Adsorptive and Diffusive Properties of Carbon Dioxide-Methane-Water in Coal-like Structures using Molecular Simulations

Alaaeldin Salih and Erich A. Müller*

Department of Chemical Engineering

Imperial College London

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Introduction (I)

One of the options for CO_2 sequestration is enhanced coalbed methane recovery (ECBM), where CO_2 is injected into coal seams with the dual purpose of desorbing coalbed methane and sequestering CO_2
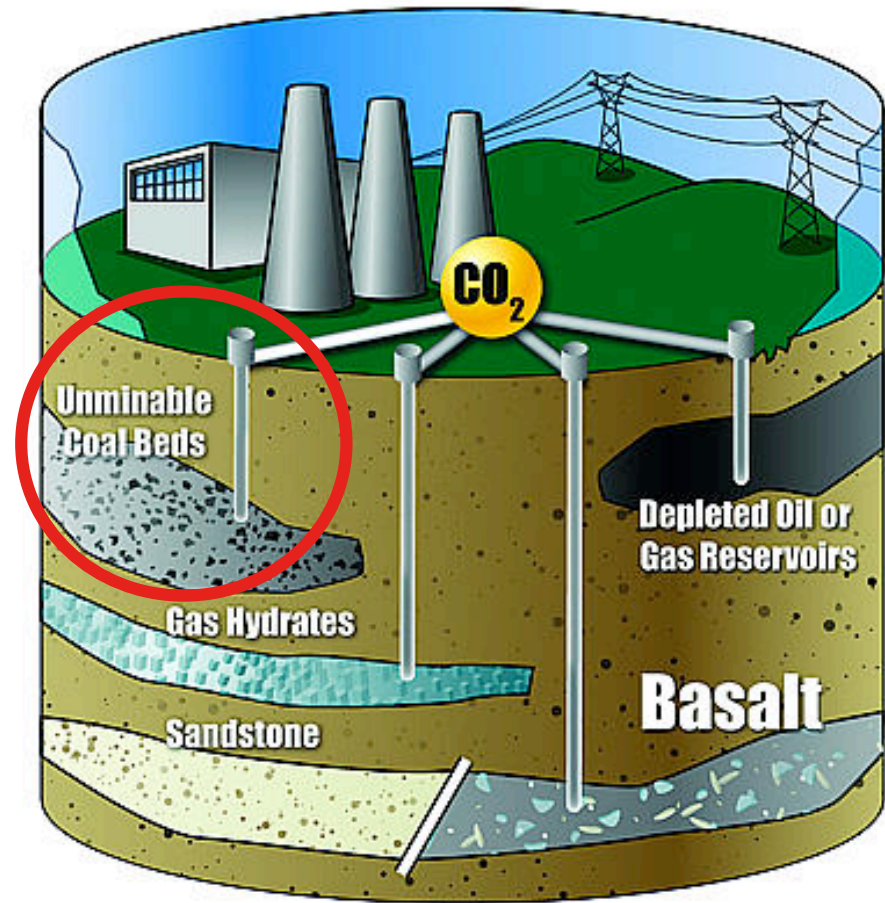
Source: **Bowen J. et al. (2008)**

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Introduction (II)

- ECBM process is plagued with operational problems, including the swelling mechanism of coal, their CO_2 adsorption capacity, and competition for available adsorption sites by underground water

- Adsorption of CO_2 in coals has been studied experimentally for decades, however, in this work we employ **molecular simulations** to model both the equilibrium and kinetic behaviour pertaining adsorption and permeation of the main three fluids (methane, carbon dioxide, water) involved in EBCM process

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Simulation Methods

Three complementary methods of simulation were used in modeling the adsorption/diffusion of the fluids in porous structures:

- Grand Canonical Monte Carlo (GCMC)
  - » Open system (μ, V, T)
  - » Boundary conditions imposed in x and y directions paralleling the pore walls
  - » Adsorption isotherms produced at T = 350K

- Equilibrium Molecular Dynamics (EMD)
  - » Simulations carried out in DL_POLY (Smith et al., 2006) using NVT ensemble
  - » Equations of motion solved by Verlet leapfrog algorithm. Temperature was kept constant using Nose'-Hoover thermostat method.
  - » Diffusion coefficients produced at T = 350K

