbate in the bulk phase.

In the NEMD simulations, we determined J_y as

$$\begin{aligned} J_y &= \rho \langle v_y \rangle \\ &= \frac{\rho}{t_{run} N} \int_0^{t_{run}} \sum_{i=1}^N v_{i,y}(t) dt \end{aligned} \quad (7)$$

where $\rho = N/V$ is the number density, t_{run} is the total simulation time, and $v_{i,y}$ is the center-of-mass velocity of adsorbed molecule i in the y -direction. Alternatively, J_y can be evaluated as

$$J_y = \frac{\rho}{t_{run} N} \sum_{i=1}^N [y_i(t_{run}) - y_i(0)] \quad (8)$$

where $y_i(0)$ and $y_i(t_{run})$ are the initial and final (without periodic boundary conditions) center-of-mass positions, respectively, of adsorbed molecule i [48]. Additional simulation details regarding the NEMD simulations can be found in the Supporting Information.

4 Results and Discussion

Experimental adsorption measurement and simulations were carried out at a temperature of 293 K. At 293 K, methane is in a supercritical state while ethane, propane and *n*-butane are in subcritical states. Experimental adsorption isotherms of methane and ethane in microporous ZSM-5/35 were measured for pressures up to 1 bar. For methane, ethane and propane, simulations were performed for pressures up to the experimental vapor pressure of propane, i.e., up to about 8 bar. For *n*-butane, the simulations were run for pressures up to its experimental vapor pressure, i.e., up to about 2 bar [51].

4.1 Adsorption in Microporous Zeolites: Molecular Model Validation

Experimentally measured adsorption isotherms of methane and ethane in the microporous ZSM-5/35 at 293 K and pressures up to about 1 bar are displayed in Fig. 2; both isotherms are Type I [52, 53]. Since this temperature is about 103 K above methane’s critical temperature and about 30 K below ethane’s critical temperature [51], both adsorbates behave as non-condensable gasses, and their adsorption isotherms can be described by the Langmuir model [54]

$$\frac{n}{n_0} = \frac{bP}{1 + bP} \quad (9)$$

In Eq. (9), n is the amount adsorbed, n_0 is the Langmuir adsorption capacity, and b is the adsorption coefficient. The coefficient b is exponentially related to the positive value of the energy of adsorption, and may be regarded as a function of enthalpy and entropy of adsorption [52]. Values of n_0 and b are: $n_0 = 2.186$ mmol/g and $b = 0.493$ 1/bar for methane, and $n_0 = 2.102$ mmol/g and $b = 13.031$ 1/bar for ethane. Comparison of the adsorption isotherms for methane and ethane in Fig. 2 suggests that the microporous zeolite has a higher affinity towards ethane than towards methane, as evidenced by both

the uptake and the value of b being higher for ethane.

We validated our molecular model against these adsorption isotherms, where the GCMC results shown in Fig. 2 exhibit excellent agreement with the experimental measurement. In addition, we performed GCMC simulations for the alkanes in both all-silica ZSM-5 and alumino-silicate ZSM-5/35 zeolites at 293 K and pressures up to 8 bar for methane, ethane and propane, and up to 2 bar for n -butane. These simulated adsorption isotherms in the ZSM-5 were compared against experimental adsorption isotherms measured by Sun et al. [55] at slightly different temperatures (277 and 308 K). The simulation results and comparison are presented in Fig. S1 of the Supporting Information. Fig. S1 indicates that (i) the simulation isotherms compare rather well with the experimental isotherms, (ii) all simulation isotherms are of Type I [52, 53], (iii) adsorption in ZSM-5/35 is lower than that in ZSM-5 due to the presence of sodium cations that restrict the space available for gas adsorption, and (iv) considering e.g., adsorption at 2 bar, the relative amount adsorbed for each alkane is $n(\text{CH}_4) < n(\text{C}_4\text{H}_{10}) < n(\text{C}_3\text{H}_8) < n(\text{C}_2\text{H}_6)$.

