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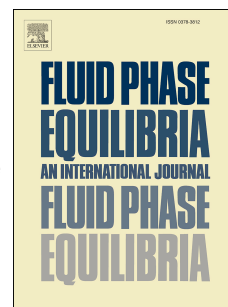
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CRediT author statement

Manuscript: Surface and confinement effects on the self-diffusion coefficients for methane-ethane mixtures within calcite nanopores, *submitted to Fluid Phase Equilibria*

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Surface and confinement effects on the self-diffusion coefficients for methane-ethane mixtures within calcite nanopores

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Abstract

The study of transport properties of unconventional oil reservoirs such as shale gas is crucial to optimize production, enhance oil extraction, and decrease costs and environmental hazards. One important dynamical property of fluids is diffusion, which is necessary to determine the oil mobility and rate of oil production from the reservoir, and can be obtained through the self-diffusion coefficient. To obtain the transport properties of fluids under confinement, one must take into account the surface and the confinement effects. Moreover, approaches that consider the position-dependency and the nonlinear particle distribution are required. Applying methods based on probability density function, the self-diffusion components of methane-ethane mixtures confined within calcite nanopores were calculated, using molecular dynamics simulations. The anisotropy between xx , yy , and zz components of the self-diffusion tensor has different effects depending on the position inside the nanopore. A surface effect causes an anisotropic behavior between parallel self-diffusion coefficients for this mixture close to the calcite walls. And at the center of the pore, the confinement effect is manifested by lowering the value of the perpendicular self-diffusion coefficient when compared to the parallel ones. Mixture composition plays an important role, since a higher ethane content shows greater anisotropy between

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parallel components.

Keywords: self-diffusion coefficients, confinement effect, Molecular Dynamics

1. Introduction

Nanoconfinement changes fluid properties because of two main phenomena: the surface effect caused by the fluid-wall interactions, and the geometric constraints resulting from the confinement itself [1, 2, 3]. The combination of these two effects impose an inhomogeneous fluid particle distribution within the confined media [4, 5, 6, 7, 8]. Predicting the surface and confinement effects is relevant for industrial applications such as separation processes [9, 10], heterogeneous catalysis [11], general adsorption phenomena [12, 13, 14, 15], and also for unconventional oil extraction, for which the fluid is found confined within porous rocks.

The understanding of fluid transport in unconventional reservoirs is crucial to optimize the production, enhance extraction performance, avoid losses, and decrease costs and undesired environmental effects [16, 17, 18]. Interfacial forces and pore geometry have strong influence on the dynamics of the confined fluids [19, 20], and the experimental challenges in probing confined media place simulations at the heart of what has been applied to investigate such nanosystems. Chen et al. [21] applied the Lattice Boltzmann Method to simulate the fluid flow and diffusion inside complex shale structures. Falk et al. [22] used Molecular Dynamics simulations to show that the continuum hypothesis is unsuitable to describe hydrocarbon transport in nanoporous media due to adsorption.

Molecular simulation has been a powerful tool to investigate confined systems, with great progress regarding the effect of confinement on fluid properties and characterization of confining surfaces for tight oil and gas reservoirs [23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33]. Regarding the diffusion process, Franco et al. [34] have shown that the parallel self-diffusion coefficients of pure methane, nitrogen, and carbon dioxide near calcite walls present an anisotropic behavior. Bui et al. [35] confirmed these results, and reported that hydration

and chemical composition of the pore can affect this phenomenon. Wu et al. [36] have addressed the dependence of the self-diffusion values on the confining mineral, as well as Fazelabdolabadi and Alizadeh-Mojarad [37]. Wu and Firoozabadi [38] claimed that the transport process affects the composition of the produced gas mixture due to selective adsorption - the fluid behavior at different compositions should be taken into account.

In this work, we analyze the surface and the confinement effect on self-diffusion data for methane-ethane mixtures confined within a calcite slit pore. Calcite is the most stable polymorph of calcium carbonate, and can be found as the most abundant mineral on some shale reservoirs [39, 40, 41]. We show the effect of the mixture composition and the position-dependency of the self-diffusion coefficients. The results were obtained with classical equilibrium Molecular Dynamics (MD) simulations, applying adequate methods that account for the effect of surface and confinement in different regions of the pore.

