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On the Peculiar Molecular Shape and Size Dependence of the Dynamics of Fluids Confined in a Small-Pore Metal-Organic Framework.

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Abstract

Force field based-Molecular dynamics simulations were deployed to systematically explore the dynamics of confined molecules of different shapes and sizes, i.e. linear (CO₂ and N₂) and spherical (CH₄) fluids, in a model small pore system, i.e. the Metal-Organic Framework SIFSIX-2-Cu-i. These computations unveil an unprecedented molecular symmetry dependence of the translational and rotational dynamics of fluids confined in channel-like nanoporous materials. In particular this peculiar behaviour is reflected by the extremely slow decay of the Legendre reorientational correlation functions of even-parity order for the linear fluids which is associated to jump-like orientation flips, while the spherical fluid shows a very fast decay taking place in a sub-picosecond time scale. Such a fundamental understanding is relevant to diverse disciplines such as in chemistry, physics, biology and materials science where diatomic or polyatomic molecules of different shapes/sizes diffuse through nanopores.

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TOC FIGURE

The scientific community has intensified its efforts over the last decades to develop novel porous adsorbents able to address societal issues including air purification, wastewater treatment, natural gas upgrading, etc.¹⁻³. Among them, metal-organic frameworks (MOFs) appear as a promising family of custom-designed adsorbents able to efficiently capture strategic gases of utmost importance in diverse energy and environment-related applications.^{4,5} The nature and strength of interactions between the internal surfaces of such nanoporous materials and the guest molecules play the predominant role in the capture/storage processes. These interactions can be tuned by changing the chemical features and both pore dimension and shape of the MOFs to modulate the thermodynamic and dynamic behaviors of the confined fluids and hence the performances of the nanoporous materials.⁵ From a more fundamental perspective, we have reported in the past that controlling the MOF/fluid interactions leads to intriguing dynamic properties such as the super-diffusivity of hydrogen in a 1D-type channel-like MOF.⁶ Moreover, when the pore sizes of the nanoporous material approach the dimensions of the molecules, their transport and dynamic properties are expected to be drastically altered in comparison with their bulk properties.⁷⁻¹⁰ Although the diffusion of fluid molecules in MOFs is nowadays relatively well-documented¹¹, only rare studies have been reported in ultra-small pore MOFs with pore aperture sizes below 5-7 Å. Interestingly, we revealed an anomalous single-file diffusion behavior of carbon dioxide in a 1D-type channel like MOF¹² with a pore size (4-5 Å) similar to the dimension of the guest (3.2 Å) that augurs more intriguing diffusion behavior to discover in this sub-class of MOFs.

This motivated us to perform a systematic computational exploration of the dynamics of model fluids with different molecular sizes/shapes, i.e. linear (CO₂, N₂) and spherical rotor (CH₄) molecules in a 1D-square channel MOF, namely the *SIFSIX-2-Cu-i* MOF with a pore size of ~5 Å, that has been very recently reported as an excellent candidate for CO₂ capture.¹³ The translational and rotational dynamics of these molecules were individually investigated by Molecular Dynamics (MD) simulations in the NVT ensemble at 303 K using the Nose-Hoover thermostat with a relaxation time of 0.5 ps and a time step of 1 fs to integrate the equations of motion, as implemented in the DL_POLY software. The same concentration of confined molecules for the three fluids was considered in a simulation box containing (3x3x5) MOF unit cells and arbitrary fixed to the loading simulated for CH₄ at 1 bar and 303 K by preliminary grand Canonical Monte Carlo (GCMC) simulations. Well-established all-atom microscopic

models for CO₂¹⁴, N₂¹⁵ and CH₄¹⁶ have been selected whereas the force field used to describe MOF-fluid interactions has been taken from our previous study.¹⁷ The employed force fields have been systematically validated in predicting a wide range of properties of the investigated fluids in previous studies^{18,19,20}. Trial GCMC runs with another reliable force field (TraPPE) for CO₂²¹ at 1 bar and 303 K revealed very small changes in the calculated adsorption enthalpy (39.00 kJ/mol for TraPPE and 38.75 kJ/mol for the employed EPM2¹⁴ force field) and very similar deviation from the available experimental value of 35.0 kJ/mol¹³. This implies that the choice of the force field for the fluids does not affect the adsorption properties of the investigated MOF. All MD simulations were equilibrated for 5 ns starting from initial configurations obtained by canonical Monte Carlo simulations and the dynamic features of the confined fluids were subsequently extracted by performing 20 ns runs.