- Non-Equilibrium Molecular Dynamics (NEMD)
  - » Dynamics of pore filling

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Coal Substrates

Three different coal models were designed to capture some of the complexity of coal:
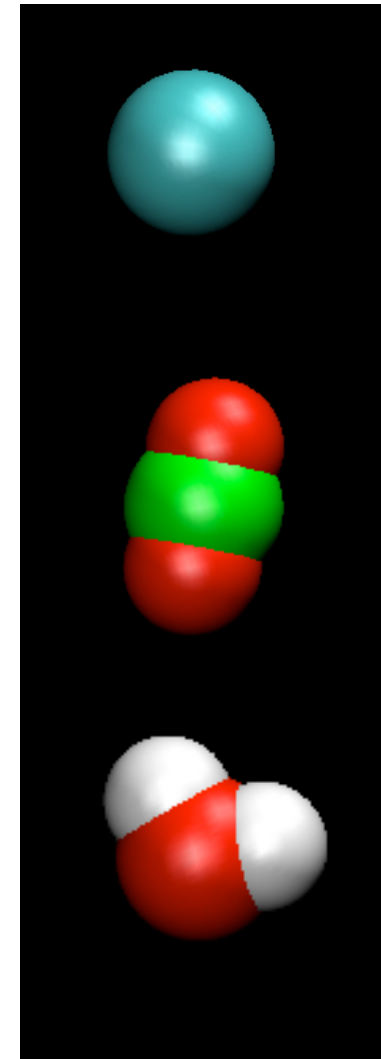
- **Slit-pore**: simple and most widely used. Each wall is made from three graphene layers. The pore width is 1.5 nm

- **Random-structure**: more complex structure made from randomly placed graphitic units (coronene-shaped)

- **Nanotubes**: these were used in order to compare with the other structures
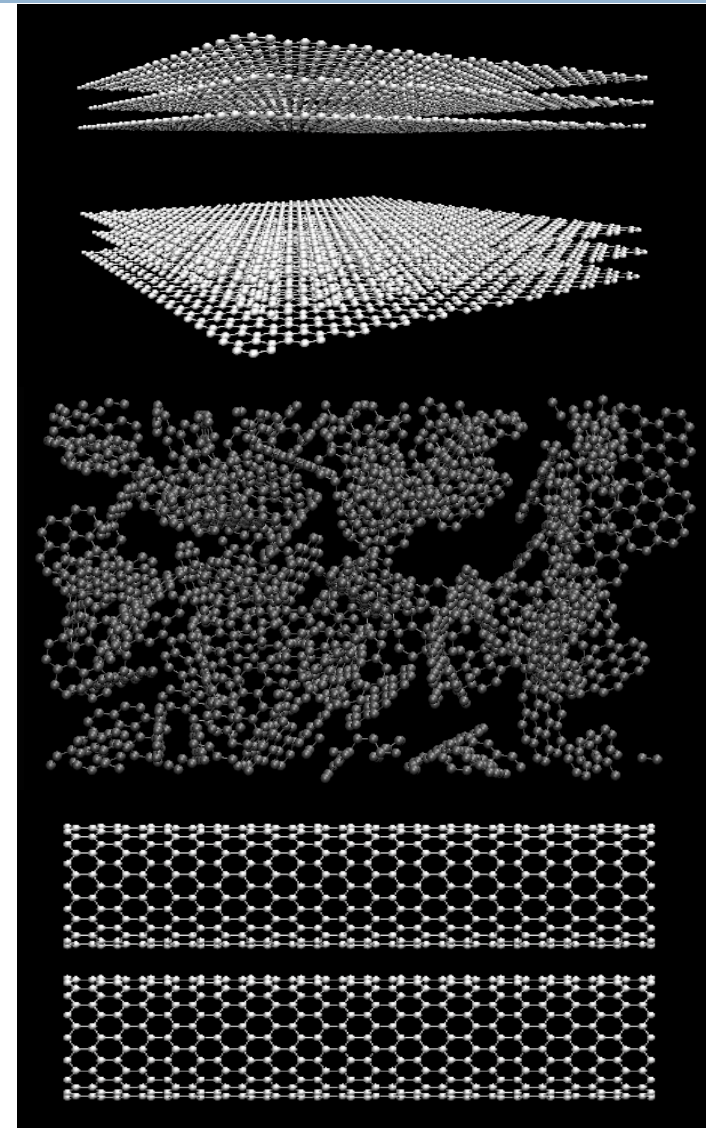
Fluid Intermolecular Potentials

The following three models were used in the simulations:

- **Methane:** is commonly modeled as a spherical Lennard-Jones (LJ) particle with one interaction site.

