

Preferential adsorption in ethane/CO₂ fluid mixtures confined within silica nanopores

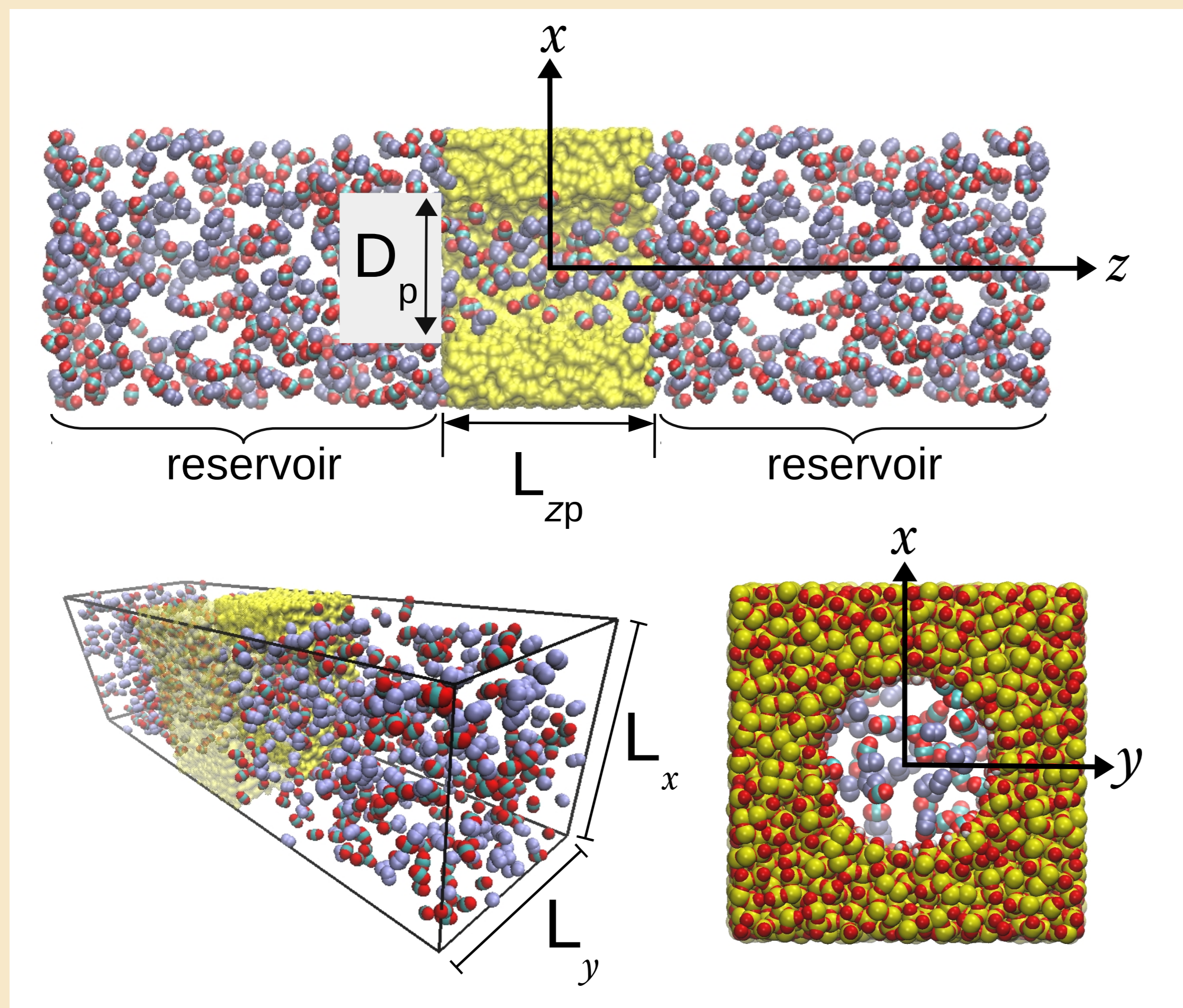
M. Dolores Elola & Javier Rodriguez

Departamento de Física de la Materia Condensada, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica (CAC-CNEA), Bs As



1. Introduction & Methodology

Structural and dynamical properties of fluid ethane confined within silica nanopores have been investigated by Molecular Dynamics simulations. The pure ethane phase and equimolar mixtures of ethane and CO₂ were considered; at densities in the range $\rho/\rho_{crit} = 0.05 - 2.18$.