The translational dynamics of the confined fluids were first explored. The corresponding self-diffusivities were extracted from the plots of the mean square displacement of the molecules using the well-known Einstein's relation. The calculated self-diffusion coefficients decrease from $6.9 \cdot 10^{-10}$ to $5.6 \cdot 10^{-10}$ and $2.3 \cdot 10^{-10}$ m²/s for N₂, CH₄ and CO₂, respectively. The fluid-fluid and fluid-MOF pair residence dynamics were calculated using the well-defined intermittent residence time correlation function (tcf) (eq. 1):

$$C_{res}(t) = \frac{\langle n_{ij}(0) \cdot n_{ij}(t) \rangle_{t^*}}{\langle n_{ij}(0)^2 \rangle} \quad (1)$$

where $n_{ij}(t)=1$ if a specific atom j is within a pre-defined cut-off distance of a second atom i at times 0 and t , and the atom j has only left the cut-off sphere for a period shorter than t^* during the time interval $[0,t]$, otherwise $n_{ij}(t)=0$ ^{17, 22}. For $t^*=\infty$, we define the intermittent residence correlation function as $C_{res}^I(t)$. The slowest decaying fluid-MOF intermittent residence tcfs, corresponding to the interactions of the center of mass (COM) of each fluid with the N- and F- atoms of the MOF framework, are depicted together with the corresponding fluid-fluid COM tcfs in Figures 1a and 1b. A reference radial cut-off of 5.25 Å, consistent with our previous studies¹⁷, was used in the calculations. The observed trend for the decay of the calculated fluid-MOF tcfs and the corresponding intermittent residence lifetimes is the inverse of the trend observed for

the self-diffusion coefficients. This result suggests that the translational dynamics of the fluids are mostly controlled by the fluid-MOF interactions. The calculated adsorption enthalpies at low coverage, obtained by GCMC simulations, reveal the following sequence: CO₂ (40.3 kJ/mol) > CH₄ (28.3 kJ/mol) > N₂ (23.4 KJ/mol). Such a finding further indicates that the strongest MOF/fluid interaction leads to the slowest diffusivity of the fluid.

Moreover, the slow decay of the fluid-fluid tcfs implies that the motion of the confined fluids is very restricted and molecular by-passing events are expected to be rare. To confirm this, the by-passing tcfs were calculated for all fluid pairs using equation 2, which was introduced previously¹⁷:

$$C_{Bypass}^c(t) = \frac{\langle h_{ij}(0) \cdot h_{ij}(t) \rangle}{\langle h_{ij}(0)^2 \rangle} \quad (2)$$

The calculation of this function was performed for specific fluid-fluid pairs, taking into account the first neighbour *j* around each molecule *i*, which was identified at the time step *t*=0. The distance difference $z_{ij}(t) = z_j(t) - z_i(t)$ for these specific tagged pairs at *t*=0 was calculated for the whole time frame considered for the calculation of the time correlation function. In this way $h_{ij}(t)$ was estimated in the following way: if $z_{ij}(0) \cdot z_{ij}(t) > 0$ and this condition remains the same during the time interval [0,*t*] then $h_{ij}(t) = 1$. However, the first time that $z_{ij}(0) \cdot z_{ij}(t) < 0$ then $h_{ij}(t) = 0$ and afterwards for all times $t' > t$ the corresponding value is $h_{ij}(t') = 0$. The calculated by-passing tcfs

(Figure 1c) verify that the by-passing time ($\tau_{Bypass}^c = \int_0^\infty C_{Bypass}^c(t) \cdot dt$) required for N₂

molecules (339 ps) to overtake their neighbors in the pore is shorter than for CO₂ (420 ps) and CH₄ (483 ps). Such a sequence is consistent with the slightly faster self-diffusivity of N₂. One can note that the longer by-passing time for CH₄ vs CO₂ does not correlate with a faster self-diffusivity for CO₂ and this clearly emphasizes that stronger CO₂-MOF interactions tend to slow down the diffusivity of the fluid.