2. Computational details

2.1. MD simulations

Mixtures of methane and ethane were confined between two parallel plates of calcite, as shown in Figure 1. The calcite plane considered was $\{10\bar{1}4\}$ orthogonal to the z direction with xyz dimensions 4.990 nm x 4.856 nm x 1.212 nm. The pore size was fixed as $H = 3.5$ nm along the z axis. All simulated systems had overall density of $250 \text{ kg}\cdot\text{m}^{-3}$, and the results shown here are for systems simulated at 375 K.

We performed MD simulations with GROMACS 5.0.2 [42], using the Leap-Frog algorithm for the numerical integration of the equations of motion, with a time step of 2 fs. TraPPE force field [43] was applied to hydrocarbons, and Xiao et al. [44] force field was applied to the calcite crystal, with a cutoff radius of 1.0 nm. Crossed parameters for fluid-wall interactions were calculated using geometrical combining rules. The Particle Mesh Ewald method [45] was used to calculate the electrostatic interactions, and a velocity-rescale thermostat [46]

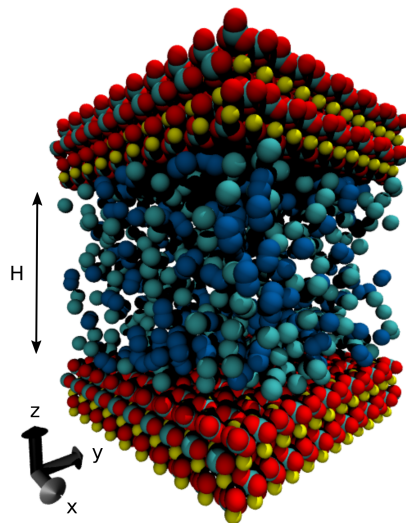


Figure 1: 3D plot of initial configuration: methane-ethane mixture confined inside calcite slit pore.

was used to control the temperature of the system, with relaxation time $\tau_T = 1.0$ ps. Periodic boundary conditions were applied to all directions, and no tail corrections were applied due to the inhomogeneity of the systems [47, 48]. Positions and velocities were stored every 0.2 ps.

Each system was equilibrated at the canonical ensemble for 20 ns followed by 50 ns of production time at the same ensemble. For statistical purposes, the trajectory was divided in 5 blocks of 10 ns each to calculate the standard deviations of self-diffusion coefficients.

2.2. Self-diffusion calculation

Self-diffusion is the average displacement of a molecule from its initial position in a system without a chemical potential gradient or external forces, being caused by thermal molecular motion. The self-diffusion coefficient is useful for estimating transport diffusion, an important dynamic property of fluids [49, 50, 51, 52].

In the case of an inhomogeneous fluid, new methods to calculate the components of the self-diffusion tensor have been proposed [53, 47, 54], considering the break of symmetry due to the confining walls. At a confined environment, there is a non-uniform particle distribution, leading to different diffusion at different regions. We calculate the position-dependent components of the self-diffusion coefficient parallel to the walls following the method of Liu et al. [53]:

$$D_{||} = \lim_{t \rightarrow +\infty} \frac{\langle \Delta r^2(t) \rangle_{\Omega}}{2tP(t)} \quad (1)$$

where $\langle \Delta r^2(t) \rangle_{\Omega}$ is the mean square displacement of the centers of mass, and the survival probability $P(t)$ is calculated as the ratio between the number of centers of mass that remain in the layer Ω between t_0 and t , $N(t_0, t_0 + t)$, and the number of centers of mass within layer Ω at t_0 , $N(t_0)$, considering multiple time origins:

$$P(t) = \frac{1}{\tau} \sum_{t_0=0}^{\tau-1} \frac{N(t_0, t_0 + t)}{N(t_0)} \quad (2)$$

The perpendicular component is obtained following the method described by Franco et al. [47]:

$$D_{\perp} = \frac{L^2}{\alpha \tau_r} \quad (3)$$

where L is the layer width, α is a parameter related to the potential mean force, and τ_r is the residence defined as (for further details, the reader is referred to Franco et al. [47]):

$$\tau_r = \lim_{t \rightarrow +\infty} \int_0^t P(t) dt \quad (4)$$

All the aforementioned approaches are based on the Smoluchowski equation (Equation 5), which describes the time evolution of the probability density, and is suitable for systems with a non-uniform spatial distribution at equilibrium [55, 53]:

$$\frac{\partial p(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{J} = \nabla \cdot D e^{-\beta W(\mathbf{r})} \cdot \nabla [e^{\beta W(\mathbf{r})} p(\mathbf{r}, t)] \quad (5)$$

where $p(\mathbf{r}, t)$ is the probability density function, \mathbf{r} the position vector, \mathbf{J} the particle flux through the boundaries, D the diffusion tensor, $\beta = 1/(k_B T)$ (k_B

being the Boltzmann constant, and T the absolute temperature), and $W(\mathbf{r})$ is the potential of the mean force.