- Molecular Dynamics simulations, times ~ 60 ns).
- Microcanonical Ensemble **NVE**, at $T \sim 320$ K.
- Inter-molecular interactions: Coulomb & Lennard-Jones; Intra-molecular interactions: stretching, bending & torsion.

2. Structural Properties: Local Densities

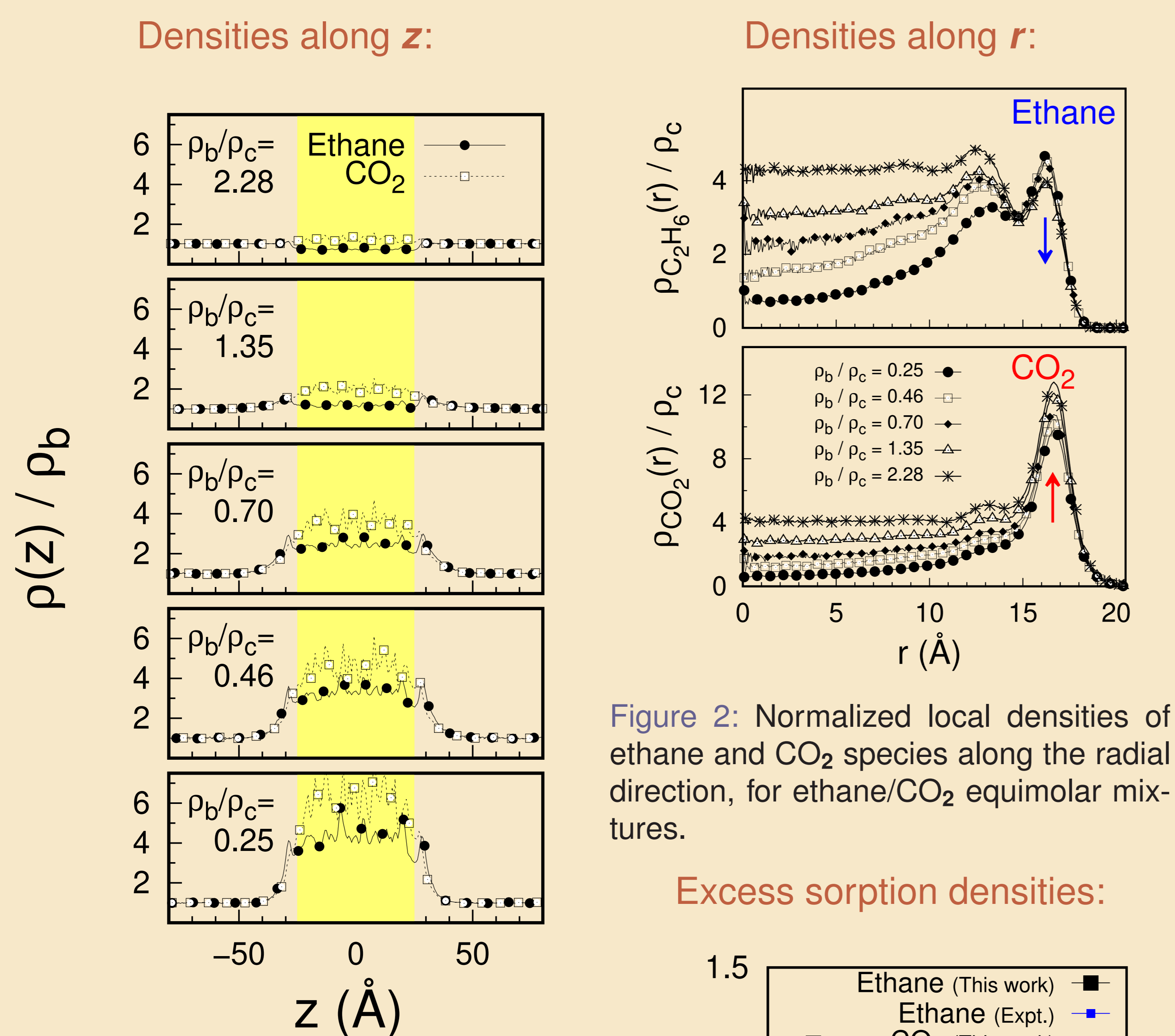


Figure 1: Normalized local densities along the axial z -axis for ethane/CO₂ equimolar mixtures.