To gain more insight into the translation dynamics of the confined fluids, the COM velocity tcfs and their corresponding spectral densities $S_v(\omega)$ ²³ were calculated (Figure

2a). The shape of these tcfs emphasizes that CH₄ exhibits more frequent ‘collisional’ effects. This is reflected especially on the shape of the velocity tcfs at the short time scale from 0-1 ps with the presence of four local minima and this is a signature of a local translational dynamics of the fluid. A relatively similar behavior has been observed for CO₂ (Figure 2b) and N₂ (Figure 2c), with a variant that the first minimum is shifted at slightly longer time scales and the other local minima are less pronounced for both fluids as compared to CH₄. The calculated spectral densities show in all cases typical low frequency peaks in the range 20-35 cm⁻¹ and additional peaks are present for CO₂ (50 cm⁻¹), N₂ (58 and 74 cm⁻¹) and CH₄ (93 and 130 cm⁻¹). These peaks may be attributed to frustrated translations due to the local structure around the fluid molecules²⁴, which results from a combination of fluid-MOF and fluid-fluid interactions. In the case of N₂ and CH₄, where fluid-MOF interactions are weaker, the blue-shifted peaks are clear indications of more strongly correlated dimer and trimer motions^{23,25,26}. The longer by-passing time for CH₄ emphasizes that the higher frequency peaks could probably be attributed to the long-lasting molecular collisional effects, which are reflected on the slower decay of its by-passing tcf.

In order to further investigate the origins of the low frequency peaks for the linear molecules, the normalized tcfs of the parallel and perpendicular projections of the COM velocity vector to the CO₂ and N₂ intramolecular axis and their corresponding spectral densities were calculated using equations 3 and 4:

$$C_{v^{\parallel}}(t) = \frac{\langle \vec{v}^{\parallel}(0) \cdot \vec{v}^{\parallel}(t) \rangle}{\langle \vec{v}^{\parallel}(0)^2 \rangle}, \quad C_{v^{\perp}}(t) = \frac{\langle \vec{v}^{\perp}(0) \cdot \vec{v}^{\perp}(t) \rangle}{\langle \vec{v}^{\perp}(0)^2 \rangle} \quad (3)$$

where the parallel and perpendicular components at each time *t* are expressed as:

$$\vec{v}^{\parallel}(t) = [\vec{v}(t) \cdot \vec{u}(t)] \cdot \vec{u}(t), \quad \vec{v}^{\perp}(t) = \vec{v}(t) - \vec{v}^{\parallel}(t) \quad (4)$$

In this equation $\vec{u}$ is a unit vector along the bond axis of CO₂ and N₂. The corresponding plots reported in Figures 2b and 2c evidence that the lowest and highest frequency translational modes correspond to the tcf of the parallel and perpendicular components respectively.

We further explored the impact of the molecular symmetry of the fluid on its reorientational dynamics. These dynamics were investigated by means of the Legendre reorientational tcfs using equation 5:

$$C_{\ell R}(t) = \langle P_{\ell}(\bar{u}(0) \cdot \bar{u}(t)) \rangle, \ell = 1-4 \quad (5)$$

