

Molecular simulations to study the effect of pore geometry and structure on the adsorption of CH₄/H₂ mixtures in carbon pores

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1 Background

Physical adsorption of methane and hydrogen gas mixtures in microporous carbons is considered to be important and fundamental in (i) heterogeneous catalytic processes, (ii) cleaner hydrogen production technologies and (iii) fuel storage applications.

Considering the significance of adsorption and separation of CH₄ and H₂ mixtures in carbon materials, in this work we carried out GCMC simulations to theoretically study the effect of pore structure and geometry on the selective separation of methane molecules from CH₄/H₂ mixtures. The pore geometries studied include slit, tube, carbon foam and a carbon with random pore configuration

2 Simulation method

The most widely applied Grand Canonical Monte Carlo simulations was used to study the adsorption behavior of hydrogen on nanoporous materials. All the GCMC simulations performed are classical ones.

In this work the hydrogen was modeled as a two-site sphere and methane was modeled as spherical. The intermolecular potentials are given in Table 1.

Reference	Molecule	No of sites	H-H distance, nm	σ_{HH} , nm	ϵ_{HH} , K
1	H ₂	2	0.074	0.259	12.5
2	CH ₄	1	--	0.381	148.1

Table 1: Lennard-Jones parameters for C-C and H-H interactions. The energy is reduced by Boltzmann's constant

3 Effect of carbon pore size on the selectivity for CH₄ molecules

In this work we carried out simulations in slit-pores of width 0.73, 1.2, 1.5, 1.9, 2.25 and 2.64 nm, that can hold up to 1-6 layers of methane molecules, respectively. The results are expressed in terms of selectivity versus pressure, as shown in Fig 1.

We noticed that the selectivity for methane in smaller pores (width ≤ 1.2 nm) was remarkably higher, which is due to the reduction in entropy of hydrogen molecules and also due to the very high zero point energy of methane molecules in smaller pores.

Snapshots showing the entropy effect associated to hydrogen molecules in smaller pores are given in Fig 2.

In larger pores these effects seems to negligible and thus, the selectivity was found to be relatively higher in pores of size that can hold 1-2 layers of methane molecules.

In any case, the selectivity remains higher than unity due to the energetic effects.

Pores that can hold 1-2 layers of CH₄ were found to be the optimum pore size for the selective adsorption of CH₄ molecules at 298 K

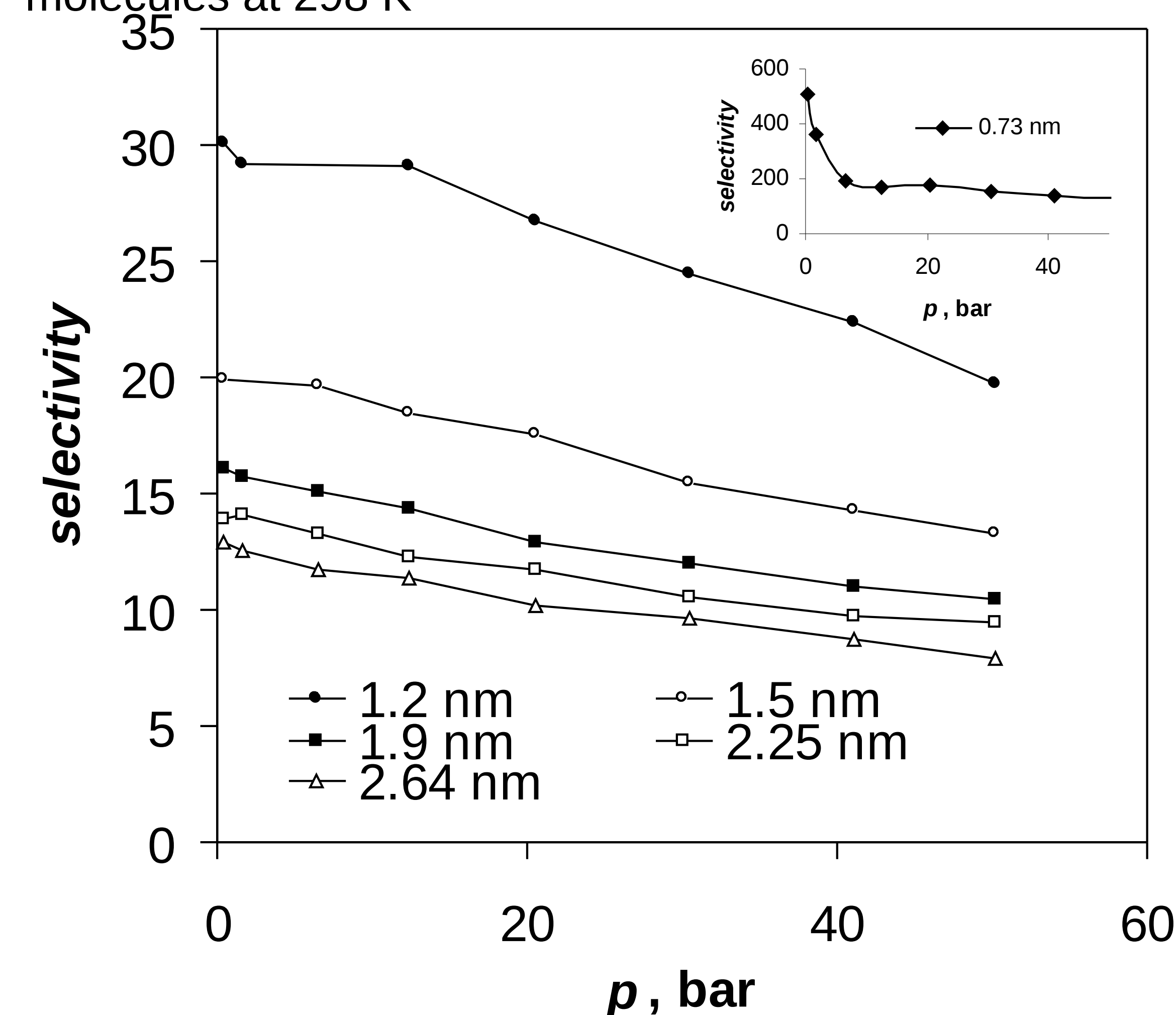


Fig 1: Effect of pore size on selectivity of methane at 298 K

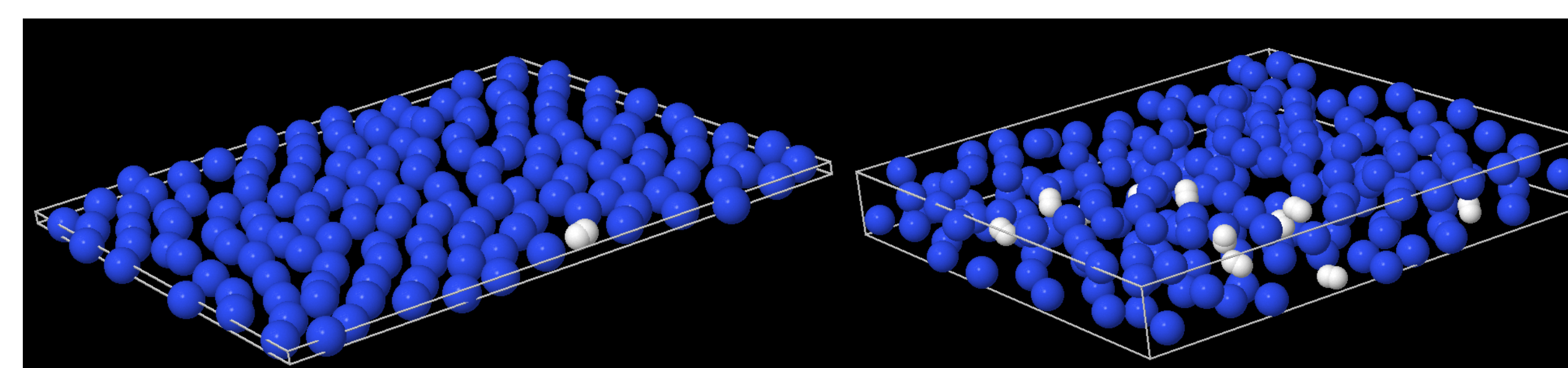


Fig 2: Snapshots showing the adsorption of CH₄/H₂ (CH₄-blue; H₂- white) in slit-pores of size 0.73 nm(left panel) and 1.2 nm (right panel)

4 Effect of pore structure on the selectivity for CH₄ molecules

An array of nanotubes that have a closed structure has the highest selectivity for methane molecules, followed by carbon foams, slit and random pore structures.

The selective adsorption of methane was influenced by both energetic and packing effects at low and high pressures, respectively.

The reduction in entropy of hydrogen favors the selectivity for methane molecules at higher pressures (Fig. 4).

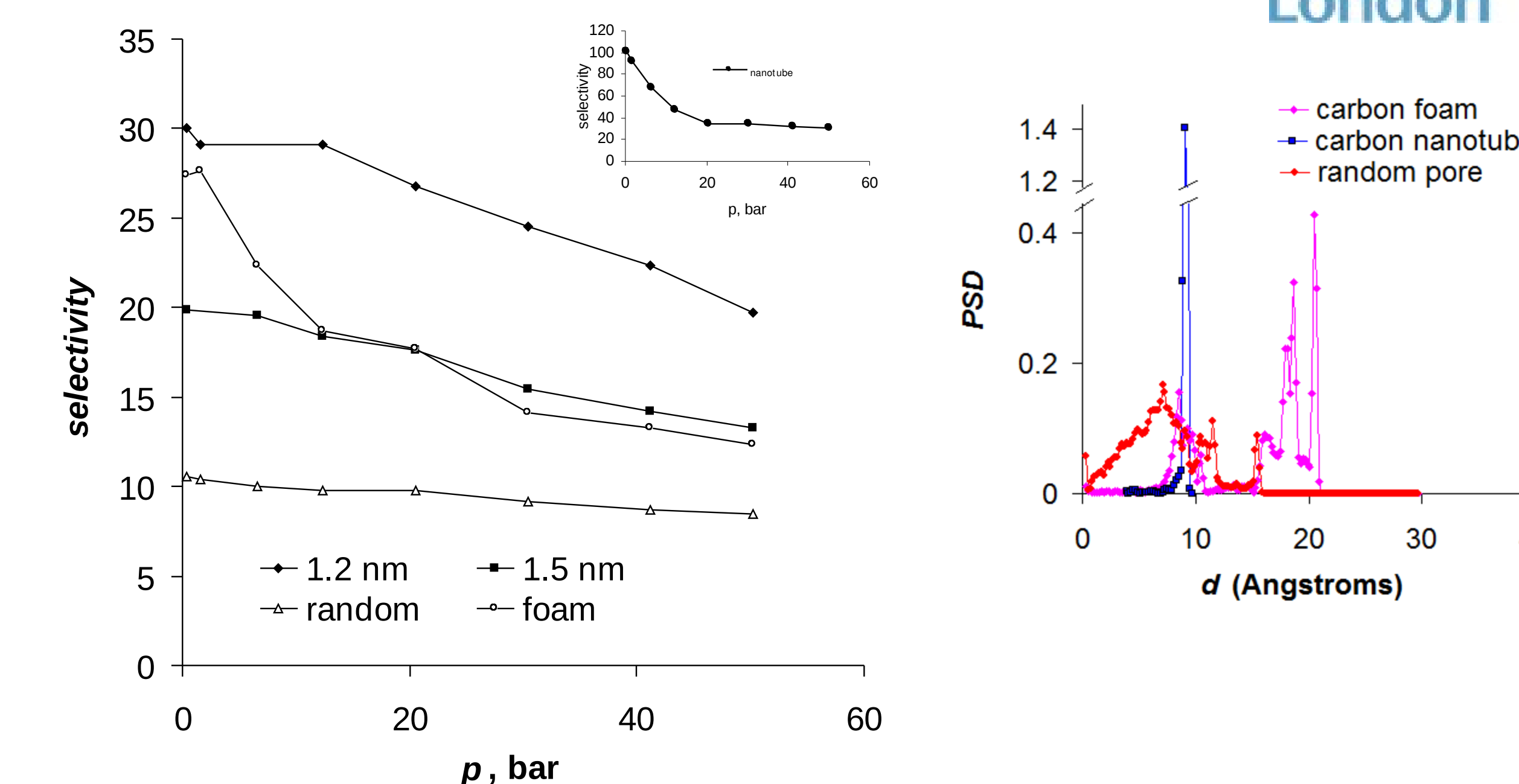


Fig 3: Effect of pore geometry on selectivity of methane at 298 K (the pore size distribution of the studied geometries determined using the geometrical methods^{3,4} is shown above (right))

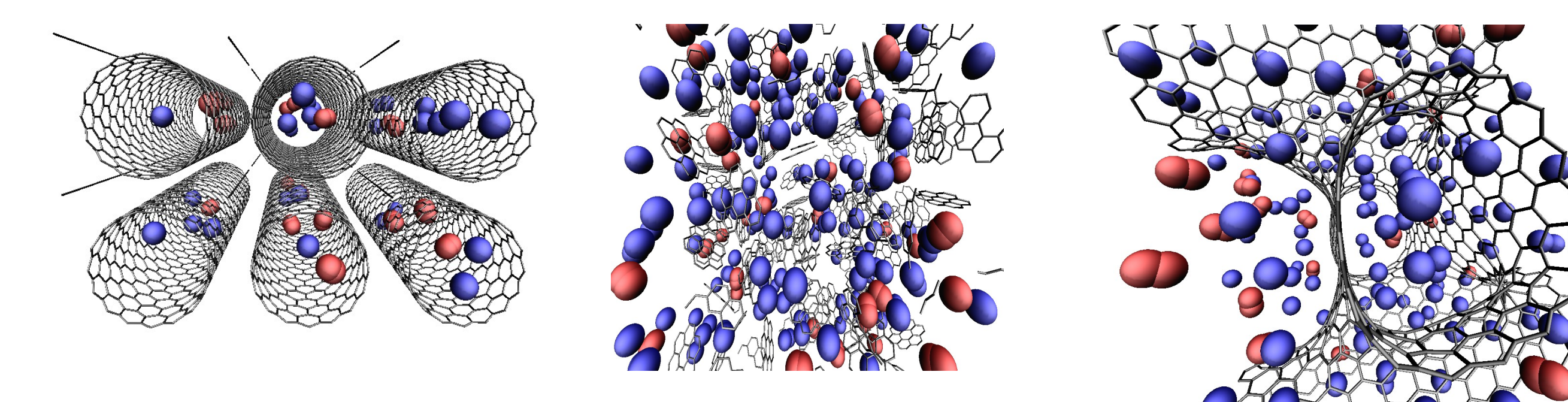


Fig 4: Snapshots showing the adsorption of CH₄ (blue) and H₂ (red) mixtures (from left to right) in nanotube, random pore and carbon foams at 50 bar and 298 K

5 Conclusions

The GCMC results shows that the pore structure and geometry have a significant effect on the selectivity of methane.

Irrespective of the carbon pore structure or geometry, the selectivity at 298K was affected by both energetic effects at low pressure and packing effects at higher pressures.

Despite the strong solid-fluid interactions, an array of nanotubes that have a closely packed structure have the highest selectivity, followed by carbon foams.

A model microporous carbon with slit-pore that can hold 1-2 layers of methane was found to be the optimum pore size for selective adsorption of methane over hydrogen molecules at 50 bar and 298 K.

The selectivity of the smaller pores was found to be influenced by entropy effects.

At the pressures and temperatures considered, the gas mixture behaves ideally in pores of width > 1.5 nm and the mixture adsorption and selectivity can be predicted from the single-component adsorption isotherms.

References

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Support from the Ministerio de Ciencia e Innovacion (Project PLE2009-0052) is acknowledged. KVK would like to thank Ministerio de Ciencia e Innovacion (Spain) for the Juan de la Cierva contract. The authors thank Prof. Boris.I. Yakobson, Rice University, for giving us the co-ordinates of carbon foam structure