- **CO_2**: EPM2 model by Harris and Yung (1995): Three LJ spheres with partial charges associated with each atomic site

- **Water**: Three-site SPC/E model (Berendsen et al., 1987): considered simple and reliable. Produces good structural and dynamical properties
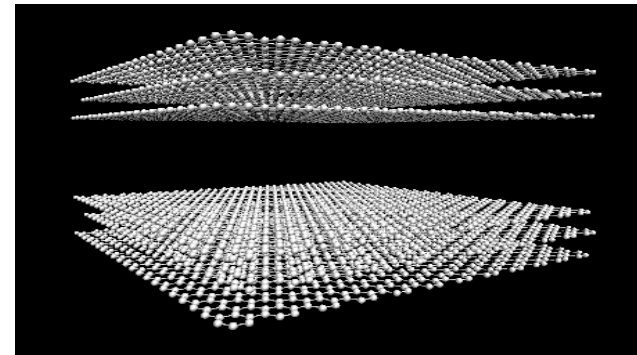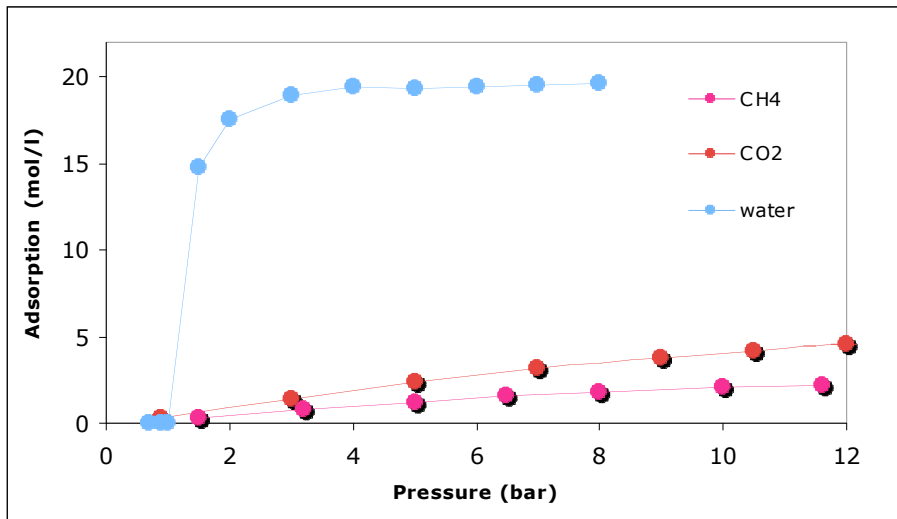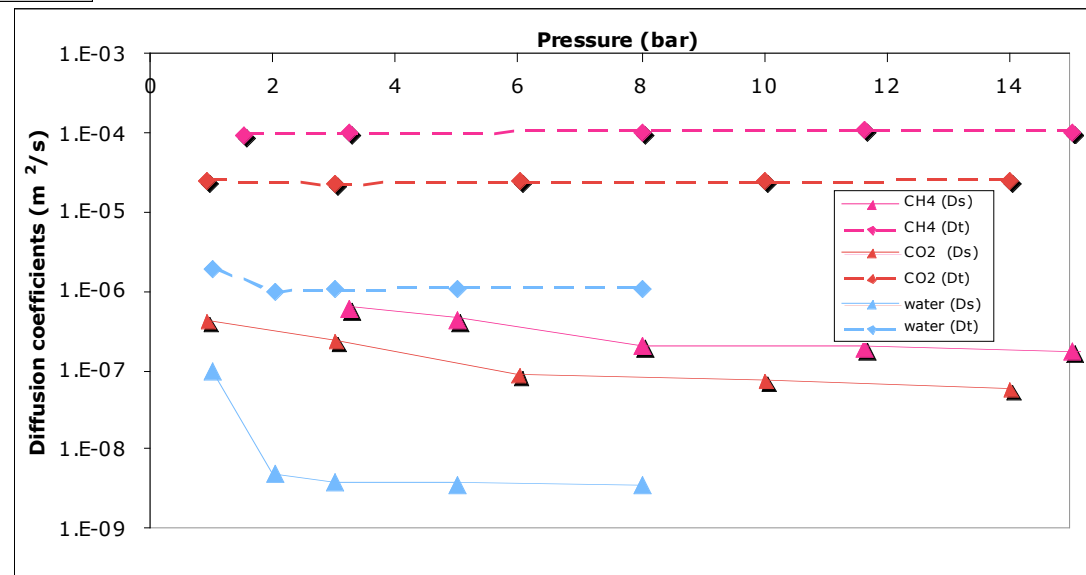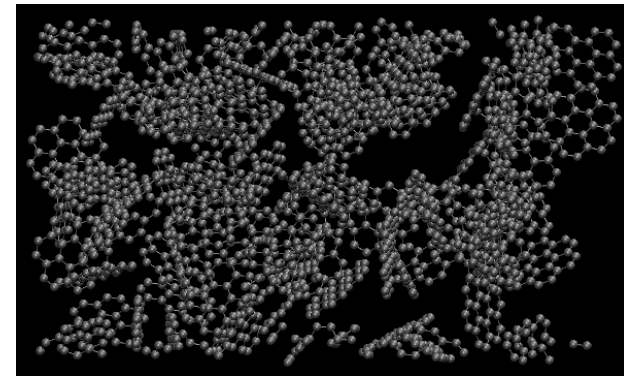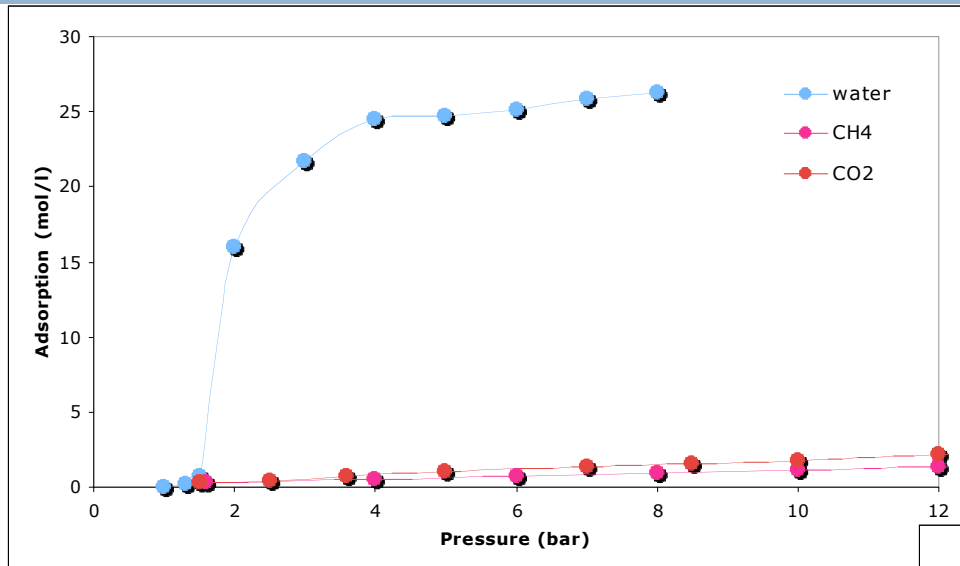
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Results (slit pores)

