

Supporting Information for:

Preferential Adsorption in Ethane/Carbon Dioxide Fluid Mixtures Confined within Silica Nanopores

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Local densities of confined Ethane along the z -axis:

Figure S1 shows the normalized density profiles of ethane confined within the smaller pores.

Density profiles of ethane species in units of g cm^{-3} are displayed in figure S2, for the pure-ethane systems. We notice that the absolute ethane density inside the cavity is very weakly sensitive to the external bulk density.

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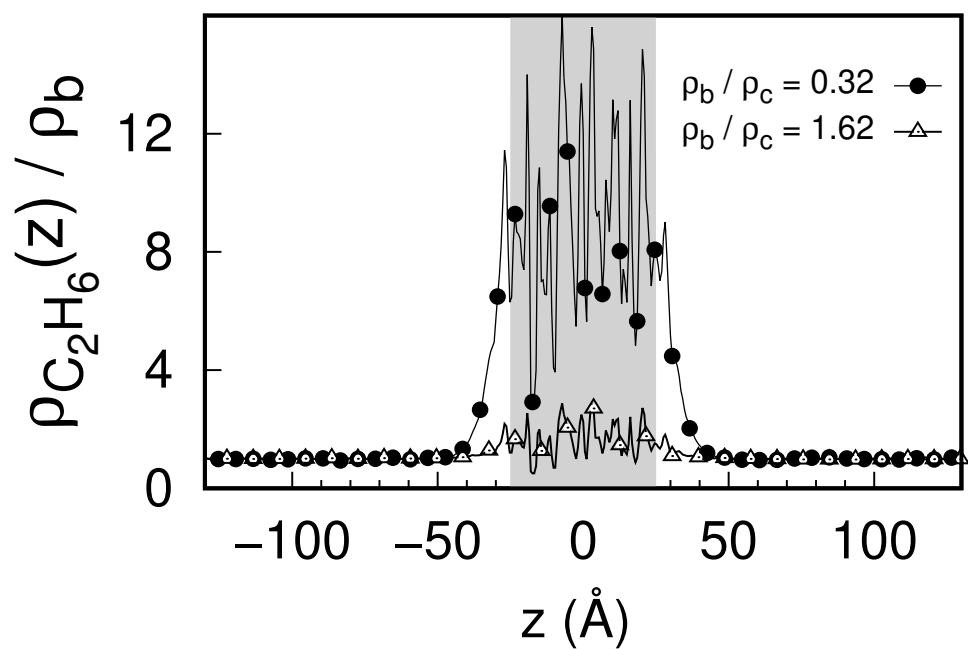


Figure S1: Local densities of ethane (normalized to ρ_b) along the axial z axis, for pure ethane confined within the smaller pore of 1 nm diameter. Densities have been computed within an axial cylinder of diameter 1 nm and length L_z . The dashed region indicates the location of the silica pore.

