Classical Density Functional Theory as a Fast and Accurate Method for Adsorption Property Prediction of Porous Materials

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Abstract

Physical adsorption separation is vital for many industrial processes, prompting researchers to develop new materials for energy-efficient processes. Porous adsorbent materials are of particular interest due to their diverse design possibilities and computational screening has accelerated the search for optimal materials. Classical density functional theory (cDFT) has recently been used as a faster alternative to state-of-the-art computational methods for screening of porous materials. However, extensive validation of cDFT predictions has not been performed for many materials, in a wide range of conditions, and with guest molecules exhibiting strong Coulombic interactions. In this paper, we validate the cDFT predictions by calculating the adsorption properties for more than 500 Metal-Organic Frameworks with three adsorbate molecules (CH$_4$, N$_2$, and CO$_2$) and comparing them to state-of-the-art results from GrandCanonical Monte Carlo (GCMC) simulations. For CO$_2$, we introduce the computation of Coulombic interactions between the MOF and the molecule, which are necessary to accurately describe this system. Our results demonstrate cDFT’s ability to accurately replicate GCMC adsorption isotherms and enthalpies of adsorption while needing a median time of only 6 minutes per material. These features position cDFT as a serious candidate for adsorption properties estimations of porous materials for a wide range of physical adsorption-based processes.

I. INTRODUCTION

Physical adsorption plays an important role across various industrial processes including separating chemicals (e.g., O$_2$/N$_2$ [1–3] or xenon from air [4]), radioactive off-gases treatment [5], climate change mitigation [6], cooling processes [7], and purification [8–10]. To lower cost, a key lever is to reduce the energy demand, leading to the ongoing development of new materials.

Porous materials, such as Metal-Organic Frameworks (MOFs), Covalent-Organic Frameworks (COFs), and zeolites, exhibit extensive design possibilities and have received considerable interest for physical adsorption [11–13]. By systematically exploring this vast design

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space, researchers can tailor materials with favorable properties for their specific application. However, experimentally studying a wide variety of porous materials can be time-consuming. To mitigate the laborious process of synthesizing an extensive array of materials, researchers perform computational screenings to find the most promising materials for their application [12–16]. These computational screenings usually rely on Monte Carlo simulations, such as configurational-bias Monte Carlo (CBMC) and Grand Canonical Monte Carlo (GCMC) [12, 14, 17, 18] or, more recently, machine learning (ML) models trained on GCMC data [16, 19, 20].

Monte Carlo simulations are state-of-the-art for computing adsorption properties and have been used for computational screenings for more than a decade [21]. In initial screenings, Monte Carlo simulations are often used to compute Henry coefficients and enthalpies of adsorption of porous materials for a few thousand materials [22, 23]. These properties are subsequently employed to evaluate the suitability of these materials for applications, e.g., carbon capture, employing metrics such as selectivity and parasitic energy. However, these simple material metrics often exhibit weak correlation with more comprehensive process metrics [12, 24], prompting contemporary investigations to incorporate an additional layer of process considerations into their screening methodologies [12, 21, 25]. For process modeling and optimization, adsorption properties of the MOFs, such as the adsorption isotherms and enthalpies of adsorption, are needed in a wide range of temperatures. To accurately extrapolate data across temperatures using the Clausius-Clapeyron equation and to model mixture behavior with the Ideal Adsorbed Solution Theory (IAST), it is essential to compute adsorption isotherms and enthalpies of adsorption across the entire range of relevant pressures [26]. This range spans pressures from the Henry’s law regime to the saturation pressure. However, computing full adsorption isotherms with GCMC simulations can take up to several days [27], which limits the scope of materials screened [12, 25]. GCMC simulations can also display numerical uncertainties in the estimation of the enthalpy of adsorption [26], propagating to the temperature extrapolation of adsorption isotherms with Clausius-Clapeyron equation.

As a faster alternative to Monte Carlo simulations, ML-based models have recently been developed and are able to accurately reproduce the Monte Carlo results [19, 20, 28]. However, training these models requires a substantial amount of data, usually coming from GCMC simulations, involving a time-intensive phase of training data generation. Furthermore,
as the ML-based methods are not physics-based, these models are usually trained on one property in specific conditions, such as the loading at a defined set of pressures for fixed temperature \cite{19, 28} or the enthalpy of adsorption at one pressure and one temperature \cite{20}. New training data must be generated when other properties or the same properties in new conditions are needed, e.g., in process optimization.

