Computer simulation of liquids with permanent porosity

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Introduction

Porous liquids (PLs) are a new class of materials that combine the fluidity of liquids with properties from porous solids. These are classified according to their composition into three types: 1) organic cages that have been functionalized to be fluid at ambient temperature, 2) organic cages disolved in an organic solvent that cannot occupy their cavities, and 3) MOF or zeolite particles in a similar energetically-impeded solvent (Fig. 1). The intrinsic cavities of the cages and particles serve as permanent, selective hosts to small molecules that can be engineered to increase the solubility of specific solutes in the liquid. Thus, an understanding the structural properties of PLs and their interaction with desirable guests becomes a required stepping stone in the development this novel technology.

In this work, we apply a combination of experimental and computational tools, namely neutron diffraction experiments and Molecular Mechanics simulations, to analyze the structure and dynamical properties of different porous liquids. We also report gas uptake simulation results for a variety of hydrocarbons and discuss the transport dynamics of these hydrocarbons inside the PLs.

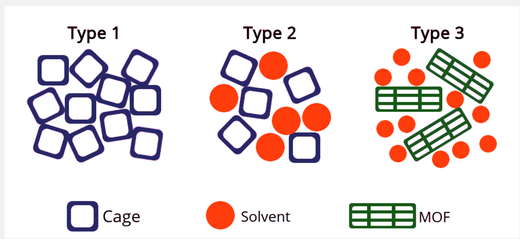

Fig. 1: Classification of porous liquids according to their chemical composition.

Goals

- To construct models and topologies for molecular mechanics simulations of porous liquids that reproduce available experimental results.
- To develop an understanding of the structural properties of the liquids and their capacity to absorb specific gases.
- To assess the viability of each system as a porous liquid and predict their experimental performance.

Systems Studied

PL-2-1

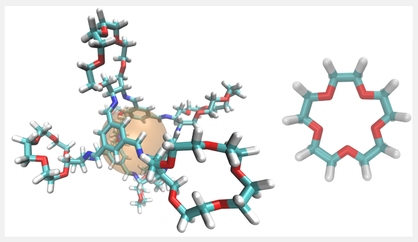

Fig. 2: Type-2 PL formed by crown ether cages (left) in 15-crown-5 ether (right).

PL-2-2

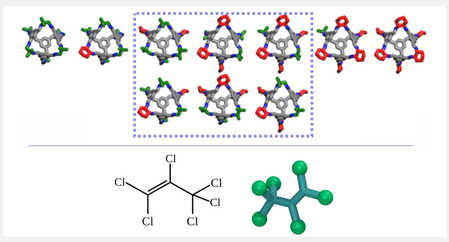

Fig. 3: Type-2 PL formed by organic cages of different types (top) disolved in perchloropropane (bottom).

PL-2-3

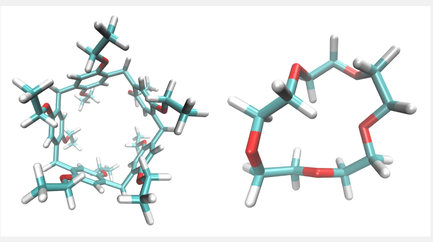

Fig. 4: Type-2 PL comprising pillar[5]arene cages (left) in 15-crown-5 ether (right).

PL-3-1

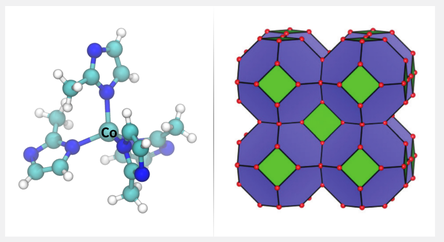

Fig. 5: Type-3 PL involving a zeolite particle is a water. This particle is a 2x2x2 supercell (right) of ZIF-67 groups (left).

Metodology

Optimization of the experimental geometries and calculation of their partial charge distribution by means of *ab-initio* DFT calculations with the CP2K software.

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Selection and construction of force-field parameters required for running Molecular Mechanics simulations with the Cassandra and GROMACS software packages.