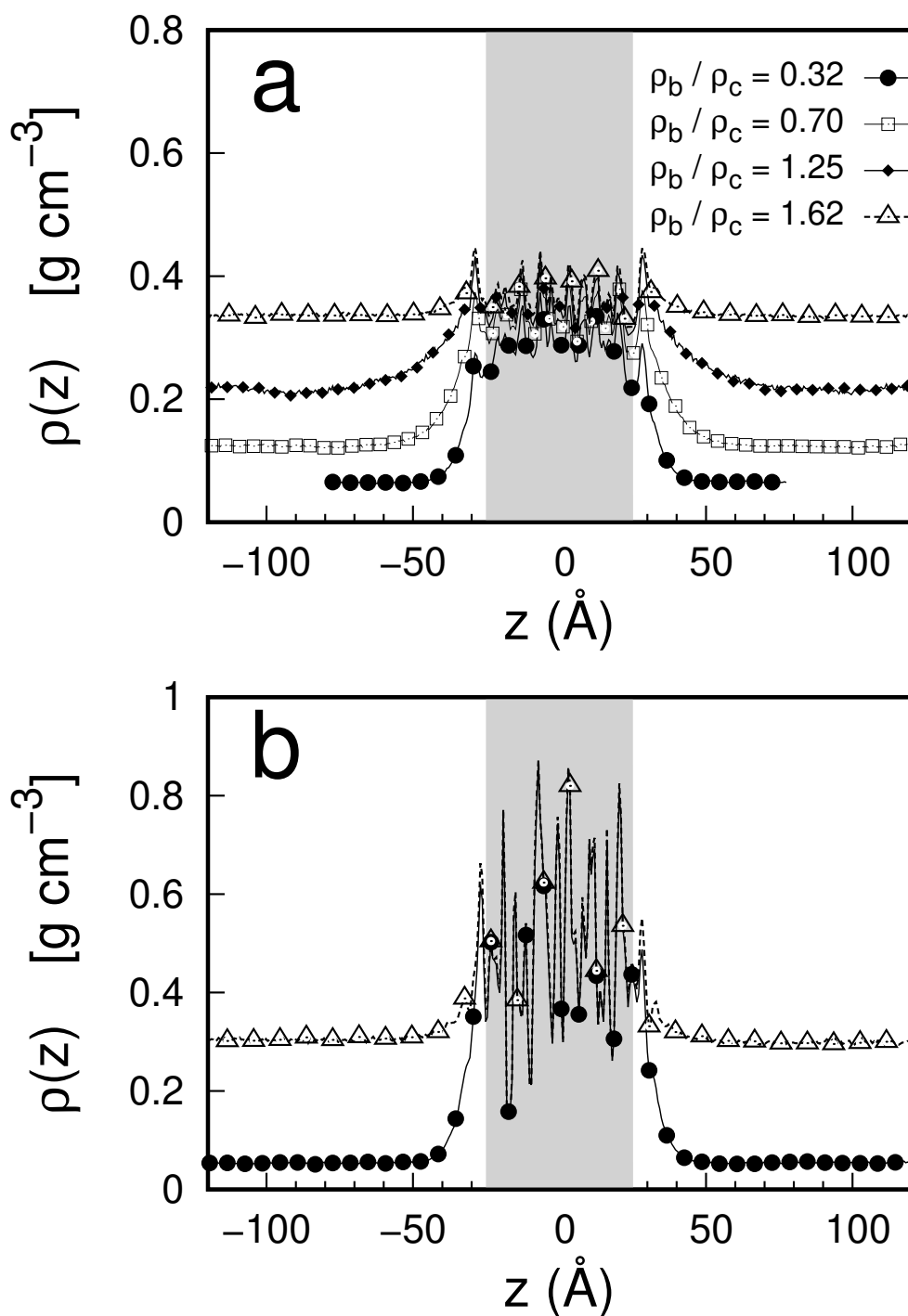


Figure S2: Local densities of ethane along the axial z axis, for pure ethane confined within (a) wider pore of diameter $D_p = 3.8$ nm, (b) small pore of diameter $D_p = 1$ nm. Densities are displayed in g cm^{-3} and have been computed within an axial cylinder of diameter D_p and length L_z . The dashed region indicates the location of the silica pore.

Orientalional correlations in hydrophobic and hydrophilic pores:

The features of the orientational correlations close to the pore walls were evaluated from the distribution function $P(\cos \theta) = \langle \delta(|\cos \theta_i| - \cos \theta) \rangle$, where $\cos \theta_i$ is shown in the inset scheme on fig S3a. The curves displayed in fig S3 show a comparison between the distribution functions $P(\cos \theta)$ for pure ethane and CO_2 and a mixture of the two, confined within hydrophobic and hydrophilic pores. Only the interfacial molecules were taken into account for the calculation. The