3. Results and discussion

Diffusion under confinement greatly differs from diffusion in unconfined media. The diffusion near the walls is influenced by adsorption, which results in a larger density of molecules at the interface [56, 57, 52]. The particle distribution for confined methane is presented in Figure 2, where the different areas, considered for calculation of the self-diffusion coefficients in this study, are highlighted.

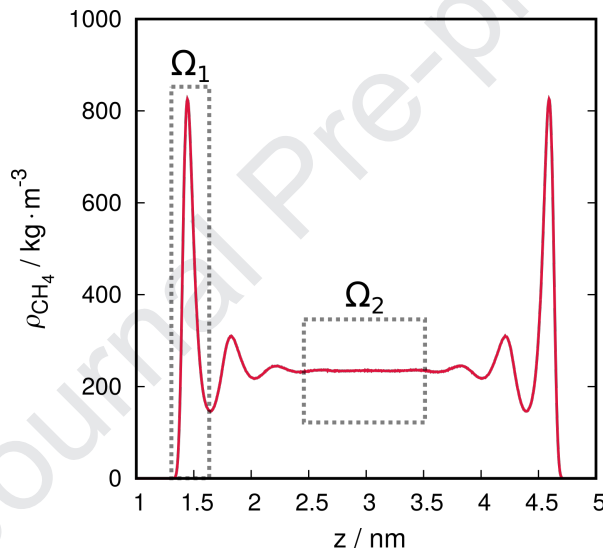


Figure 2: Density profile showing areas Ω_1 (wall) and Ω_2 (center) considered for calculation of the self-diffusion coefficients. Data for pure methane confined within calcite walls.

Figure 3 shows the density profile of pure hydrocarbons confined within calcite walls at the same density and pore size as the mixtures. At the center of the pore, further from the walls, the effect of the confining surface, that restricts the movement on the direction of confinement, can be observed. The parallel self-diffusion coefficients have essentially the same value in this region, but the perpendicular self-diffusion coefficient is much lower. Close to the walls, a large density variation is observed due to the fluid-surface interactions, but

at the center of the pore, the density is uniform. Therefore, the differences between the parallel and the perpendicular diffusion coefficients entail a pure confinement effect. The trace of the resulting self-diffusion tensor in this region, however, is comparable to the unconfined self-diffusion values. Franco et al. [34] have shown that, increasing the pore size, the differences between the parallel and perpendicular self-diffusion coefficients at the center of the pore decreases.

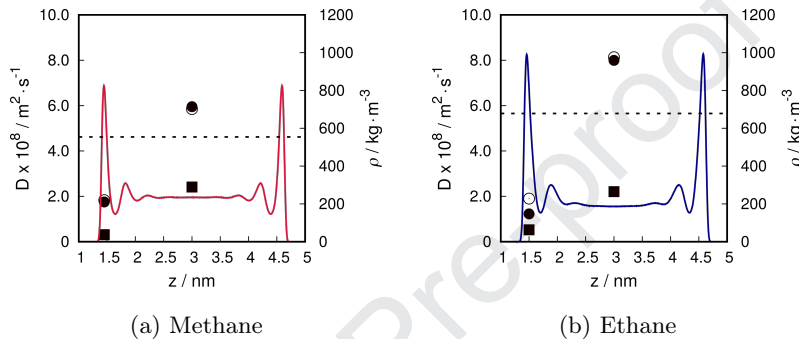


Figure 3: Position-dependent self-diffusion coefficients of pure components. D_{XX} : filled circles; D_{YY} : open circles; D_{\perp} : squares. The filled line shows the density profile inside the pore. The dashed line shows the unconfined self-diffusion average value calculated with Einstein's method at the temperature and density, and corrected for finite-size effects [58].

Close to the walls, an anisotropic behavior between the parallel self-diffusion coefficients emerges [34], as one can see in Figure 3b. This anisotropy has been explained as a consequence of the surface effect, in particular, due to the structural arrangement of the calcite crystal and the first fluid adsorbed layer. The question that is yet to be addressed is whether or not the same phenomena are observed for mixtures, and how the mixture composition affects such phenomena. Figure 4 shows the results for different regions of the pore for confined methane-ethane mixtures with different compositions at 375 K, with a pore size of 3.5 nm.

