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Molecular motion of propane in silica pores: computer simulations compared with neutron scattering experiments

Understanding how fluids, and notably hydrocarbon gases, seep through porous rocks in the terrestrial environment is essential to understand the fundamental processes involved and also to aid better recovery of these gases from the earth. It is known that the behavior of fluids in general is altered on confining them in nanopores. It can be expected that the motion of hydrocarbons through porous rocks will be affected too. One way of investigating this is using neutron scattering experiments to probe the motion of confined hydrocarbon molecules. In such experiments, a beam of neutrons with a known energy and momentum is bombarded on a material to be studied. The neutrons get scattered by the molecules in the material and in the process exchange some momentum and energy with these molecules. The scattered neutrons are detected and the energy and momentum they exchanged with the molecules is also recorded.

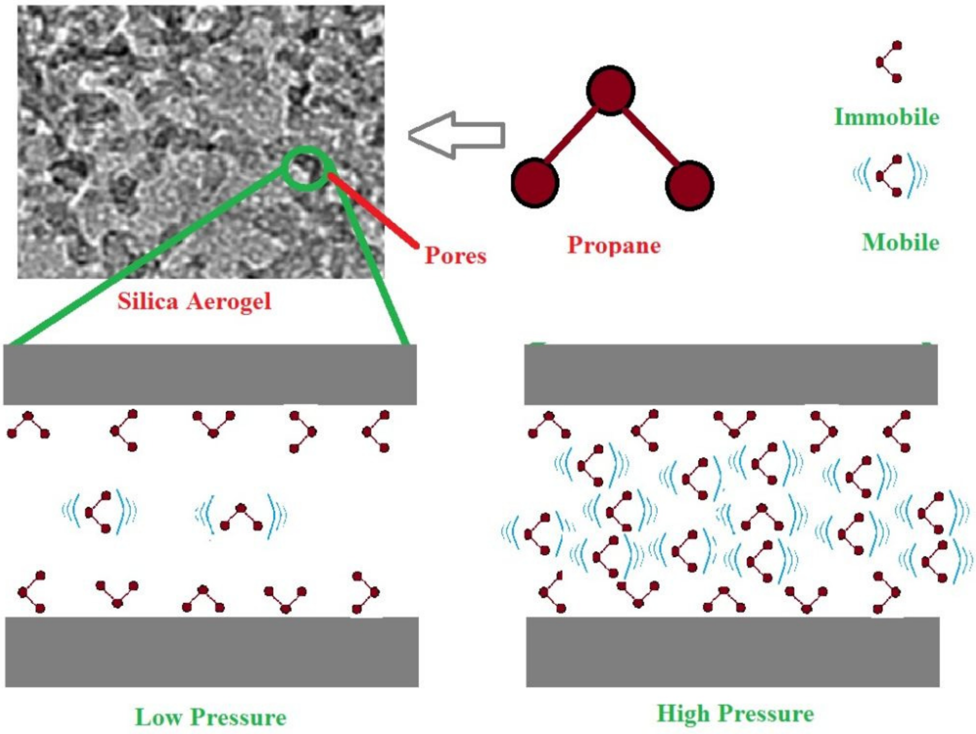

Fig. 1. A schematic explanation of the main findings in the simulation. The system studied is propane (top center) confined in the silica aerogel pores (top left, an SEM image of silica aerogel, with a representative pore marked by a green circle). Molecular model of the system (bottom) were made and computer simulations carried out at low (left) and high pressures (right) of propane loading in a pore represented by the space between two grey slabs. The grey slabs represent silica matrix. At low pressures, most propane molecules are adsorbed at the pore surface and are therefore unable to move. At high pressures, the newly added molecules can only occupy the central regions of the pore where they are free from the interaction with the silica surface and are therefore able to move. A higher fraction of mobile molecules at higher pressures leads to higher diffusion coefficient at high pressure.

This exchange of energy and momentum encodes information, respectively, on the motion and structural arrangements of the molecules in the material being studied. In a recent experiment, we used quasielastic neutron scattering (QENS – a type of neutron scattering specifically suited to study diffusive motion) to study the diffusive motion of propane inside 20 nm wide pores of silica aerogel. These experiments revealed a counter-intuitive behavior of propane diffusive motion as a function of pressure. In general, at higher pressure, crowding of molecules is expected to result in a slower motion. However, in case of propane confined in silica aerogel, we found that the diffusive motion gets faster as the pressure is increased from 8 bar to 58 bar. To understand this counter-intuitive finding we carried out computer experiments using molecular dynamics simulations. In these experiments models of the real system are made and Newton's equations of motion for the system are solved numerically. These calculations provide trajectories of each molecule constituting the system in time. Properties of interest can then be calculated from these trajectories. We calculated the experimental observables measured in the QENS experiments directly from the simulated trajectories and compared the two. Good agreement was achieved between the experimentally obtained quantities and those calculated from the simulation. We used the simulation data to further calculate quantities inaccessible with experiments. For example, we calculated quantities related to the rotational motion of propane. An inspection of the time scales involved in the rotational motion of propane helped explain why only translational motion of propane was observed in the experiments while the rotational motion is too fast to be captured by the neutron scattering instrument used. We also calculated the distribution of molecules in the pore as a function of their location. At low pressures, most of the propane molecules in the pores are adsorbed at the pore walls and are immobile due to the intermolecular binding forces from the pore walls. The remaining molecules that are away from the pore walls do not feel these forces and remain mobile. At higher pressures, more propane molecules are added to the pores. As the pore wall is already saturated, the newly added propane molecules have to occupy the central regions of the pore and are therefore mobile. Thus the ratio of mobile to immobile propane molecules increases at higher pressure, thereby increasing the overall diffusion coefficient which translates to faster motion at higher pressure. Our MD simulations thus explain the counter-intuitive experimental findings. These findings are important for gas extraction and recovery from sub terrestrial environment.

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