Adsorption and diffusion
of fluids at 350K

D_s Self-diffusion

D_t Transport diffusion

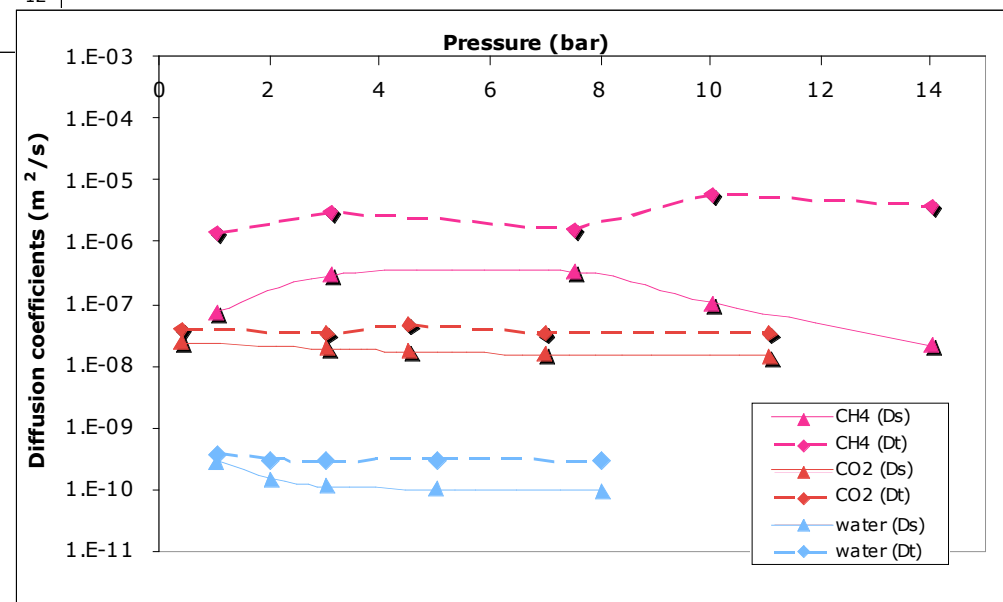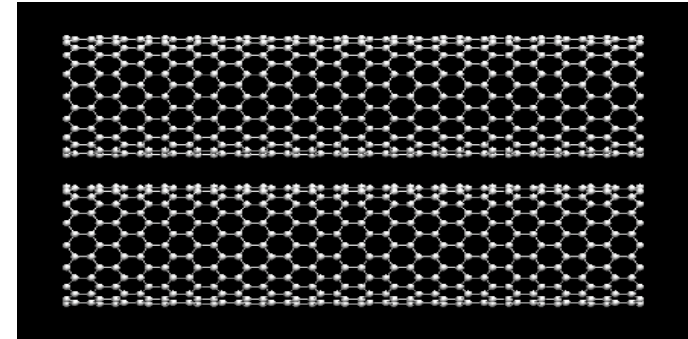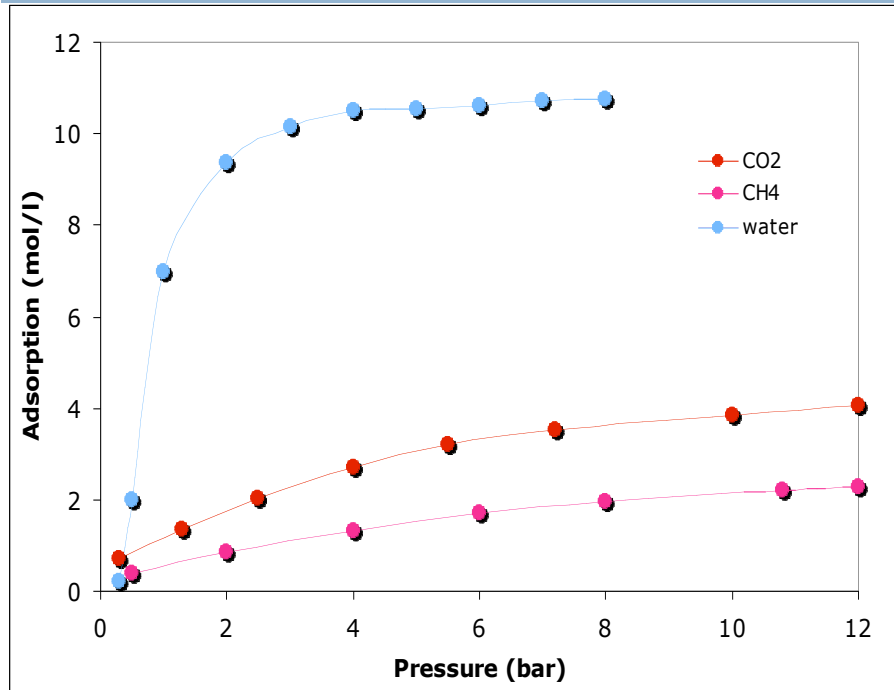**Imperial College
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Results (random structure)