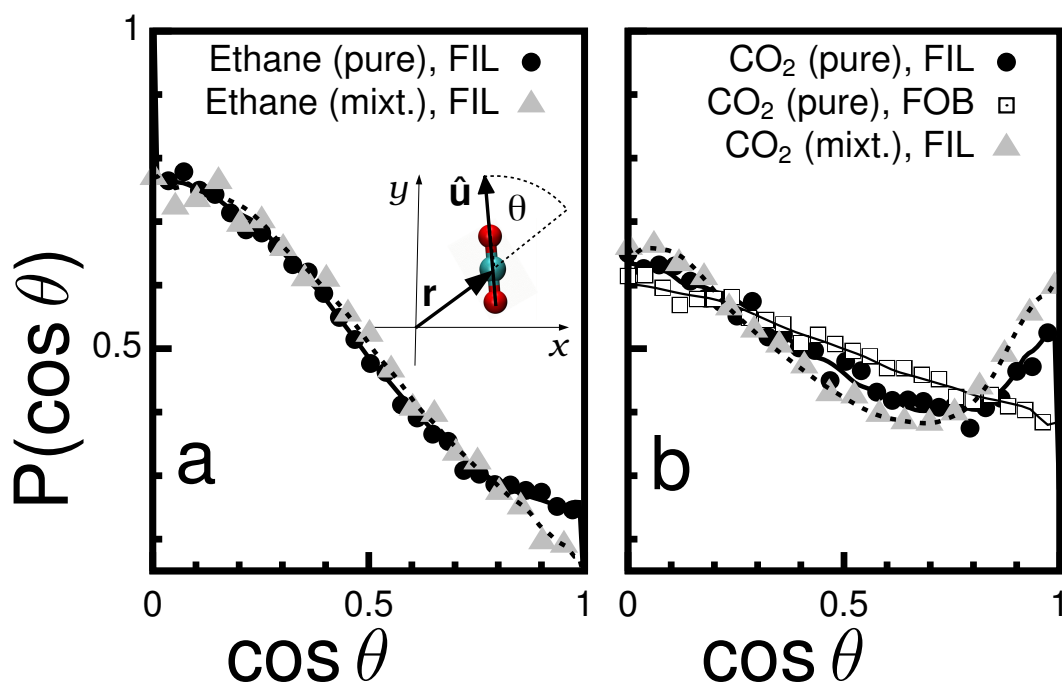


Figure S3: Probability distribution $P(\cos \theta)$ as a function of the angle between the molecular axis and the center-of-mass vector, for confined (a) ethane and (b) CO_2 molecules located at the interfacial layer, in hydrophobic (FOB) and hydrophilic (FIL) silica pores.

curves associated to CO_2 species, on fig S3b, reveal that it is the change in the chemistry of the pore walls that drives changes in the orientations of the molecules near the silica surface (and not the presence of ethane molecules). Actually, the shape of the curve for pure CO_2 confined in a hydrophobic pore is similar to those of ethane, with a single maximum at $\cos \theta = 0$, indicating the prevalence of parallel arrangements of the molecules near the walls. However, the curve of pure CO_2 in hydrophilic pores exhibits already a bimodal distribution with maxima at $\cos \theta = 0$ and $\cos \theta = 1$, indicating the existence of parallel and perpendicular orientations of the molecules with

respect to the silica surface.

The effect of the presence of SiOH groups at the pore wall has been qualitatively evaluated by inspecting a few snapshots of the system. We have identified the SiOH-CO₂ pairs that are forming a hydrogen bond (HB), based on a usual geometric criterion ($d(\text{O} \cdots \text{H}) \leq 3.5 \text{ \AA}$ and $\angle[\text{O} \cdots \text{H} - \text{O}] \geq 120^\circ$), and noticed that the CO₂ molecules involved in HBs have perpendicular orientations. We also found a minor fraction of interfacial CO₂ molecules that are in perpendicular arrangements but are not explicitly forming HBs. A typical snapshot illustrating these configurations is provided in fig S4a.

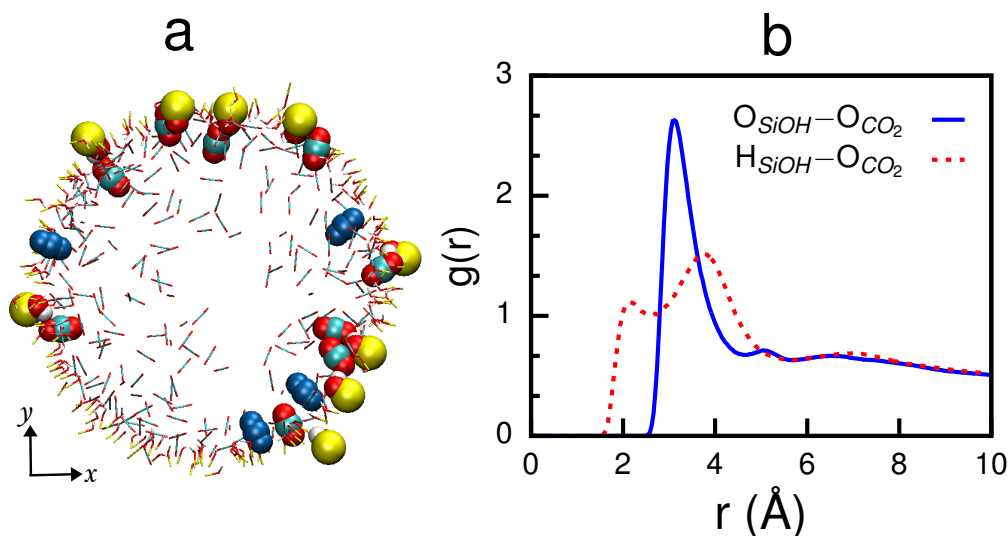


Figure S4: Axial view of a typical snapshot of the Mix-57 system. Only the CO₂ confined species are shown in licorice style; the CO₂ and SiOH groups forming hydrogen bonds are represented in spacefill style. The interfacial CO₂ molecules with perpendicular orientations, but not directly H-bonded to SiOH, are displayed in blue. Panel (b) shows the pair correlation functions of O-O and O-H pairs between SiOH and CO₂ molecules.

We have also included in fig S4b the results of pair correlation functions for O-O and H-O pairs between SiOH and CO₂ molecules, where an intense O-O maximum can be observed at $r = 3 \text{ \AA}$, flanked by two lower peaks arising from H-O pairs, at $r = 2 \text{ \AA}$ and $3.7 \text{ \AA}$. This arrangement is consistent with H-bonding formation between SiOH groups and interfacial CO₂ molecules. As can be observed, due to the lack of spherical symmetry in these systems, a gradual decrease of the asymptotic long- r behavior is expected.

Local Diffusion:

Based on the formalism of Berne and co-workers,¹ we computed the modified mean square displacements in the direction parallel to the pore walls, $\mathcal{R}_z^2(r;t)/P(t)$, along with the survival probabilities, $P(t)$. These functions are displayed for ethane species in fig S5, for two typical cases of low and high pressure: Eth-40 and Eth-400 systems. MSDs and the survival probabilities have been evaluated within cylindrical concentric shells of width 3 Å.

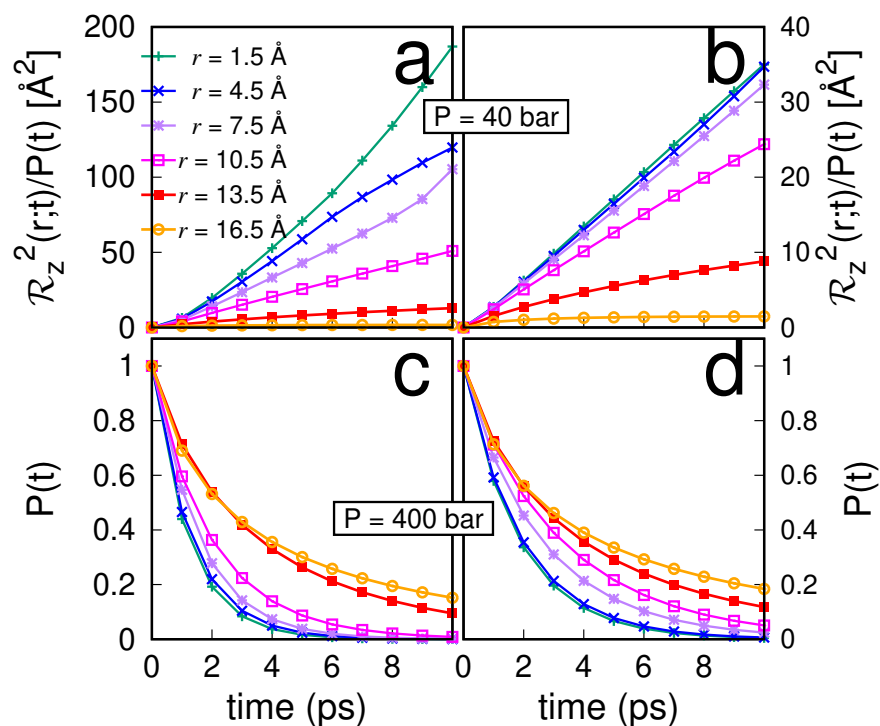


Figure S5: Mean square displacements of the generalized Einstein formalism, $\mathcal{R}_z^2(r;t)/P(t)$, in the direction parallel to the pore walls, computed within cylindrical concentric shells of width $\Delta r = 3$ Å, centered at r , as indicated, for (a) Eth-40 and (b) Eth-400 systems. Bottom panels show the corresponding survival functions, $P(t)$.

References

- (1) Liu, P.; Harder, E.; Berne, B. J. On the calculation of diffusion coefficients in confined fluids and interfaces with an application to the liquid-vapor interface of water. *J. Phys. Chem. B* **2004**, *108*, 6595–6602.