An anisotropic behavior between the parallel components of the self-diffusion tensor is observed near the walls regardless of the mixture composition, which implies that the same surface effect observed for the pure systems is found for adsorbed mixtures. The anisotropy is greater between ethane parallel self-

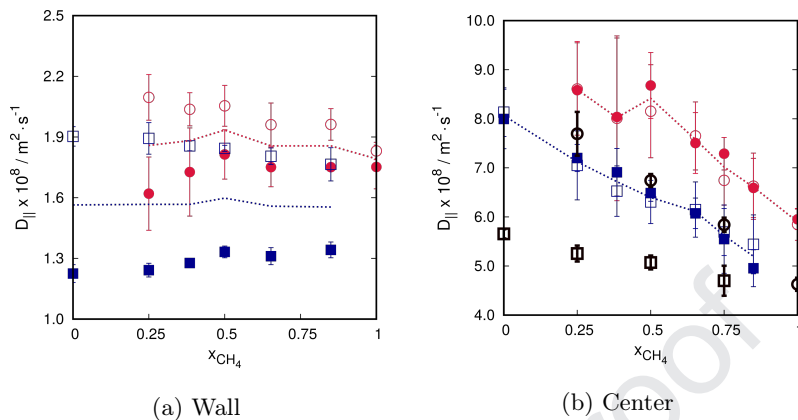


Figure 4: Effect of mixture composition on the parallel components of the self-diffusion for different regions of the pore. D_{XX} : filled symbols; D_{YY} : open symbols. Red circles for methane, blue squares for ethane, and black symbols for the unconfined mixture, for which $D_{XX} = D_{YY}$. The dashed line is the arithmetic average between D_{XX} and D_{YY} of each components.

diffusion components than between methane parallel self-diffusion components, and the difference between D_{XX} and D_{YY} also decreases increasing methane mole fraction. This implies that the presence of ethane alters methane self-diffusion, increasing the anisotropic behavior between methane parallel self-diffusion coefficients. Nevertheless, the average value of the parallel components near the walls remains reasonably constant. At the center of the pore (Figure 4b), no anisotropic behavior between parallel components is observed, and the magnitude of self-diffusion coefficients is 3-4 times higher than near the walls. This is most probably related to the density variation within the pore. The total density is much larger close to the walls, decreasing particles mobility.

As for the perpendicular component, to calculate the α parameter from Equation 3, we assumed that the layer is sufficiently small so that the potential of the mean force can be considered linear. For that reason, the layer considered for this calculation near the wall was $\Omega_1/2$, i.e., a linear density profile. The calculation of the perpendicular self-diffusion coefficient is unfeasible for some systems using this method because the relaxation time of local density

fluctuations may become faster than the time required for particles to diffuse, considering the evaluated small layer [54]. A possible solution is to increase the system size, but this has an enormous impact on the required computational effort. For the center of the pore, the whole length of Ω_2 can be used.

The values obtained for the perpendicular component near the walls were one order of magnitude smaller than the values of the parallel components (Figure 5a), and they seem to remain unaffected by changes in mixture composition. The slower motion of the molecules near the walls in the direction of confinement is due to layering, which creates a barrier for diffusion in z direction.

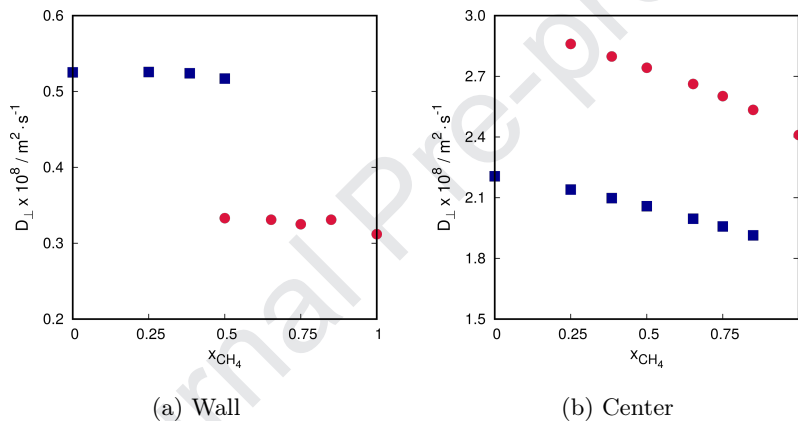


Figure 5: Composition dependency of the perpendicular coefficients of the self-diffusion tensor for different regions of the pore. Circles for methane and squares for ethane.