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Simulation of different porous liquid configurations using periodic boundary conditions.

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Analysis of simulated systems and comparison to experimental references.

Results

PL-2-1

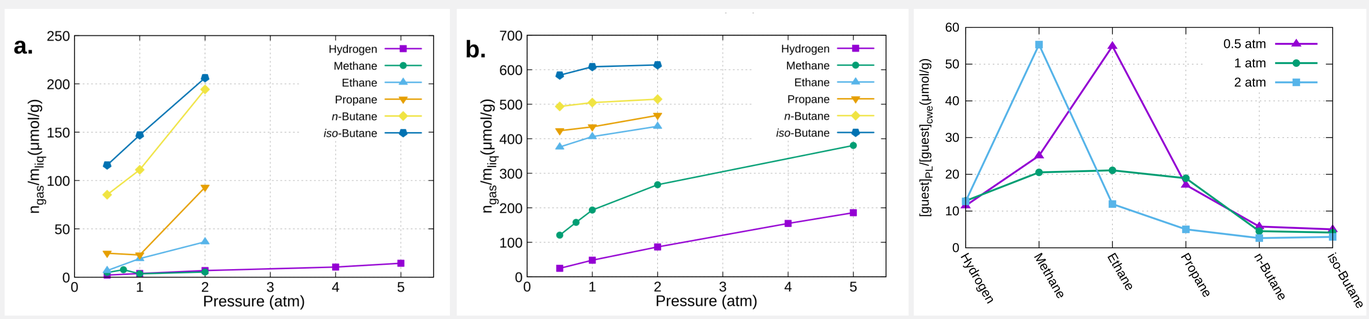

Fig. 6: Guest absorption isotherms at different pressures computed by Grand Canonical Monte Carlo simulations at 300 K for **a.** the pure solvent (15-crown-5 ether) and **b.** the Type-2 porous liquid.

Fig. 7: Change in ratio of equilibrium concentrations of studied gases in the type-2 porous liquid (PL) relative to the solvent (CWE) at different pressures.

Guests No.	Guest	τ_{InC} [ps]	τ_{ExC} [ps]
10	Methane	400	30
	Ethane	3700	10
	n-Butane	7500	30
	iso-Butane	--	8600
50	Methane	200	30
	Ethane	500	100
	n-Butane	16500	3900
	iso-Butane	--	--

Table 1: Residence time spend by guests inside intrinsic (τ_{InC}) and extrinsic (τ_{InC}) cavities.

PL-2-2

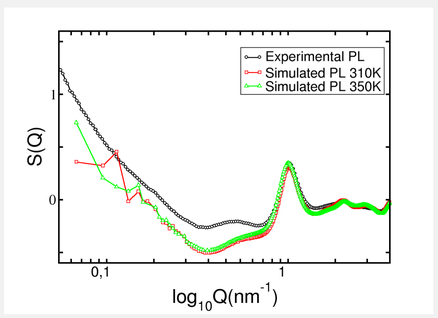

Fig. 8: Comparison of static structure factor values obtained from experiments and simulations of the PL.

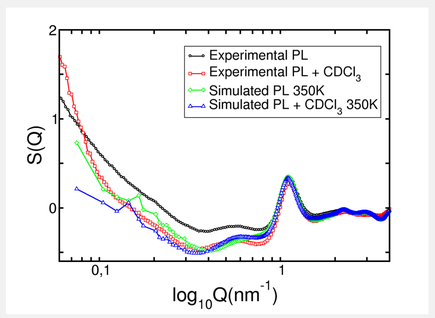

Fig. 9: Comparison of experimental and simulated static structure factor values of the pure PL and the PL with deuterochloroform.

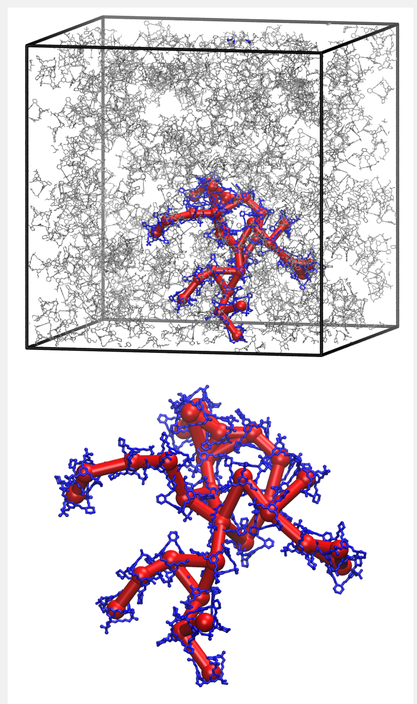

Fig. 10: Linear aggregate formed by cage molecules in the porous liquid. Such aggregates change dynamically in size and shape.

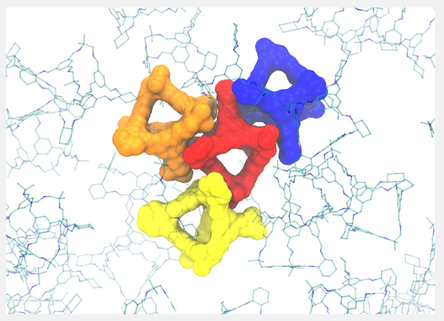

Fig. 11: A linear aggregate shown in the PL at a mesoscopic scale.

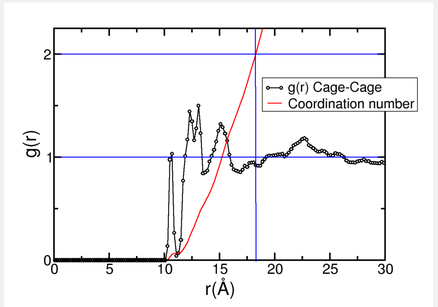

Fig. 12: Radial distribution function and coordination number of cages relative to other cages.

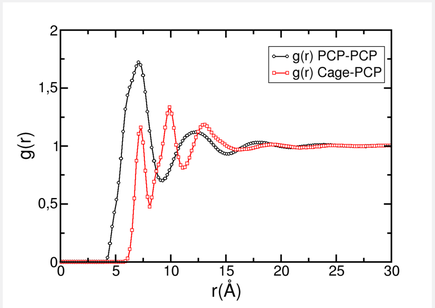

Fig. 13: Radial distribution function and coordination number of cages relative to solvent molecules.

Video 1: Linear aggregation of scrambled cages in perchloropropane.

PL-2-3

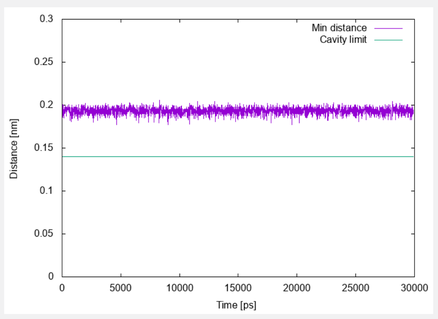

Fig. 14: Minimum distance between cages and solvent in an NPT run at 350 K.

Video 2: Evolution of a pillar[5]arene cage in 15-crown-5 ether at 350 K.

PL-3-1

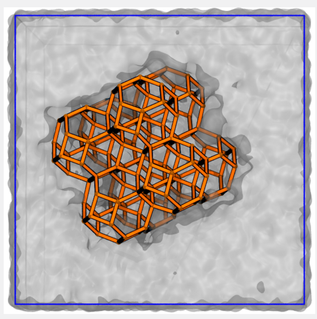

Fig. 15: Snapshot of a NVT simulation involving a ZIF-67 particle in water.

Video 3: Evolution of a ZIF-67 particle in water at 298 K.

Conclusions

The results arising from computational and experimental analysis of PL-2-1 and PL-2-2 have permitted the description of their structure and properties. Moreover, these techniques have provided insight into the dynamics and absorption of relevant small molecules acting as guests. From the study and understanding of these systems, candidates such as PL-2-3 and PL-3-3 are introduced as possible novel porous liquids.

Special note should be paid to the conflux of computational and experimental work, requirement for the fulfillment of the goals set in this study.

References

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