Adsorption and diffusion
of fluids at 350K

D_s Self-diffusion

D_t Transport diffusion

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Results (nanotubes)

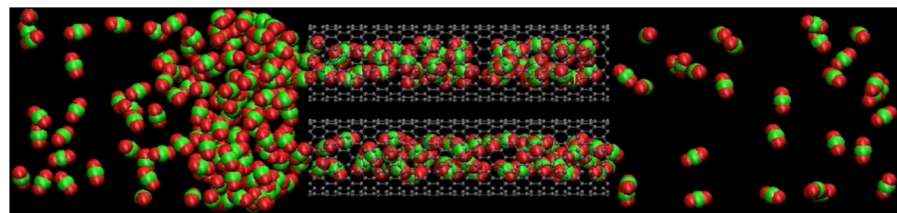
Adsorption and diffusion
of fluids at 350K

D_s Self-diffusion

D_t Transport diffusion

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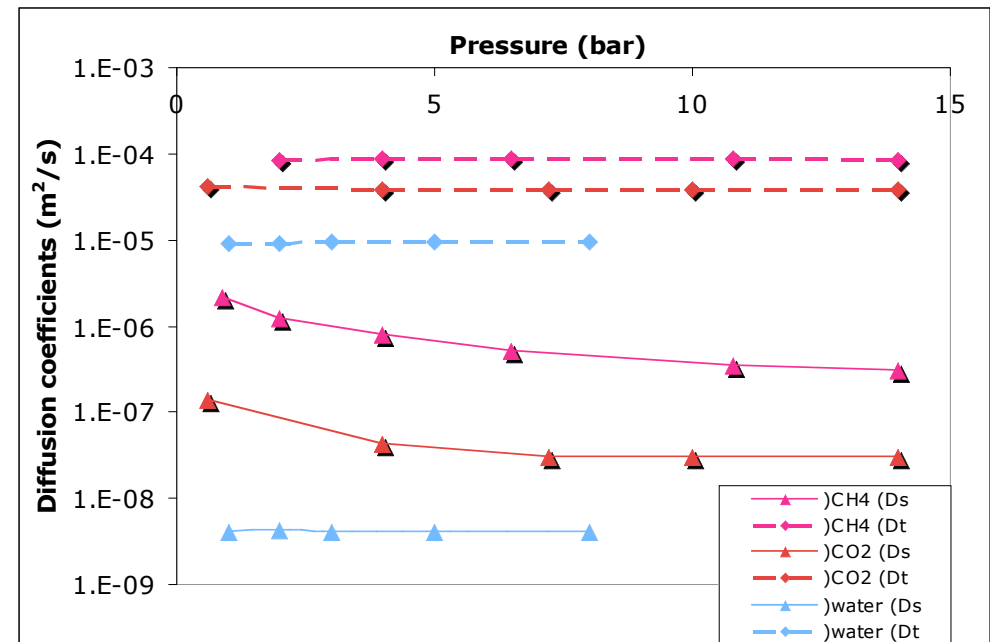
Comparison of CO₂ flow in different structures

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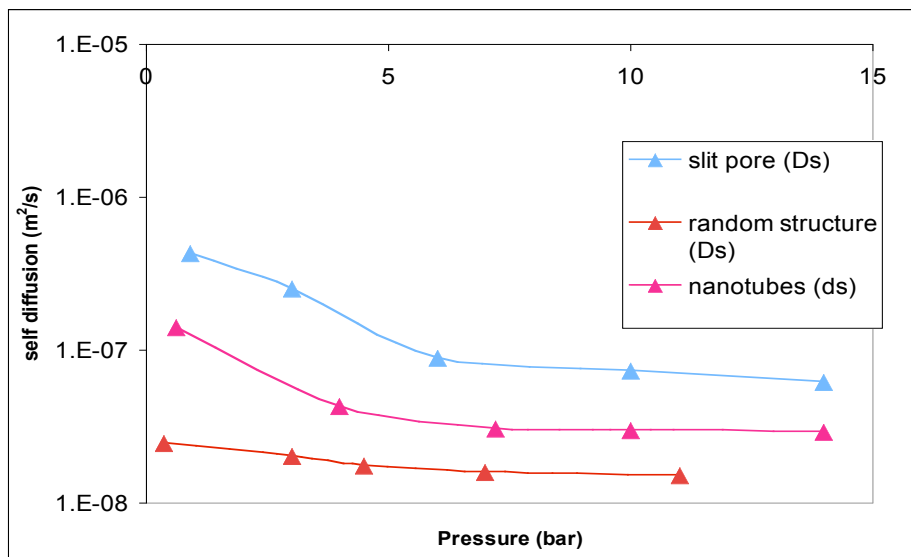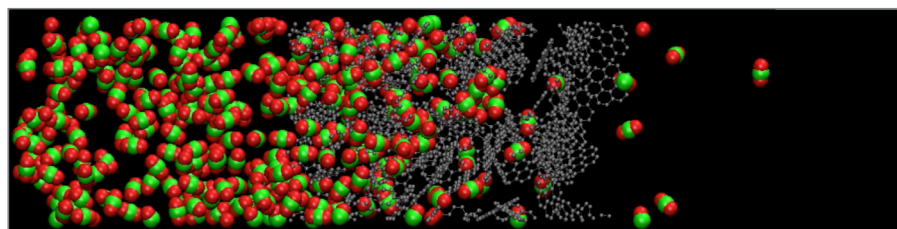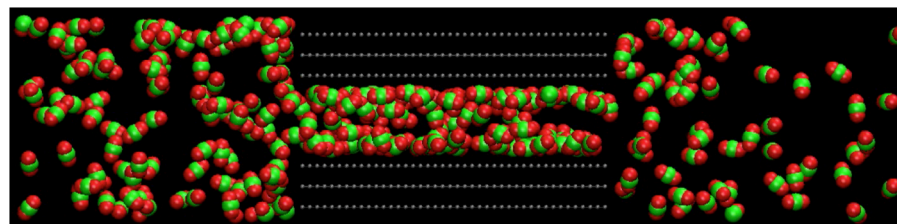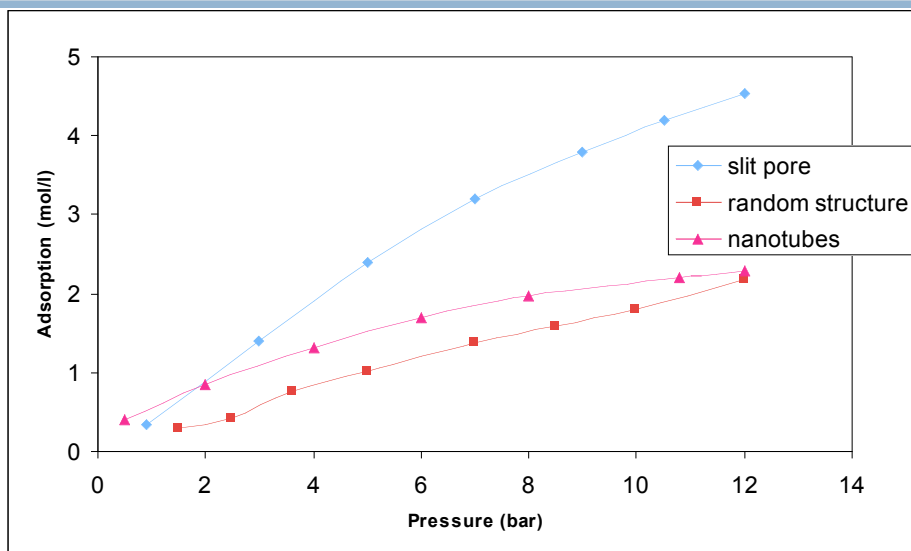
Conclusions

- The geometry of the pores is significant in determining the adsorption and diffusion properties of the three fluids studied (methane, CO_2 and water).

- The presence of water, even in small quantities, can radically change the dynamics of the adsorption and diffusion processes. Water clusters can block the pores which in turn reduce the adsorption capacity of the structures for CO_2 and CH_4.

- It is important to study the kinetics of the system when studying the adsorption properties as it gives better understanding of the system specially when looking at mixtures.

- Swelling, although not discussed herein, can affect the adsorption process in a significant way.

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Further info:

Erich A. Müller

Department of Chemical Engineering

Imperial College London

e.muller@imperial.ac.uk

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