The presence of confining walls affects the diffusion at the center of the pore for small pore sizes. At the center of the pore (Figure 5b), the values of the perpendicular self-diffusion coefficients were about 3 times smaller than the parallel ones, following the same trend of decreasing with the increase of methane content. Franco et al. [34] have shown that bulk-like behavior is only observed for pure methane confined within calcite nanopores for pores larger than 15 nm.

Two interesting points emerge from the results. The first one, shown in Figure 5a, is that the diffusion of ethane is higher than that for methane. This can be explained by the preferential adsorption of ethane by the calcite crystals.

In Figure 6, the average mole fraction of methane in each region (close to the walls and at the center of the pore) is shown. The methane content close to the calcite walls is smaller than the global composition, and higher at the center.

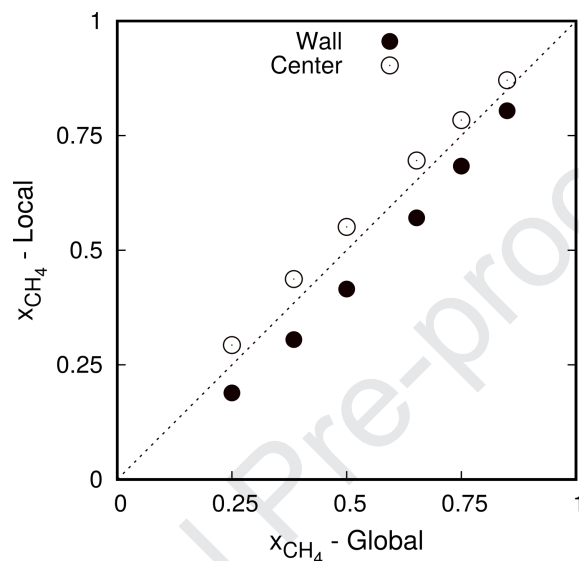


Figure 6: Average mole fraction of methane at regions Ω_1 (wall) and Ω_2 (center) for each mixture composition. Dashed line for $y = x$.

The second point is the behavior of the self-diffusion with the increase of methane mole fraction. Keffer and Adhangale [52] have studied the composition dependency of self-diffusion of an unconfined methane-ethane mixture, and have shown that the self-diffusion coefficients of both components increase with methane mole fraction, which is the opposite of what we have observed for the confined mixture. Pressure may be the answer for such a different behavior. Our systems were simulated at same mass density, temperature, and volume. This implies that the higher the methane content, the higher the number of molecules within the pore to keep the same mass density, which increases the pressure of the system. And, increasing pressure, the values of the self-diffusion coefficients of methane and ethane under confinement are decreased, as shown by Sharma et al. [31], which corroborates our results.

4. Conclusion

We have studied the surface and the confinement effect on the self-diffusion coefficients of methane-ethane mixtures confined by calcite nanopores, using classical equilibrium molecular dynamics simulations.

Close to the calcite walls, the same anisotropic behavior previously observed for pure components was found for confined methane-ethane mixtures. This surface effect significantly affects the mobility of the adsorbed fluids in all directions. This means that parallel self-diffusion coefficients are different in different directions, and achieve much higher values than the perpendicular self-diffusion coefficient.

At the center of the pore, the surface effect that causes the anisotropic behavior between parallel self-diffusion coefficients vanishes, and the confinement effect acts on the perpendicular self-diffusion coefficient. The mixture composition plays an important role in the dynamics at the center of the pore, and, increasing methane mole fraction, keeping the same density and temperature, all diagonal components values of self-diffusion tensor decrease, which is probably a consequence of the higher pressures.

The surface and the confinement effects are usually mixed terms in the literature, and, in fact, they are often coupled. Nevertheless, in this work, we have shown that, even for a tight nanopore (3.5 nm), they play different roles. The anisotropic behavior between the parallel self-diffusion coefficients close to the walls vanishes at the center of the pore, which means that the surface itself is sufficiently far from the center of the pore. But, at the same time, the proximity of the two walls is enough to cause an anisotropic behavior for the perpendicular self-diffusion coefficients, when compared to the parallel ones, and this is a direct consequence of the confinement effect. Because of these effects, the determination of each component of the self-diffusion tensor in confined media is necessary, and adequate methods to calculate such diffusion coefficients must be employed.

Acknowledgments

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: