**CO₂ packing polymorphism under confinement in cylindrical nanopores:**  
**Supplementary Information**

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*Collective Variables (CVs).* In this work, we perform WTMetaD with different \(\lambda\) order parameters, as CVs; in particular we test \(\lambda_I\), which we tuned in our previous work\(^\text{[5]}\) and \(\lambda_B\), based on structure B found in the present analysis. As mention in the main manuscript, we refer to Salvalaglio et al.\(^\text{[2, 3]}\) and Giberti et al.\(^\text{[4]}\) for the formulation of this parameter. Nonetheless, we present hereafter further details.

The order parameter \(\lambda\) represents the degree of crystallinity of a system based on the local environment around each molecule; indeed, \(\lambda\) is the sum of each local contribution, \(\Gamma_i\) (Eq (1)), which spans 0 to 1, as we will describe in the following.

\[
\lambda = \frac{1}{N} \sum_{i=1}^{N} \Gamma_i
\]

Dividing by the total number of molecules in the system, \(N\), ensures that \(\lambda\) similarly to a molecular fraction, expresses the portion of particles organized alike a defined crystal structure, ranging from 0 to 1.

The core of this formulation is thus \(\Gamma_i\), which accounts for the local density, \(\rho_i\), and orientation with respect to neighbours, \(\theta_{ij}\), of each \(i\)th molecule (Eq (2)).

\[
\Gamma_i = \frac{\rho_i}{n_i} \sum_{j=1}^{N} f_{ij} \Theta_{ij}
\]

The contributions to \(\Gamma_i\) are based on tunable switching functions to have continuous and differentiable CVs. In particular, the local density, \(\rho_i\), is expressed as (Eq (3)):

\[
\rho_i = \frac{1}{1 + e^{-b(n_i - n_{\text{cut}})}}
\]

where \(b\) tunes the slope of the switching function, \(n_i\) is the coordination number, and \(n_{\text{cut}}\) a well-defined cut-off so that for \(n_i > n_{\text{cut}}\) the molecule is considered crystalline.

The coordination number \(n_i\) is expressed as (Eq (4)):

\[
n_i = \sum_{j=1}^{N} f_{ij} \quad (j \neq i)
\]

where:

\[
f_{ij} = \frac{1}{1 + e^{a(r_{\text{cut}} - r_{ij})}}
\]

where \(a\) tunes the slope, \(r_{ij}\) is the distance between the \(i\)th and the \(j\)th molecules, and \(r_{\text{cut}}\) is the cut-off that defines the first coordination shell within which the local environment is studied.

The other feature considered is the orientation between neighbouring molecules, i.e. the polar angle \(\theta_{ij}\) between the neighbouring \(i\)th and \(j\)th molecules. As mention in the main manuscript, the angle distribution of molecules within the first coordination shell is a fingerprint of each crystal structure, which displays peaks corresponding to the characteristic orientations \(\theta_k\); \(\theta_{ij}\) in a crystal fluctuates around these peaks according to a Gaussian distribution (with width \(\sigma_k\)). \(\Theta_{ij}\) accounts for this behaviour (Eq (5)) and it is weighted by \(f_{ij}\) (Eq (6)) to consider only neighbouring particles.

Overall, if the local environment around the \(i\)th molecule is the one of the crystal structure it is tuned accordingly to, in terms of density and orientation, \(\Gamma_i\) will tend to 1.

In Table 1 we report the values for the tuning of \(\lambda_I\) and \(\lambda_B\).

**TABLE I.** Tuning of the \(\lambda\)-order parameters. The table reports \(\theta_1\), its supplementary \(\theta_2\), the associated width of the Gaussian \(\sigma\), which for symmetry reasons is the same for both angles. The cut-off values for the number of neighbours and the coordination shell are presented as well. The characteristic angles selected are the ones of bulk phase I for \(\lambda_I\) and confined structure B for \(\lambda_B\), so that the first expresses the fraction of molecules organised as bulk phase I, while the latter as structure B.