Excess density:

Difference between the average density inside the pore and the bulk density,

$$\Delta\rho_{exc} = \langle\rho_{pore}\rangle - \rho_b$$

Density profiles reveal the formation of a dense adsorption layer, rich in CO₂.

Excess sorption densities:

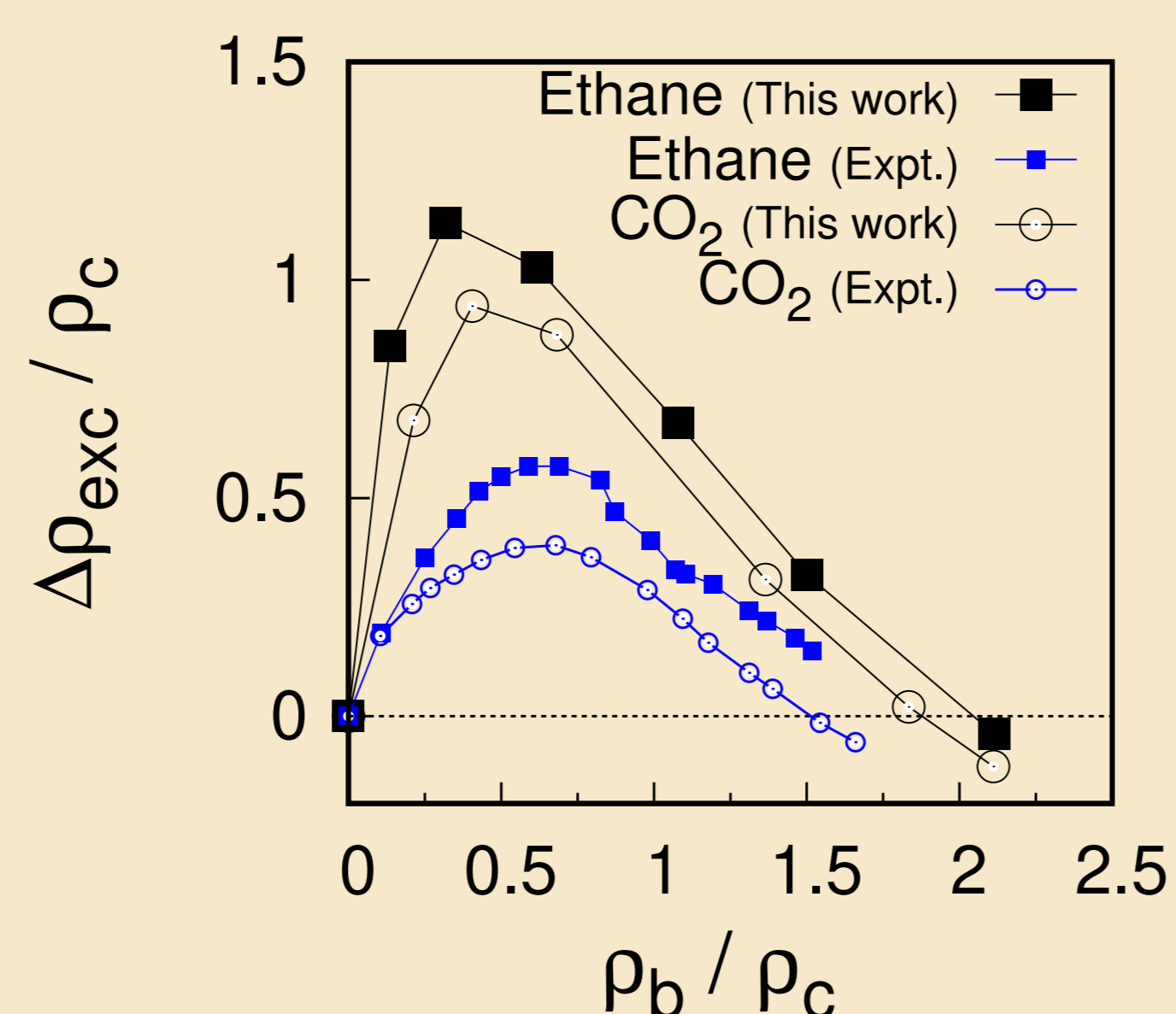


Figure 3: Excess densities of confined ethane and CO₂ in the pure fluids. Experimental data measured on 11.1 nm CPG-75 silica glass pores.