4.2 Adsorption Isotherms

Simulation adsorption isotherms of the C_1 to C_4 alkanes in both microporous and dual-porosity ZSM-5/35 zeolites at 293 K and up to high pressures are shown in Fig. 3. All adsorption isotherms in the microporous zeolite, and adsorption isotherms of methane and ethane in the dual-porosity zeolite can be correlated by the semi-empirical Jensen-Seaton model [56]

$$n = KP \left\{ 1 + \left[\frac{KP}{n_0(1 + \kappa P)} \right]^c \right\}^{-\frac{1}{c}} \quad (10)$$

In Eq. (10), K is the Henry law constant, n_0 is a measure of saturation loading, κ represents an adsorbed phase compressibility, and c determines the curvature of the isotherm. All isotherms are Type I, except for propane and n -butane in the dual-porosity zeolite, which have Type II character.

For methane (Fig. 3a), the adsorption in the dual-porosity zeolite is lower

than in the microporous zeolite, indicating methane is preferentially adsorbed in the zeolite micropores rather than in the mesopores, where the analogous behavior occurs for ethane (Fig. 3b) up to pressures of about 5.5 bar. However, above this crossover pressure, the adsorption in the dual-porosity zeolite is higher than in the microporous zeolite, suggesting enhancement of ethane adsorption in the mesopores. With increasing number of carbon atoms in the alkanes, propane (Fig. 3c) and *n*-butane (Fig. 3d), the crossover shifts to lower pressures and the uptake in the dual-porosity zeolite is higher than the uptake in the microporous zeolite, and increases non-linearly with pressure. In the dual-porosity zeolite, both propane and *n*-butane appear to be approaching condensation in the mesopores at the highest pressures considered.

Fig. 4 corroborates the adsorption behavior of the alkanes inside the cylindrical mesopores of the dual-porosity zeolite through radial density profiles, $\rho(r)$, at pressures of 2 and 7 bar. From Fig. 4, we see that methane is nearly homogeneously adsorbed within the mesopores, i.e., $\rho(r)$ increases but the fluid structure remains homogenous, where the presence of a monolayer near the surface is only just beginning to appear (cf. Fig. 4a and Fig. 4b). In contrast to methane, the other alkanes show preferential adsorption at the mesopore surface, forming one or two molecular layers on the surface. This is due to multi-interaction sites in ethane, propane and *n*-butane molecules, which leads to enhancement of the adsorbate-pore surface interactions. With increasing pressure, both the preferential adsorption and density increase away from the mesopore surface (cf. Fig. 4a and Fig. 4b). For both ethane and propane, more distinct second molecular layers are exhibited at the higher pressure, while a third layer is beginning to form for propane (consistent with the non-linear uptake shown in Fig. 3c). The preferential adsorption of ethane, propane, and *n*-butane at the mesopore surface thus explains their higher adsorption in the dual-porosity zeolite in comparison with the microporous zeolite at higher pressures.

4.3 Self-Diffusivity

Self-diffusion coefficients, D_α^s ($\alpha \equiv x, y, z$), for the alkanes in both microporous and dual-porosity ZSM-5/35 zeolites as a function of pressure, P , are displayed in Fig. 5. Additional details regarding the determination of D_α^s from MD simulations are provided in the Supporting Information. The self-diffusion coefficient describes the diffusion of a single molecule moving around amongst other particles, and is a measure of the average MSD that a molecule has travelled in a given time interval. Experimentally, D^s can be measured by a pulsed field gradient nuclear magnetic resonance or quasi-elastic neutron spectroscopy, where its accurate measurement is rather challenging. Depending on the experimental technique, values of D^s may vary by orders of magnitude [57].

The MFI framework has a three-dimensional channel structure with straight channels of $0.54 \text{ nm} \times 0.56 \text{ nm}$ in the y -direction, zigzag channels of 0.56 nm in the x -direction, and tortuous connections through straight-zigzag channel intersections in the z -direction. The molecular diameters of the alkanes are about 0.4 nm (cf. Table 1 and [55]). We can see from Fig. 5 that for both microporous and dual-porosity zeolites, the self-diffusion coefficients exhibit behavior dependent upon the connectivity of the channel structure, i.e., $D_y^s > D_x^s > D_z^s$.