<table>
<thead>
<tr>
<th>(\theta_1) [°]</th>
<th>(\theta_2) [°]</th>
<th>(\sigma) [°]</th>
<th>(n_{\text{cut}}) [-]</th>
<th>(r_{\text{cut}}) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_I)</td>
<td>(\lambda_B)</td>
<td>(\lambda_I)</td>
<td>(\lambda_B)</td>
<td></td>
</tr>
<tr>
<td>70.47</td>
<td>108.86</td>
<td>14.32</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>46.18</td>
<td>133.82</td>
<td>5.21</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

WTMetaD set-up. Well-Tempered Metadynamics simulations are performed biasing either \(\lambda_I\) or \(\lambda_B\). A typical simulation has initial Gaussian height equal to 4 kJ/mol, i.e. \(\sim 1.5\) kT; the width of such Gaussian depends instead on the \(r^2\)-\(\rho_{CO_2}\) conditions, and spans from

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ideal random distribution of relative orientations. All possible relative orientations of two unit vectors in three dimensional space can be mapped in spherical coordinates as a function of the polar angle $\theta$ and the azimuthal angle $\phi$. Randomly oriented molecules are characterised by a flat probability distribution across all possible orientations. The homogeneous probability density on the surface of a sphere of unit radius has the constant value $P_{\text{rand}}(\theta, \phi) = 1/4\pi$, which satisfies the normalization condition:

$$\int_0^\pi \int_0^{2\pi} \frac{1}{4\pi} \sin \theta d\theta d\phi = 1 \quad (7)$$

The angle used to map relative orientation between two neighbouring molecules in this work corresponds to the polar angle $\theta$. The probability in $\theta$ associated with a random arrangement in spherical coordinates can thus be obtained by integrating out $\phi$ as follows:

$$P_{\text{ref}}(\theta) = \int_0^{2\pi} \frac{1}{4\pi} \sin \theta d\theta = \frac{1}{2} \sin \theta \quad (8)$$

The probability density in $\theta$, in this work used as a fingerprint of the molecular arrangement is then obtained by differentiating $P_{\text{ref}}(\theta)$ with respect to $\theta$:

$$p_{\text{ref}}(\theta) = \frac{dP_{\text{ref}}(\theta)}{d\theta} = \frac{1}{2} \sin \theta \quad (9)$$

One CO$_2$ molecule. Initially, we perform standard MD runs with only one particle confined in differently sized pores ($d_{\text{pore}} = 1, 2, 5, 10$ nm, $l_z = 10$ nm). These simulations last for about 95, 138, 125 and 30 ns, respectively and the potential of the wall is set to the reference $\sigma_{\text{wall}} = 0.34$ nm; the initial position of CO$_2$ is random, but clearly detached from the confinement barrier. This analysis aims at giving an insight into the sole effect of the wall on the motion of a particle when the interaction with other CO$_2$ is absent.

Figure 1 shows that the single molecule tends to adsorb on the pore, positioning at a distance from the wall that is slightly smaller than the location of the Lennard-Jones well, i.e. $\sigma_{m,C-\text{wall}} (0.345$ nm). Moreover, all the positions along the pore axis are equally likely, and thus the height does not play a major role in the outcome. The noise in the probability density along $z$ (Figure 1(a)) is probably due to limited sampling of the area, related to the computational time allowed.

These simulations confirm the strong impact that the pore has on confined CO$_2$ in the radial direction, in particular the tendency of adsorbing them.

Analysis of the radial distribution of molecules in the pore. We present in Figure 2 the analysis of unbiased MD trajectories, focusing on the position of CO$_2$ molecule in the radial direction of the pore, for two examples not reported in section 3, namely $r' = 6.847$ (a) and 0.961 (b). In these two cases as well, it is possible to notice that if the pore allows the formation of more layers of molecules or a bulk-like filling, the height of the first peak corresponding to the adsorbed layer decreases with growing density (a); on the other hand, if the pore has no space to accommodate more layers, the height of the peaks increases with $\rho_{\text{CO}_2}$.

$\text{WTMetaD trajectories.}$ We here present two representative examples of explorative WTMetaD simulations employing $\lambda_1$ as CV: one in case of liquid conditions (Figure 3 (a), at $r' = 2.075 - \rho_{\text{CO}_2} = 8.15$ molecules/nm$^3$), and the other for ordered structures (Figure 3 (b-c), at $r' = 2.075 - \rho_{\text{CO}_2} = 12.73$ molecules/nm$^3$). As discussed in section 3, WTMetaD did not enhance the sampling of either ordering phenomena in $r'-\rho_{\text{CO}_2}$ conditions identified as liquid from MD or melting events for organized structures; however, some interesting results can be observed. In the case of liquid state, biasing $\lambda_1$ leads to the creation of an unstable droplet with higher density than the nominal one, that migrates along the $z$-axis, as shown in Figure 3 (a). On the other hand, in WTMetaD simulations in ordered areas of the $r'-\rho_{\text{CO}_2}$ phase diagram, despite not observing melting, many transitions between ordered structures take place, as reported in Figure 3 (b-c). In these explicative plots, we present a B-C conversion, where B is characterised by low value of $\lambda_1$ and a 2-peak angle distribution, while C has higher $\lambda_1$ and a sharp peak on 90$^\circ$ in its angle distribution. Interestingly, it is also possible to notice that during a transition, $\lambda_1$ changes gradually: indeed, as we highlighted in the results, the interconversion between ordered structures generally takes place by progressive rearrangement of unit cells along the $z$-axis.

Unstable ordered structures. Thanks to both MD and WTMetaD, we identify four stable ordered structures. However, WTMetaD simulations explore a bigger number of configurations that instead are not stable in unbiased simulations, and reorganise in one of the main four. Two significant examples are reported in Figure 3. The first of these two structures (Figure 3(a-c)) has CO$_2$ molecules parallel to each other, aligned along the $z$-axis, and the density is the same throughout the pore length; the second arrangement presented in Figure 4(d-f) has well-defined characteristic angles, similar to bulk phase I, as well as a more compact packing than the other phases; such compact packing is achieved by locally increasing the molecular density, which results in areas of the pore with $\rho_{\text{CO}_2}$ below the nominal value.

REFERENCES

FIG. 1. Probability density of the location of a single CO$_2$ molecule inside pores with $\sigma_{\text{wall}} = 0.34$ nm and diameter 1 nm (a-c), 2 nm (d), 5 nm (e) and 10 nm (f). In (a) and (b) we report the probability density as a function of only the location along the molecular axis, $z$ (a), and of only the radial position, $r$ (b), to better visualise the different role they play: negligible $z$, while determinant $r$. In all graphs, the radial position axis ranges from zero, i.e. the pore axis, to the value of the pore radius, reported in Å.

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FIG. 2. Probability density profiles of the position of CO$_2$ molecules in the radial direction of the pore, for the range of densities investigated at different values of $r'$, namely 6.847 in (a), and 0.961 in (b). Along the pore radius, zero corresponds to the cylinder axis, while the maximum value reported to the radius of the pore.

FIG. 3. Explorative WTMetaD biasing $\lambda_I$. (a) Axial density profile over time for the creation of a droplet at $r' = 2.075 - \rho_{CO_2} = 8.15$ molecules/nm$^3$. (b-c) Time-evolution of the CV $\lambda_I$ in (b) and of the characteristic angles over the first 20 ns in (c) at $r' = 0.484 - \rho_{CO_2} = 12.73$ molecules/nm$^3$. The time scale for the orientation distribution in (c) is highlighted in (b) by dark blue to light blue shades on the time axis.
FIG. 4. Examples of unstable ordered structures emerging from WTMetaD with $\lambda_1$ at $r' = 0.961 - \rho_{\text{CO}_2} = 9.87$ molecules/nm$^3$. In particular, (a) to (c) report snapshots, density profile in the pore over WTMetaD time (shading from black to red for growing time), and angle distribution for the first arrangement presented; (d) to (f), instead, present the same analysis for the second one.