3. Structural Properties: Orientations

Orientation wrt the silica wall

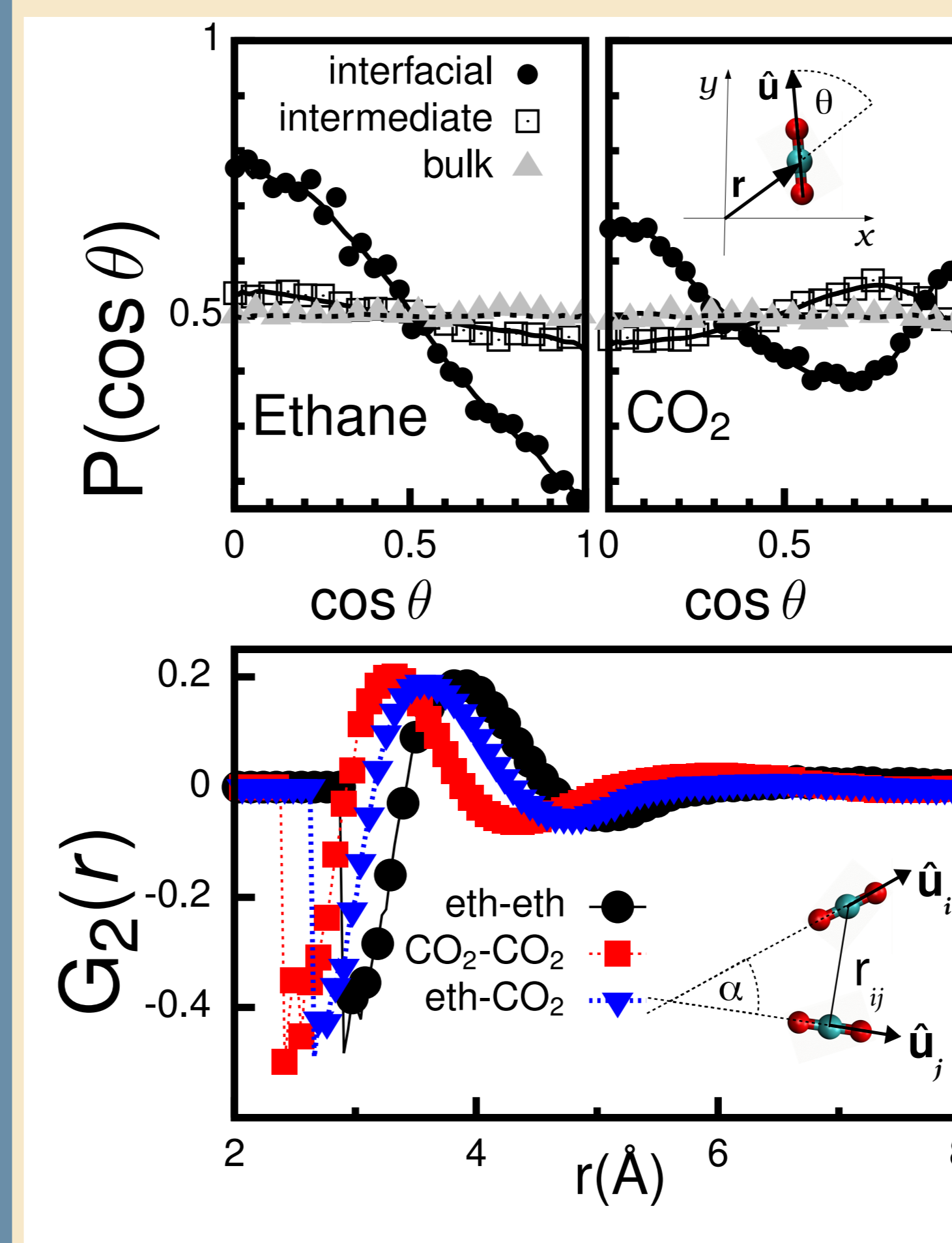


Figure 4: Top: Probability distribution $P(\cos\theta)$ for ethane and CO₂ confined species; bottom: Legendre polynomials of the intermolecular cosine angle vs. center-of-mass separation. Curves correspond to equimolar mixture with $\rho_b/\rho_c = 0.46$.

- Interfacial Ethane \rightarrow parallel to surface.
- Interfacial CO₂ \rightarrow bimodal distribution, parallel and perpendicular to surface. Due to directional hydrogen-bond like interactions $[O=C=O \cdots H-O-Si]$ with the silica walls
- Bulk region \rightarrow no preferential orientations.

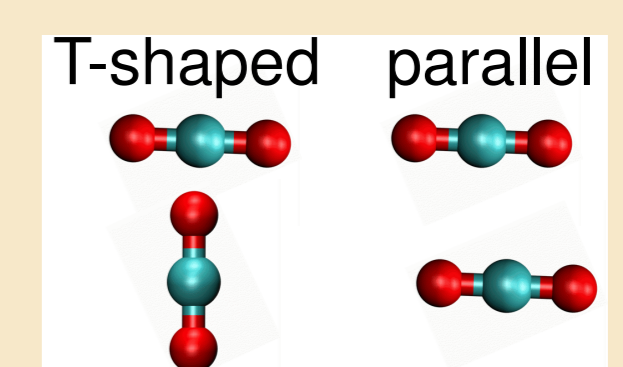
Orientalional function

$$G_2(r) = \langle P_2(\hat{u}_i \cdot \hat{u}_j) \delta(r_{ij} - r) \rangle,$$

where

$$P_2(x) = (3x^2 - 1)/2$$

is the 2nd-rank Legendre polynomial.



- $G_2 < 0$ at small $r \rightarrow$ T-shaped configurations;
- $G_2 \sim 0.2$ at $r \sim 3 - 4$ Å \rightarrow intermediate between T-shaped and parallel arrangements.

4. Dynamical Properties

Diffusion: Self-diffusion coefficients were computed from the classical Einstein relation for the mean squared displacements.

Table 1: Diffusion coefficients (in $10^{-4} \text{cm}^2 \text{s}^{-1}$).

P (bar)	pure Ethane		mixture 50% CO ₂			
	D_{eth}^{blk}	D_{eth}^{conf}	D_{eth}^{blk}	D_{eth}^{conf}	$D_{CO_2}^{blk}$	$D_{CO_2}^{conf}$
20	20.8	2.71	24.2	2.88	24.6	2.06
40	7.44	2.25	8.85	2.64	8.88	1.83
57	6.99	1.85	8.86	2.38	8.96	1.59
70	4.91	1.88	7.67	2.02	7.74	1.43
100	3.15	1.43	3.79	1.80	3.84	1.22
400	1.60	1.15	1.51	1.98	1.55	0.84

Local diffusion along r

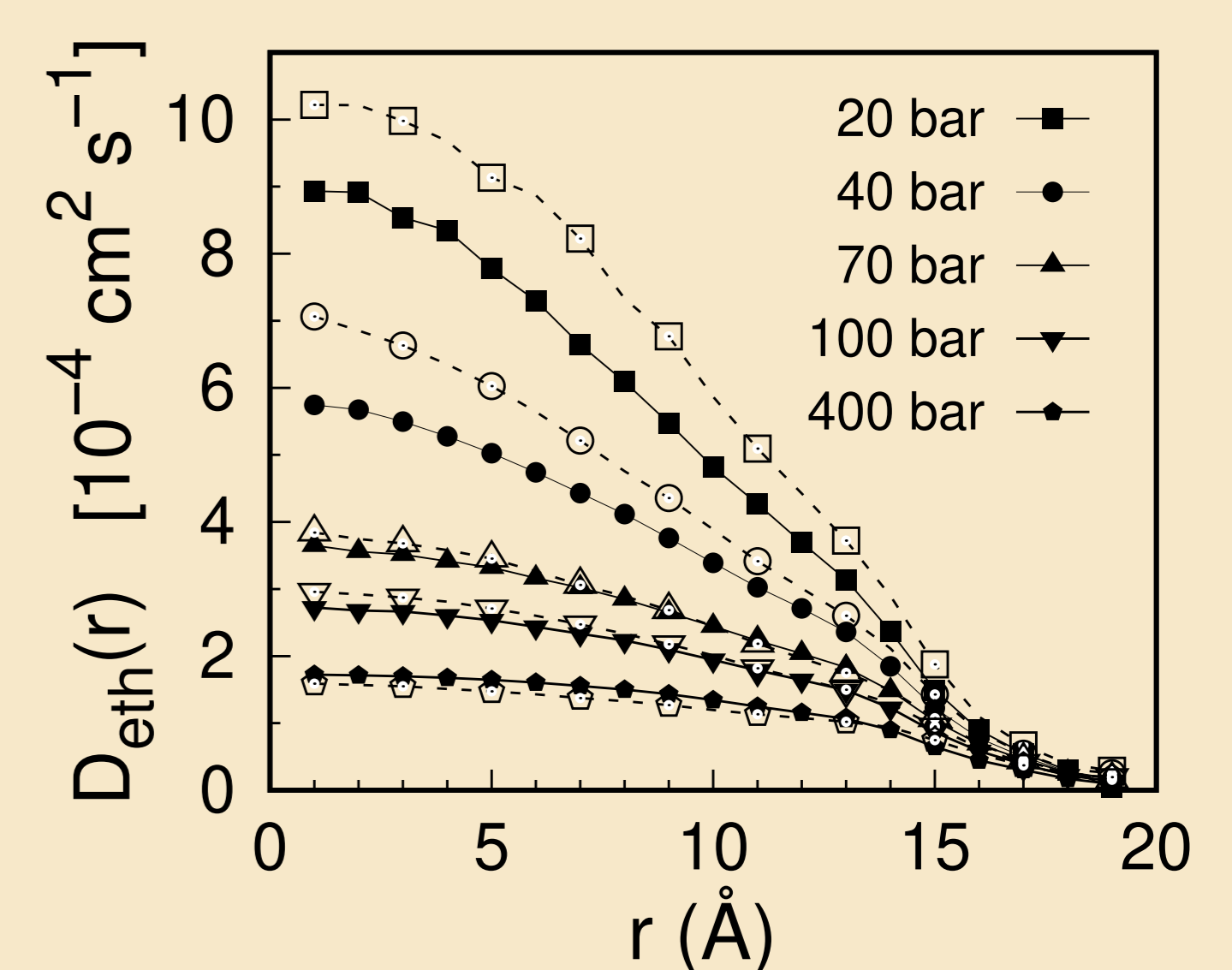


Figure 5: Local diffusion coefficients of confined ethane species. Filled and empty symbols correspond to pure ethane and equimolar mixture, respectively.

- Diffusion is *reduced* under confinement and increasing Pressure.
- Incorporation of CO₂ into the fluid *enhances* the diffusion of ethane species.
- Coexistence of fast and slow translational modes within the cavity.
- Orientational correlations of interfacial molecules decay more slowly than bulk-like ones; CO₂ correlations being the slowest.

5. Conclusions

Preferential adsorption of CO₂ over ethane within the adsorbed layer inside the pores led to significant increments in ethane mobility, due to displacements of interfacial ethane molecules towards more internal, bulk-like, locations. These effects were found to be more pronounced at low densities and under strong confinement.