For microporous zeolites, the self-diffusivity of the C_1 to C_4 alkanes follows general trends associated with the pressure (loading) dependence found experimentally, and by molecular simulations for the alkanes in intersecting channel type zeolite structures [58, 59]. Specifically, as the occupancy of adsorbed alkane molecules increases, alkane-alkane interactions tend to decorrelate molecular velocities faster than when the neighboring particles have less influence on the adsorbed molecules. The increased adsorbed density restricts individual mobility, and consequently the self-diffusion decreases. As the number of carbon atoms increases for the alkane species type, the self-diffusivity of the alkanes at the same loading also decreases. Further, cations slow down the self-diffusivity of the alkanes [60]. Accord-

ingly, we see in Fig. 5 that the self-diffusivity in all directions for methane to *n*-butane in the microporous zeolite decrease with increasing pressure, and $D_\alpha^s(\text{methane}) > D_\alpha^s(\text{ethane}) > D_\alpha^s(\text{propane})$. The values of D_α^s for *n*-butane are, as expected, lower than those for methane and ethane, but slightly higher than those for propane due to lower occupancy of *n*-butane in the zeolite (about 8 to 9 molecules per unit cell) in comparison with the occupancy of propane in the zeolite (about 10 to 11 molecules per unit cell).

Introducing transport mesopores oriented in the *y*-direction into the MFI structure has a tremendous effect on the self-diffusivity of the short alkanes in the dual-porosity zeolite, as can be further seen from Fig. 5. When compared with the microporous zeolite, the self-diffusivity of the alkanes in the dual-porosity zeolite increased in all directions by about one to two orders, depending on the pressure, and the increase is more pronounced in the *y*-direction (transport direction) than in the *x*- and *z*-directions. The increase in D_α^s is caused by alkane molecules adsorbed in the mesopore (cf. Fig. 4), which have a higher mobility than the adsorbed molecules at the microporosity scale. With increasing pressure, the values of D_x^s and D_z^s , analogous to the behavior in the microporous zeolite, decrease while the values of D_y^s for methane, ethane, and propane, however unlike in the microporous zeolite, increase; for *n*-butane, D_y^s slightly decreases with increasing pressure. In the *x*- and *y*-directions, mobility of the molecules confined in the mesopore is restricted by the mesopore confining surface, and the effect of the higher mobility on D_x^s and D_z^s is weaker than in the *y*-direction. This may explain the different pressure dependence of D_x^s and D_z^s compared to D_y^s . Molecules of *n*-butane exhibit stronger adsorption on the mesopore surface with respect to the C₁ to C₃ alkanes (cf. Fig. 4a), which may explain the slight decrease of D_y^s for *n*-butane when the pressure increased.

4.4 Transport Diffusivity

Figs. 6 and 7 display the transport and collective diffusion coefficients in the y -direction, D_y^t and D_y^c , respectively, for the C₁ to C₄ alkanes in both microporous and dual-porosity ZSM-5/35 zeolites as a function of pressure, P , along with comparison of D_y^t and D_y^c with D_y^s . Figs. 6 and 7 also present the corresponding thermodynamic correction factors, Γ , as a function of P . Additional details regarding the determination of D_y^t and D_y^c from NEMD simulations are given in the Supporting Information.

The transport diffusivity determines the efficiency of mass transport while the collective diffusivity measures the displacement of the center-of-mass of the system. In general in microporous zeolites, the collective diffusion is higher than the self-diffusion since the collective diffusion contains interparticle correlations, which have a positive contribution; or viewed differently, the self-diffusion is lowered by single particle back-correlations, i.e., by the increased probability of a particle jumping back to its previous position since this position has a higher probability of being unoccupied [28]. The transport diffusivity, D^t , is the product of D^c and Γ , and the actual values of Γ determine whether D^t is higher or lower than D^c . For example, the Langmuir isotherm, $\Gamma = 1/(1 - n/n_0) > 1$, which leads to $D^t > D^c$. In the limit of zero loading, $D^t = D^c = D^s$ and $\Gamma = 1$. Many engineering applications of zeolites use the Darken assumption that the collective diffusion is independent of the pressure (loading). This allows us to estimate the transport diffusivity from knowledge of the self-diffusivity at low pressure and adsorption isotherm. However, Skoulidas et al. [61], and Krishna and van Baten [62] have shown by MD simulations that for most zeolites the Darken assumption does not hold and depending on the pore topology the collective diffusivity can both increase or decrease as a function of pressure.

