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 λ order parameters, as CVs; in particular we test λ_I , which we tuned in our previous work¹ and λ_B , based on structure B found in the present analysis. As mention in the main manuscript, we refer to Salvalaglio et al.^{2–4} and Giberti et al.⁵ for the formulation of this parameter. Nonetheless, we present hereafter further details.

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

$$\lambda = \frac{1}{N} \sum_{i=1}^{N} \Gamma_i \tag{1}$$

Dividing by the total number of molecules in the system, N, ensures that λ , 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 Γ_i , which accounts for the local density, ρ_i , and orientation with respect to neighbours, θ_{ij} , of each i-th molecule (Eq (2)).

$$\Gamma_i = \frac{\rho_i}{n_i} \sum_{j=1}^N f_{ij} \Theta_{ij} \tag{2}$$

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

$$\rho_i = \frac{1}{1 + e^{-b(n_i - n_{cut})}} \tag{3}$$

where b tunes the slope of the switching function, n_i is the coordination number, and n_{cut} a well-defined *cut-off* so that for $n_i > n_{cut}$ the molecule is considered crystallike.

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

$$n_i = \sum_{\substack{j=1\\j\neq i}}^N f_{ij} \tag{4}$$

where:

$$f_{ij} = \frac{1}{1 + e^{a(r_{cut} - r_i)}} \tag{5}$$

where a tunes the slope, r_{ij} is the distance between the i-th and the j-th molecules, and r_{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 θ_{ij} between the neighbouring i-th and the j-th molecules. As mentioned 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 θ_k ; θ_{ij} in a crystal fluctuates around these peaks according to a Gaussian distribution (with width σ_k). Θ_{ij} accounts for this behaviour (Eq (6)) and it is weighted by f_{ij} (Eq (5)) to consider only neighbouring particles.

$$\Theta_{ij} = \sum_{k=1}^{k_{max}} e^{-\frac{(\theta_{ij} - \theta_k)^2}{2\sigma_k^2}} \tag{6}$$

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, Γ_i will tend to 1.

In Table I we report the values for the tuning of λ_I and λ_B .

TABLE I. Tuning of the λ -order parameters. The table reports θ_1 , its supplementary θ_2 , the associated width of the Gaussian σ , 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 λ_I and confined structure B for λ_B , so that the first expresses the fraction of molecules organised as bulk phase I, while the latter as structure B.

	θ_1 [°]	$\theta_2 \ [^\circ]$	$\sigma_1 = \sigma_2 \ [^\circ]$	n _{cut}	$[-] r_{cut} [Å]$
λ_I	70.47	108.86	14.32	5	4
λ_B	46.18	133.82	5.21	3	4

WTMetaD set-up. Well-Tempered Metadynamics simulations are performed biasing either λ_I or λ_B . A typical simulation has initial Gaussian height equal to 4 kJ/mol, i.e. ~ 1.5 kT; the width of such Gaussian depends instead on the r'- ρ_{CO_2} conditions, and spans from

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 3×10^{-4} to 0.6. A biasfactor of 20 is generally employed, but some conditions were explored also with a higher value of this parameter (50).

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 θ and the azimuthal angle ϕ . 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 $p_{rand}(\theta, \phi) = 1/4\pi$, which satisfies the normalization condition:

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \sin\theta d\theta = 1 \tag{7}$$

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

$$P_{ref}(\theta) = \int \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \sin \theta d\theta = \int \frac{1}{2} \sin \theta d\theta \qquad (8)$$

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

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

One CO_2 molecule. Initially, we perform standard MD runs with only one particle confined in differently sized pores ($d_{pore} = 1, 2, 5, 10 \text{ nm}, l_z = 10 \text{ nm}$). These simulations last for about 95, 138, 125 and 30 ns, respectively and the potential of the wall is set to the reference $\sigma_{wall} = 0.34 \text{ nm}$; the initial position of CO_2 is random, but clearly detached from the confinement barrier. This analysis aims at giving an insight into the solely 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. $\sigma_{m,C-wall}$ (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 ρ_{CO_2} .

WTMetaD trajectories. We hereafter present two representative examples of explorative WTMetaD simulations employing λ_I as CV: one in case of liquid conditions (Figure 3 (a), at $r' = 2.075 - \rho_{CO_2} =$ 8.15 molecules/nm³), and the other for ordered structures (Figure 3 (b-c), at $r' = 2.075 - \rho_{CO_2} = 12.73$ molecules/nm³). As discussed in section 3, WTMetaD did not enhance the sampling of either ordering phenomena in $r' - \rho_{CO_2}$ 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 λ_I 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 $r' - \rho_{CO_2}$ 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 λ_I and a 2-peak angle distribution, while C has higher λ_I and a sharp peak on 90° in its angle distribution. Interestingly, it is also possible to notice that during a transition, λ_I 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 4. The first of these two structures (Figure 4 (a-c)) has CO₂ 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 ρ_{CO_2} below the nominal value.

REFERENCES

- ¹Ilaria Gimondi and Matteo Salvalaglio. Co2 packing polymorphism under pressure: mechanism and thermodynamics of the i-iii polymorphic transition. J. Chem. Phys., 2017.
- ²Matteo Salvalaglio, Thomas Vetter, Federico Giberti, Marco Mazzotti, and Michele Parrinello. Uncovering Molecular Details of Urea Crystal Growth in the Presence of Additives. J. Ame. Chem. Soc., 134(41):17221–17233, oct 2012.



FIG. 1. Probability density of the location of a single CO₂ molecule inside pores with $\sigma_{wall} = 0.34$ 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.

 ³Matteo Salvalaglio, Thomas Vetter, Marco Mazzotti, and Michele Parrinello. Controlling and Predicting Crystal Shapes: The Case of Urea. Angew. Chem. Int. Ed., 52(50):13369–13372, dec 2013.
⁴Matteo Salvalaglio, Claudio Perego, Federico Giberti, Marco Mazzotti, and Michele Parrinello. Molecular-dynamics simulations of urea nucleation from aqueous solution. *Proc. Natl. Acad. Sci.*, 112(1):E6–E14, jan 2015.

⁵Federico Giberti, Matteo Salvalaglio, Marco Mazzotti, and Michele Parrinello. Insight into the nucleation of urea crystals from the melt. *Chem. Eng. Sci.*, 121:51–59, jan 2015.



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 λ_I . (a) Axial density profile over time for the creation of a droplet at $r' = 2.075 - \rho_{CO_2}$ = 8.15 molecules/nm³. (b-c) Time-evolution of the CV λ_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/nm³. 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 λ_I at $r' = 0.961 - \rho_{CO_2} = 9.87$ molecules/nm³. 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.