As a fast, accurate, physics-based alternative, classical Density Functional Theory (cDFT) has recently emerged to compute adsorption properties of porous materials. Screenings of MOFs have already been performed for applications separating or storing noble gas \cite{29}, toxic gases \cite{30}, dihydrogen \cite{31, 32}, and carbon isotopes \cite{33}. The computational cost of cDFT was shown to be much lower compared to GCMC simulations, on the order of tens of seconds for the computation of one loading \cite{32}. To test the reliability of cDFT predictions, validation has been performed by comparing cDFT predictions with GCMC results or experiments. Fu et al. \cite{32, 34} compare Monte Carlo and cDFT results for the loading of methane and dihydrogen for 1200 MOFs and show very good agreement. However, in both of these studies, the molecules are considered a single Lennard-Jones site and the comparisons were done for two pressures at one temperature. Other validations compare full adsorption isotherms predicted by cDFT with GCMC simulations or experiments, but they are limited to fewer than 10 MOFs \cite{28–31, 33, 35, 36}. Therefore, a comprehensive validation of cDFT predictions with GCMC results is needed on a wide range of pressures and temperatures for single and non-single Lennard-Jones site molecules to test the reliability of cDFT predictions for screenings of thousands of MOFs. In addition, the studies mentioned above do not include validation of the cDFT predictions of the enthalpies of adsorption, which is a crucial property for process modeling and optimization as it is used to extrapolate isotherms in temperatures and to study heat exchanges.

In this research paper, we perform this comprehensive validation of cDFT by comparing cDFT predictions of adsorption isotherms and enthalpies of adsorption with GCMC results for more than 500 MOFs, using CH\textsubscript{4}, N\textsubscript{2}, and CO\textsubscript{2} as guest molecules. N\textsubscript{2} and CO\textsubscript{2} are important molecules to study as they appear in important separation processes such as carbon capture and no extensive validation for these molecules have been performed. To improve cDFT predictions accuracy for CO\textsubscript{2}, Coulombic interactions between the porous material and the guest molecule are introduced in the framework. We confirm the low computational time of cDFT by computing adsorption isotherms in a median time of 6
CPU-minutes on one node of an AMD Ryzen Threadripper PRO 3975WX, while closely reproducing GCMC simulation results for the three adsorbate molecules. We demonstrate the ability of cDFT to faithfully replicate GCMC predictions of enthalpies of adsorption while exhibiting low numerical error. These comprehensive comparisons underscore the potential of cDFT as a relevant option in the computational assessment of porous materials for physical adsorption.

In Sec. II, we present the cDFT method and the key developments to generalize this method. We then present the GCMC calculations that are used as a benchmark in our study and how the cDFT setup is designed to match GCMC results (Sec. III). In Sec. IV, we compare the cDFT predictions to the GCMC benchmark for a set of adsorption isotherms, enthalpy of adsorption curves, and their computational cost. In Sec. V, we explore the underlying reasons for cDFT deviations from GCMC results. We finally conclude in Sec. VI on the potential of cDFT in the context of materials screening for physical adsorption-based processes.

II. VERSATILE AND EFFICIENT: CLASSICAL DENSITY FUNCTIONAL THEORY

In this section, we present a succinct overview of the computational procedure to calculate the adsorbate molecule loading within a porous material using cDFT. We emphasize key advancements that broaden the scope of the cDFT framework used here [37], specifically its applicability to 1) solids featuring non-orthorhombic unit cells and 2) adsorbate molecules that exhibit strong Coulombic interactions with the material. We also detail how we incorporate enthalpies of adsorption calculations.

A. Overview of classical Density Functional Theory based on PC-SAFT

The cDFT framework describes systems in the grand canonical ensemble $\mu VT$ where the grand potential $\Omega$ represents the thermodynamic potential. In cDFT, the grand potential $\Omega$ is minimized with respect to the density profiles $\rho_k(r)$ of every adsorbate $k$ to find the equilibrium state of the system. The grand potential is described with the following
relationship:
\[
\Omega \{ \rho_k(r) \} = F \{ \rho_k(r) \} + \sum_i N_c \int \rho_i(r)(V_i^\text{ext}(r) - \mu_i)dr.
\]

\( \rho_k(r) \) is the density profile of adsorbate \( k \) which depends on the position \( r \). \( N_c \) is the number of adsorbates, and \( V_i^\text{ext} \) is the external potential used to describe the interactions between the adsorbate \( k \) and the porous material. The external potential \( V_i^\text{ext} \) includes the van der Waals interactions and the Coulombic interactions:

\[
V_i^\text{ext}(r) = V_i^{\text{VdW}}(r) + V_i^{\text{Coulomb}}(r).
\]

The van der Waals term \( V_i^{\text{VdW}} \) is computed as described by Kessler \textit{et al.} [38] and the Coulombic term \( V_i^{\text{Coulomb}} \) is described in Sec. II B. \( \mu_k \) is the chemical potential of the adsorbate \( k \). \( F \) is the Helmholtz energy functional describing interactions within the fluid phase and is described here by the functional developed by Sauer and Gross [39] based on the PC-SAFT equation of state [40].