where $\bar{u}$ is a unit vector along the bond axis vectors of CO₂ and N₂ and the C-H bond vector of CH₄. P_{ℓ} is a Legendre polynomial ($P_1(x) = x$, $P_2(x) = \frac{1}{2} \cdot (3x^2 - 1)$, $P_3(x) = \frac{1}{2} \cdot (5x^3 - 3x)$, $P_4(x) = \frac{1}{8} \cdot (35x^4 - 30x^2 + 3)$). The calculated Legendre reorientational tcfs, reported in Figure 3, highlight that all the calculated Legendre tcfs for CH₄ decay very fast to zero, in the time scale 0.1 - 1 ps. However this fast decay is not purely exponential, implying that these fast dynamics cannot be properly described by the Debye model of reorientational diffusive motions.²⁷ This finding can be further supported by the fact that the obtained reorientational relaxation times of methane $\tau_{1R} = 0.19 \text{ ps}$ and $\tau_{2R} = 0.10 \text{ ps}$ ($\tau_{\ell R} = \int_0^{\infty} C_{\ell R}(t) \cdot dt$) don't fulfill the well-known Hubbard relation ($\tau_{1R} = 3 \cdot \tau_{2R}$)²⁸. This very fast initial decay of the reorientational tcfs of CH₄, apart from its substantially different molecular shape in comparison with CO₂ and N₂, could be also related to its low moment of inertia, which has been found to affect the short-time decay of these tcfs.²⁹ On the other hand, the decay of the reorientational tcfs for the linear molecules shows a very interesting peculiarity. In the case of CO₂, Figure 3a shows that the relaxation of the even order Legendre tcfs $C_{1R}(t)$ and $C_{3R}(t)$ is significantly faster than the relaxation of the odd order ones $C_{2R}(t)$ and $C_{4R}(t)$, especially in the limit of long-time scales. The odd order tcfs decay very fast in the time scale from 0-1 ps and then much slower up to 1 ns. For the less elongated N₂ molecule the behavior is only apparent in the case of the second order Legendre tcfs, while for CO₂ it occurs for both second and fourth order Legendre tcfs. The decay of all the Legendre reorientational tcfs is also faster for N₂. Interestingly, a similar behavior has been evidenced by Kämmerer *et al* for supercooled liquids consisting of rigid diatomic molecules³⁰. They reported that a 180° flip of the molecules is an important component of the relaxation dynamics for the orientational degrees of freedom. In order to gain a complete picture of the reorientation mechanisms, we calculated the self, angular Van Hove correlation functions³¹ for the three fluids using equation 6:

$$G(\theta, t) = \frac{2}{N \sin \theta} \sum_{i=1}^N \left\langle \delta \left[\theta - \cos^{-1} (\bar{u}_i(0) \cdot \bar{u}_i(t)) \right] \right\rangle \quad (6)$$

The calculated $1/2 \cdot \sin \theta \cdot G(\theta, t)$ functions are presented in Figure 4. The shape of these functions clearly indicates that the effect of molecular symmetry on the reorientational dynamics of the confined fluids is very strong. At long time scale the functions for CO₂ exhibit two peaks at 14° and 160°. Such a finding clearly indicates that CO₂ molecules perform jump-like orientational flips of nearly 180°, leading to a very slow relaxation of the reorientational correlators. On the other hand, the short time peak at 30° for N₂ disappears at longer time and a plateau appears. The existence of this plateau indicates that the rotation of the less elongated N₂ molecules can be described in terms of successive smaller jumps in the range of 30°-150°. In the case of CH₄ the functions at large time scales exhibit a Gaussian-like shape, with a peak centered around 90°. Such behaviour indicates that the reorientational dynamics of spherical is much less hindered in comparison with that of linear molecules. The strongly hindered reorientational motions of the linear molecules are reflected on the decay of the even-parity reorientational correlators and especially in the more elongated CO₂ molecules. In the case of the less elongated and much faster diffusing N₂ molecules this hindered rotation is mainly reflected in the extremely slow decay of $C_{2R}(t)$, but not on the decay of $C_{4R}(t)$, probably due to the existence of successive smaller jumps. This suggests that successive small angular hopping and translation-rotation coupling are more prominent in the case of N₂³².

In order to provide deeper insights on the rotational motions of the three different confined fluids the mean squared angular displacement ($\langle \Delta \varphi^2(t) \rangle$) was calculated, following the methodology proposed in previous studies^{33,34}, and further related to the rotational diffusivity (D_R), using the Einstein's formalism:

$$D_R = \lim_{t \rightarrow \infty} \frac{1}{4t} \langle \Delta \varphi^2(t) \rangle \quad (7)$$

The calculated $\langle \Delta \varphi^2(t) \rangle$ for the bond axis vector of CO₂ and N₂ and the C-H vector of CH₄ are presented in Figure 5a. From this figure it can be clearly observed that the displacements corresponding to N₂ and CH₄ are much higher than the one assigned to CO₂. The corresponding D_R for CO₂, CH₄ and N₂ are 0.138, 3.053 and 7.014 rad²/ps,

respectively. The fact that the slightly less elongated N₂ shows a rotational diffusion coefficient about 50 times higher than the one for CO₂ clearly emphasizes the strong effect of the molecular elongation on the rotational dynamics of the confined molecules. It is also interesting to point out that at very short time scales, less than 1 ps, the $\langle \Delta \phi^2(t) \rangle$ for CH₄ is higher than the one corresponding to N₂, due to the very fast reorientational relaxation of the C-H bond which can be reflected on the decay of the Legendre tcfs in Figure 3. At longer time scales, due to the successive jumps during the rotation of N₂ molecules, the $\langle \Delta \phi^2(t) \rangle$ for N₂ becomes larger resulting in a higher D_R value.

