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## Linking DFT and MD to simulate grand canonical ensemble: selectivity of binary mixtures in nanopores

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We present an approach linking molecular Density Functional Theory (DFT) and Molecular Dynamics (MD) to the study of inhomogeneous fluids behavior in the nanoporous media. It is aimed at describing composition, volumetric and transport properties of the fluid confined within a nanopore that is connected with bulk (macropore). This problem is of interest for unconventional hydrocarbon reservoirs development, geologic carbon sequestration, gas separation and other industrial applications.

While DFT has been shown to reproduce adsorption and density distribution of confined fluid well, it is not applicable to describe transport phenomena. MD simulation can be used to obtain both structural and dynamic properties, but it is computationally expensive (especially in the case of modeling a large “bulk+nanopore” system). We propose an approach, in which MD simulation is performed only for confined fluid, and its initial configuration is based on DFT calculation of the fluid composition in a nanopore under given conditions in bulk.

In this work, we apply the proposed approach to study binary mixtures of methane, ethane and carbon dioxide in slit-like nanopores with carbon walls. Previously we validated both DFT and MD molecular models independently on experimental isotherms for the studied mixtures in bulk. We consider filling the nanopores of different widths with the fluid mixture when increasing bulk pressure. Detailed understanding of these processes is important for the petroleum industry (in particular, for enhanced gas recovery using CO<sub>2</sub> injection).

For each mixture we provide the dependencies of adsorption selectivity on bulk pressure and pore size obtained by DFT along with corresponding MD equilibration results. Bulk fluid composition is also varied and its effect on selectivity is analyzed. We consider typical reservoir conditions: pressures up to 30 MPa and temperatures up to 400 K. Filling the pores with a width of 1–5 nm is studied in detail since the structure of fluid density profile varies most significantly in this range. DFT calculations are also provided for pore widths up to 50 nm to cover pore size distribution of unconventional reservoirs and observe stabilization of selectivity in larger pores.

Equilibrium density profiles of each component obtained by DFT and MD are compared. Both theory and simulation reproduce the layering structure of a confined fluid well. We observe the formation of an equal number of adsorption layers and (in the pores wider than 1 nm) the bulk-like region with constant density in the center of the pore. With increasing bulk pressure capillary condensation occurs, while the mixture in bulk is still gaseous. This can be observed from the density profiles and is visualized in snapshots from MD simulation.

Thus, in this work we apply a combination of theoretical (DFT) and simulation (MD) approaches to study the behavior of confined binary mixtures in equilibrium with bulk. The presented approach can be used to provide essential information for optimal design of CO<sub>2</sub> EOR in unconventional reservoirs and CO<sub>2</sub> sequestration.

### Time Block Preference

Time Block A (09:00-12:00 CET)

## References

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