For microporous zeolites, D_y^c of the C₁ to C₄ alkanes exhibits deviation from the Darken assumption, although D_y^c for ethane (Fig. 6b) becomes roughly constant at high pressures. Values of D_y^c for methane (Fig. 6a)

increase while values for ethane (Fig. 6b), propane (Fig. 7a), and *n*-butane (Fig. 7b) decrease when the pressure is increased; the latter corresponds to a general trend of D^c vs. P for alkanes in intersecting channel type zeolite structures [58, 59]. The increase of D_y^c for methane was also observed by Beerdsen et al. in the MFI zeolite [58, 59]; here, D_y^c increased, as in our case, while D_x^c and D_z^c decreased with the net effect of a slight decrease of the overall collective diffusivity with increasing P . Variations of D_y^t with P are results of the pressure dependences of both D_y^c and Γ . For methane (Fig. 6a), Γ increases with P , while for ethane (Fig. 6b), propane (Fig. 7a), and *n*-butane (Fig. 7b), Γ first increases up to a certain pressure and then it decreases when P is further increased. The pressure corresponding to a maximum in Γ shifts to lower P with increasing number of carbon atoms in the alkanes. As a consequence, D_y^t for methane increases with P in the whole pressure range, while D_y^t for ethane to *n*-butane increases at lower pressures, and decreases at higher pressures when P is increased. At high pressures, $D_y^c(\text{CH}_4) > D_y^c(\text{C}_2\text{H}_6) > D_y^c(\text{C}_3\text{H}_8) > D_y^c(\text{C}_4\text{H}_{10})$ together with $D_y^t > D_y^c > D_y^s$.

The presence of 4 nm mesopores in the MFI structure leads to substantial enhancement of transport for the alkanes in the dual-porosity zeolite, as can be further seen from Figs. 6 and 7. When compared with the microporous zeolite, D_y^c of the alkanes in the dual-porosity zeolite at high pressures increased by about one order for methane, ethane and *n*-butane, and more than two orders for propane. For all the alkanes, D_y^c increases with P , and $D_y^c > D_y^s$, except for *n*-butane at lower pressures, where $D_y^c \approx D_y^s$. The pressure dependences of Γ in the dual-porosity zeolite follow those in the microporous zeolite, but the values of Γ are lower when compared with the microporous zeolite. The latter leads to a less pronounced enhancement of D_y^t in comparison with the enhancement of D_y^c in the dual-porosity zeolite. Variations of D_y^t with P reflect combined effects of D_y^c and Γ : D_y^t for methane (Fig. 6a) and ethane (Fig. 6b) increases with P , D_y^t for propane (Fig. 7a) also increases with P up to the vicinity of its vapor pressure, and then sharply

decreases, and D_y^t for *n*-butane (Fig. 7b) decreases with P . Except for propane at pressures close to its saturation pressure, $D_y^t > D_y^c$ for all the alkanes in the dual-porosity zeolite.

Fig. 8 displays radial velocity profiles in the y -direction, $v_y(r)$, in the mesopores at pressures of 2 and 7 bar. Fig. 8 along with Fig. 4 provide evidence of the enhancement of D_y^c and the increase of D_y^c with P in the dual-porosity zeolite with respect to the microporous zeolite. In general, the collective diffusivity is directly proportional to the flux and inversely proportional to the number of adsorbed molecules (see Eq. (5)). The values of J_y obtained by the NEMD simulations increase with P (not shown). The increase in J_y is more pronounced than the increase in N when P is increased, which provides an explanation for the values of D_y^c in the dual-porosity zeolite increasing with P . Moreover, the flux J_y can be considered as a sum of fluxes in micropores and mesopores, J_y^{micro} and J_y^{meso} , respectively, with $J_y^{\text{meso}} > J_y^{\text{micro}}$ due to high mobility of adsorbed molecules in the mesopores. The simulation results for D_y^c in the microporous zeolite suggest that J_y^{micro} may either slightly increase with P for methane, or decrease with P for ethane to *n*-butane. J_y^{meso} is directly proportional to the density and (average) velocity in the mesopores. Fig. 4 indicates that the density in the mesopores increases with P , and close inspection of Fig. 8 reveals that the velocities within the mesopores increase with P , although marginally. This results in a pronounced increase of J_y^{meso} when P is increased. Hence, the increase of J_y is caused by the contribution from the mesoporosity. Fig. 8 further shows that the velocity profiles are not parabolic and, except *n*-butane, $v_y(r)$ display slip (non-zero) velocities at the mesopore surface, and their shapes correlate with $\rho(r)$ in Fig. 4. The values of the slip velocity decrease with increase of the adsorbate-pore surface interactions; the slip velocity is the highest for methane and zero for *n*-butane.

5 Conclusions

Using Monte Carlo and molecular dynamics simulations, we predicted adsorption isotherms and the dependences of the self-, collective and transport diffusivities on the reservoir pressure (loading) in microporous and hierarchical ZSM-5 zeolites. The hierarchical ZSM-5 zeolite with dual micro/mesoporosities was modeled as an MFI structure, where a cylindrical mesopore with a 4 nm diameter was introduced. The adsorbate-adsorbate and adsorbate-adsorbent interactions were described by the TraPPE and Vujić-Lyubartsev’s force fields, along with the Lorentz-Berthelot mixing rules. The force fields almost exactly reproduced both the experimental single-component adsorption isotherms of methane and ethane in microporous aluminosilicate ZSM-5 zeolite (which were measured as part of this work), and the published experimental high-pressure single-component adsorption isotherms of methane to *n*-butane in microporous all-silica ZSM-5 zeolite.

We found that all isotherms were Type I, except for propane and *n*-butane in the dual-porosity zeolite, which were Type II. In the dual-porosity zeolite, methane was preferentially adsorbed in the zeolite micropores rather than in the mesopores, and as a result, the adsorption was lower than in the microporous zeolite. The analogous behavior occurred for ethane up to a crossover pressure, where above the crossover pressure, the adsorption in the dual-porosity zeolite was higher than in the microporous zeolite due to enhancement of ethane adsorption in the mesopores. With increasing number of carbon atoms in the propane and *n*-butane molecules, the crossover shifted to lower pressures, and the uptake in the dual-porosity zeolite became higher than the uptake in the microporous zeolite. This was due to multi-interaction sites in ethane, propane and *n*-butane molecules, which increased the adsorbate-pore surface interactions, and led to enhancement of adsorption of these alkanes in the zeolite mesopores.

Due to alkane molecules adsorbed in the mesopores, which have a higher mobility in comparison with the adsorbed molecules at the micropore scale,

the self-diffusivity of the alkanes in the dual-porosity zeolite increased in all directions by about one to two orders, and the increase was more pronounced in the transport direction (direction of the cylindrical mesopores) than in the other directions. Unlike in the microporous zeolite, the self-diffusivity for methane, ethane, and propane increased with the pressure. Introducing transport mesopores into the MFI structure also had a tremendous effect on the transport of the alkanes in the dual-porosity zeolite. When compared with the microporous zeolite, the collective diffusivity increased by about one to nearly two orders, and except for *n*-butane, the collective diffusivity is higher than the self-diffusivity. In addition, the collective diffusivity for all the alkanes increased with the pressure. For both microporous and dual-porosity zeolites, the collective diffusivity exhibited deviation from the Darken assumption.

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Table 1: Lennard-Jones parameters ε and σ , and partial atomic charges, q , for zeolite atoms [38] and adsorbate pseudo-atoms [39] along with the torsional potential, u_{tors} , for n -butane; k is the Boltzmann constant.

Atom	ε/k (K)	σ (nm)	q (e)
Si _Z	31.98	0.2970	1.413
Al _Z	24.0	0.3140	1.072
O _Z	52.0	0.3011	-0.7065
O _{Z2}	55.04	0.3011	-0.87125
H _Z	0	0.1	0.3438112
Na ⁺	234.13	0.3230	1
CH ₄	148.0	0.373	0
CH ₃	98.0	0.375	0
CH ₂	46.0	0.395	0

$u_{tors} = c_1 (1 + \cos \Phi) + c_2 [1 - \cos (2\Phi)] + c_3 [1 + \cos (3\Phi)]$, where $c_1/k = 355.03$ K, $c_2/k = -68.19$ K, and $c_3/k = 791.32$ K.

Figure 1: (a) The x - y view of the microporous zeolite supercell. (b) The x - y and y - z views of the dual-porosity zeolite supercell with a cylindrical mesopore of diameter 4 nm. Atoms are coloured as follows: Si, yellow; O, red; Al, magenta; H, white.

Figure 2: Experimental and simulation adsorption isotherms of (a) methane and (b) ethane in the microporous ZSM-5/35 zeolite at 293 K. The solid lines represent correlation of the experimental data by the Langmuir isotherm [54].

Figure 3: Simulation adsorption isotherms of (a) methane, (b) ethane, (c) propane and (d) n -butane in the microporous and dual-porosity ZSM-5/35 zeolites at 293 K. The solid lines represent correlation of the simulation results for the microporous zeolite by the semi-empirical Jensen-Seaton isotherm [56], and dotted lines are a guide to the eye for the dual-porosity zeolite.

Figure 4: Radial density profiles, $\rho(r)$, for methane, ethane, propane, and *n*-butane in the 4 nm mesopores of the dual-porosity ZSM-5/35 zeolite at 293 K and pressures of (a) 2 bar, and (b) 7 bar; r is the distance of a molecule from the center of the cylindrical mesopore, which is located at $r = 0$.

Figure 5: Self-diffusion coefficients in the x -, y - and z -directions, D^s , for (a) methane, (b) ethane, (c) propane and (d) *n*-butane in the microporous and dual-porosity ZSM-5/35 zeolites as a function of pressure, P , at 293 K. Open and filled symbols are for the microporous and dual-porosity zeolites, respectively. Circles, triangles and squares correspond to D^s in the x -, y - and z -directions, respectively. The dotted and dashed lines are a guide to the eye for the microporous and dual-porosity zeolites, respectively.

Figure 6: Transport, collective and self-diffusion coefficients in the y -direction, D_y^t , D_y^c and D_y^s , respectively, (left column) and thermodynamic correction factor, Γ , (right column) for (a) methane and (b) ethane in the microporous and dual-porosity ZSM-5/35 zeolites as a function of pressure, P , at 293 K. Open and filled symbols are for the microporous and dual-porosity zeolites, respectively. Triangles, squares and circles correspond to D_y^t , D_y^c and D_y^s , respectively. The dotted and dashed lines are a guide to the eye for the microporous and dual-porosity zeolites, respectively.

Figure 7: Transport, collective and self-diffusion coefficients in the y -direction, D_y^t , D_y^c and D_y^s , respectively, (left column) and thermodynamic correction factor, Γ , (right column) for (a) propane and (b) n -butane in the microporous and dual-porosity ZSM-5/35 zeolites as a function of pressure, P , at 293 K. Open and filled symbols are for the microporous and dual-porosity zeolites, respectively. Triangles, squares and circles correspond to D_y^t , D_y^c and D_y^s , respectively. The dotted and dashed lines are a guide to the eye for the microporous and dual-porosity zeolites, respectively.

Figure 8: Radial velocity profiles in the y -direction, $v_y(r)$, for methane, ethane, propane, and n -butane in the 4 nm mesopore of the dual-porosity ZSM-5/35 zeolite at 293 K, pressures of (a) 2 bar, and (b) 7 bar, and the external force of 0.3 kcal/(mol nm); r is the distance of a molecule from the center of the cylindrical mesopore, which is located at $r = 0$.

References

- [1] J. Čejka, H. van Bekkum, A. Corma, and F. Schüth (Eds.), *Introduction to Zeolite Science and Practice*, Elsevier: Amsterdam, The Netherlands, 2007.
- [2] D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons: New York, NY, 1984.
- [3] J. Kärger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids*, John Wiley & Sons: New York, NY, 1992.
- [4] N.Y. Chen, T. F. Degnan Jr., and C. M. Smith, *Molecular Transport and Reaction in Zeolites*, VCH Publishers: New York, NY, 1994.
- [5] M. Manko, R. Chal, P. Trens, D. Minoux, C. Gerardin, and C. Makowski, *Microporous Mesoporous Mater.* **170**, 243, 2013.
- [6] D. P. Serrano, J. M. Escola, and P. Pizarro, *Chem. Soc. Rev.* **42**, 4004, 2013.
- [7] I. I. Ivanova and E. E. Knyazeva, *Chem. Soc. Rev.* **42**, 3671, 2013.
- [8] K. Möller and T. Bein, *Chem. Soc. Rev.* **42**, 3689, 2013.
- [9] L. Deliere, F. Villemot, D. Farrusseng, A. Galarneau, S. Topin, and B. Coasne, *Microporous Mesoporous Mater.* **229**, 145, 2016.
- [10] R. Ameloot, A. Liekens, L. Alaerts, M. Maes, A. Galarneau, B. Coq, G. Desmet, B. F. Sels, J. F. M. Denayer, and D. E. De Vos, *Eur. J. Inorg. Chem.* **24**, 3735, 2010.
- [11] A. Sachse, R. Ameloot, B. Coq, F. Fajula, B. Coasne, D. E. De Vos, and A. Galarneau, *Chem. Commun.* **48**, 4749, 2012.
- [12] D. Qian, C. Lei, G.-P. Hao, W.-C. Li, and A.-H. Lu, *ACS Appl. Mater. Interfaces* **4**, 6125, 2012.

- [13] P. Eliášová, M. Opanasenko, P. S. Wheatley, M. Shamzhy, M. Mazur, P. Nachtigall, W. J. Roth, R. E. Morris, and J. Čejka, *Chem. Soc. Rev.* **44**, 7177, 2015.
- [14] M. Mazur, P. S. Wheatley, M. Navarro, W. J. Roth, M. Položij, A. Mayoral, P. Eliášová, P. Nachtigall, J. Čejka, and R. E. Morris, *Nature Chemistry* **8**, 58, 2016.
- [15] S. Gheorghiu and M.-O. Coppens, *Proc. Natl Acad. Sci. USA* **101**, 15853, 2004.
- [16] A. Byfut, T. Backers, A. Schroeder, and C. Carstensen, *Appliance of the Extended Finite Element Method in Geomechanics*, 71st EAGE Conference and Exhibition 2009, Amsterdam, The Netherlands, 2009.
- [17] A. Striolo, F. Klaessig, D. R. Cole, J. Wilcox, G. G. Chase, C. H. Sondergeld, and M. Pasquali, *Identification of Fundamental Interfacial and Transport Phenomena for the Sustainable Deployment of Hydraulic Shale Fracturing? Role of Chemicals Used*, Workshop Report, NSF Grant Number CBET-1229931, 2012.
- [18] A. Yethiraj and A. Striolo, *J. Phys. Chem. Lett.* **4**, 687, 2013.
- [19] ShaleXenvironmenT: <https://shalexenvironment.org>
- [20] L. Michalec and M. Lísal, *Molec. Phys.* in press, 2017.
- [21] T. Backers, C. Gruehser, T. Meier, and G. Dresen, *Fracture Pattern of Borehole Breakouts in Shale-Comparison of Physical and Numerical Experiments*, EAGE, Copenhagen, Denmark, 2012.
- [22] H. Mischo and T. Backers, *Analysis of Fracture Coalescence by Fracture Mechanics Simulation*, EUROCK, Stockholm, Sweden, 2012.
- [23] S. L. Montgomery, D. M. Jarvie, K. A. Bowker, and R. M. Pollastro, *AAPG Bull.* **89**, 155, 2005.

- [24] C. Baerlocher, L. McCusker, and D. Olson, *Atlas of Zeolite Framework Types*, Amsterdam: Elsevier, The Netherlands, 2007.
- [25] B. Coasne, A. Galarneau, C. Gerardin, F. Fajula, and F. Villemot, *Langmuir* **29**, 7864, 2013.
- [26] F. Villemot, A. Galarneau, and B. Coasne, *J. Phys. Chem. C* **118**, 7423, 2014.
- [27] P. Demontis and G. B. Suffritti, *Chem. Rev.* **97**, 2845, 1997.
- [28] B. Smit and T. L. M. Maesen, *Chem. Rev.* **108**, 4125, 2008.
- [29] J. Jiang, R. Babarao, and Z. Hu, *Chem. Soc. Rev.* **40**, 3599, 2011.
- [30] E. Haldoupis, S. Nair, and D. S. Sholl, *Phys. Chem. Chem. Phys.* **13**, 5053, 2011.
- [31] C. D. Williams, K. P. Travis, N. A. Burton, and J. H. Harding, *Microporous Mesoporous Mater.* **228**, 215, 2016.
- [32] R. J. M. Pellenq, B. Coasne, and P. E. Levitz, *Molecular Simulation of Adsorption Phenomena*, N. Quirke and D. Nicholson (Eds.), Taylor and Francis: London, UK, 2005.
- [33] S. M. Rao and M.-O. Coppens, *Chem. Eng. Sci.* **83**, 66, 2012.
- [34] K. Chae, Y. Shi, and L. Huang, *J. Mater. Chem. A* **1**, 3886, 2013.
- [35] W. Löwenstein, *Am. Mineral.* **39**, 92, 1954.
- [36] L. Sarkisov and A. Harrison, *Molec. Simul.* **37**, 1248, 2011.
- [37] L. D. Gelb and K. E. Gubbins, *Langmuir* **15**, 305, 1999.
- [38] B. Vujić and A. P. Lyubartsev, *Modelling Simul. Mater. Sci. Eng.* **24**, 045002, 2016.

- [39] M. G. Martin and J. I. Siepmann, *J. Phys. Chem. B* **102**, 2569, 1998.
- [40] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press: Oxford, UK, 1987.
- [41] D. Frenkel and B. Smit, *Understanding Molecular Simulation. From Algorithms to Applications*, Elsevier: Amsterdam, The Netherlands, 2002.
- [42] B. Widom, *J. Chem. Phys.* **39**, 2808, 1963.
- [43] S. Nosé, *J. Chem. Phys.* **81**, 511, 1984.
- [44] W. G. Hoover, *Phys. Rev. A* **31**, 1695, 1985.
- [45] M. Svoboda, J. K. Brennan, and M. Lísal, *Molec. Phys.* **113**, 1124, 2015.
- [46] E. J. Maginn, A. T. Bell, and D. N. Theodorou, *J. Phys. Chem.* **97**, 4173, 1993.
- [47] G. Arya, H.-C. Chang, and E. J. Maginn, *J. Chem. Phys.* **115**, 8112, 2001.
- [48] S. Chempath, R. Krishna, and R. Q. Snurr, *J. Phys. Chem. B* **108**, 13481, 2004.
- [49] D. Dubbeldam and R. Q. Snurr, *Molec. Simul.* **33**, 305, 2007.
- [50] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, John Wiley & Sons: New York, NY, 1976.
- [51] Thermophysical Properties of Fluid Systems:
<http://webbook.nist.gov/chemistry/fluid>
- [52] J. R. F. Rouquerol, K. S. W. Sing, P. Llewellyn, and G. Maurin, *Adsorption by Powders and Porous Solids*, Elsevier: Amsterdam, The Netherlands, 2014.

- [53] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, and K. S. W. Sing, *Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution*, IUPAC Technical Report, Pure Appl. Chem. 2015.
- [54] I. Langmuir, *J. Am. Chem. Soc.* **38**, 2221, 1916.
- [55] M. S. Sun, D. B. Shah, H. H. Xu, and O. Talu, *J. Phys. Chem. B* **102**, 1466, 1998.
- [56] C. R. C. Jensen and N. A. Seaton, *Langmuir* **12**, 2866, 1996.
- [57] J. Kärger and D. M. Ruthven, *J. Chem. Soc. Faraday Trans. 1* **77**, 1485, 1981.
- [58] E. Beerdsen, D. Dubbeldam, and B. Smit, *Phys. Rev. Lett.* **96**, 044501, 2006.
- [59] E. Beerdsen, D. Dubbeldam, and B. Smit, *J. Phys. Chem. B* **110**, 22754, 2006.
- [60] F. Leroy, B. Rousseau, and A. H. Fuchs, *Phys. Chem. Chem. Phys.* **6**, 775, 2004.
- [61] A. I. Skoulidas, D. S. Sholl, and R. Krishna, *Langmuir* **19**, 7977, 2003.
- [62] R. Krishna and J. M. van Baten, *Microporous Mesoporous Mater.* **109**, 91, 2008.