To further investigate the contribution of local collective effects to this rotational behavior, the angular Van Hove correlation function was calculated for the angular difference $\Delta\theta = |\theta(t) - \theta(0)|$. In this case θ is the angle formed by a specific unit vector of a reference molecule i with the same corresponding vector of its nearest neighbor at $t=0$, $i^{\text{near}(0)}$. The corresponding angular Van Hove correlation function can be expressed as equation 8.

$$G(\Delta\theta, t) = \frac{2}{N \sin \Delta\theta} \sum_{i=1}^N \left\langle \delta \left[\Delta\theta - \left| \cos^{-1}(\vec{u}_i(t) \cdot \vec{u}_{i^{\text{near}(0)}}(t)) - \cos^{-1}(\vec{u}_i(0) \cdot \vec{u}_{i^{\text{near}(0)}}(0)) \right| \right] \right\rangle \quad (8)$$

The calculated $1/2 \cdot \sin \Delta\theta \cdot G(\Delta\theta, t)$ functions corresponding to a long-time scale (200 ps) are presented in Figure 5b. The maximum of these functions is observed for $\Delta\theta=0$ for all molecules, while an additional peak is present at $\Delta\theta \sim 140^\circ$ for CO₂. The identical shape of these functions observed for N₂ and CH₄ indicates that the mutual reorientation of the closest neighbors is very similar for these two molecules and hence the linearity of N₂ does not promote significant local steric hindrance effects. This finding, in combination with the successive angular rotational step mechanism in the reorientation of N₂ is consistent with a faster rotational diffusivity calculated for this molecule. In the case of CO₂, the higher elongation of the molecule causes more pronounced local steric hindrance effects and the large angular flips are also reflected on the existence of the second peak at $\Delta\theta \sim 140^\circ$. This observation clearly emphasizes that the extent of molecular elongation in the case of linear molecules significantly influences the mechanism of rotational relaxation.

Our findings provide for the first time a clear evidence of the effects of the molecular symmetry on the mechanisms controlling the translational and rotational dynamics of confined linear and spherical molecules in channel-like nanoporous materials. Such a conclusion is highly relevant for diverse disciplines such as in chemistry, physics, biology and materials science where diatomic or polyatomic molecules which can be effectively considered as linear, such as short chains or peptides, diffuse through nanopores³⁵. These processes can also be of significance in transport of biomolecules in living cells³⁵ and in molecular recognition and manipulation of molecular machines³⁶.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure Captions

Figure 1: **a)** and **b)** Calculated MOF/fluid and fluid/fluid tcfs for representative pairs
c) Calculated fluid/fluid by-passing tcfs.

Figure 2: Calculated tcfs and their corresponding spectral densities for **a)** the COM velocities, **b)** the parallel and perpendicular projections of the COM velocity vector to the CO₂ intramolecular axis and **c)** the parallel and perpendicular projections of the COM velocity vector to the N₂ intramolecular axis

Figure 3: Calculated Legendre reorientational tcfs for the bond axis vectors of **a)** CO₂ and **b)** N₂ and **c)** the C-H bond vector of CH₄.

Figure 4: Calculated $1/2 \cdot \sin \theta \cdot G(\theta, t)$ functions for **a)** CO₂, **b)** N₂ and **c)** CH₄.

Figure 5: Calculated **a)** mean squared angular displacements for the bond axis vector of CO₂ and N₂ and the C-H vector of CH₄. **b)** Calculated $1/2 \cdot \sin \Delta \theta \cdot G(\Delta \theta, t)$ functions for a long-time scale of $t=200$ ps.