PC-SAFT calculates the Helmholtz energy as the sum of contributions from intermolecular interactions. In this study, we consider the following contributions:

\[
F[\{\rho(r)\}] = F^{\text{ig}}[\{\rho(r)\}] + F^{\text{hs}}[\{\rho(r)\}] + F^{\text{hc}}[\{\rho(r)\}] + F^{\text{disp}}[\{\rho(r)\}] + F^{\text{mp}}[\{\rho(r)\}],
\]

where the individual contributions are the ideal gas reference (ig), hard-sphere repulsion (hs), hard-chain formation (hc), dispersive attraction (disp), and multipolar interactions (mp) [39].

The evaluation of the Helmholtz energy functional and the minimization of the grand potential is provided by the FeO\textsubscript{s} Python package [37]. Once the grand potential is minimized, the equilibrium density is integrated over a unit cell to calculate the loading. Repeating the calculations for multiple bulk pressures yields adsorption isotherms, i.e., the loading as a function of the pressure at constant temperature. The enthalpy of adsorption at each pressure gives the enthalpy of adsorption curves as detailed in Sec. II B.

We also compute the Henry coefficients and zero-loading enthalpy using a pragmatic approach. The lowest pressure of the isotherms is chosen to be at the end of the Henry regime [26], ensuring that any lower pressure will also be in the Henry regime. We calculate the loading and enthalpy of adsorption at half of this lowest pressure to provide an additional point within the Henry regime. To determine the Henry coefficient, we perform a linear
regression using three points: zero pressure, half of the lowest pressure, and the lowest pressure. The slope of this regression gives us the Henry coefficient. To determine the zero-loading enthalpy, we first perform a linear regression using the enthalpy of adsorption values at half of the lowest pressure and at the lowest pressure. By extrapolating this regression to zero pressure, we obtain the zero-loading enthalpy.

B. Key developments for generalizable cDFT

To generalize the cDFT framework used here, we extend it by three key developments: 1) extension for non-orthorhombic unit cells, 2) adding Coulombic interactions in the external potential, and 3) calculation of the enthalpy of adsorption. Here, we describe these developments succinctly and give more details in the Supplementary Materials, Sec. S1.

To generalize cDFT to more porous materials, the cDFT method is extended to non-orthorhombic unit cells. The unit cell is discretized along its skewed axes and a coordinate transform is applied to obtain Cartesian coordinates, which are required to calculate distances for the external potential. In cDFT, the skewness of the coordinate system also needs to be accounted for when evaluating the (non-local) Helmholtz energy functional. The applied coordinate transform and rapid evaluation of convolution integrals in skewed coordinates are included in the Supplementary Information, Sec. S1A.

Previous work [30] only considers the Van der Waals interactions between the MOF and the guest molecules, even if the guest molecules could exhibit Coulombic interactions with the MOF. As guest molecules of high interest, such as CO$_2$, can have strong Coulombic interactions with porous materials, considering these interactions is crucial to obtain accurate predictions of adsorption properties. To describe these Coulombic interactions, we employ a method similar to that used by Hong et al. [41] in a different context. To account for the orientation of the guest molecule within the external potential, they sample the Van der Waals interactions between a guest molecule and the solid at various orientations at a given position $\mathbf{r}$. We extend this approach by including the Coulombic interactions $V^{\text{Coulomb}}$ between the guest molecule and the MOF. To minimize the number of orientations sampled and consequently the computational cost, preliminary calculations of likely orientations are estimated, and then 10 orientations are computed. The minimum energy is used for the external potential at this position $\mathbf{r}$. More details on the initial estimate of optimal directions...
are included in the Supplementary Materials, Sec. S1B.

In addition to the adsorption isotherm, an important property for modeling and designing adsorption processes is the enthalpy of adsorption. The enthalpy of adsorption is needed, for example, to calculate heat requirements in adsorption processes or to extrapolate adsorption isotherms with the Clausius-Clapeyron relation. In this work, we calculate the enthalpy of adsorption analytically from cDFT. The enthalpy of adsorption for every adsorbate $\Delta h^\text{ads}_k$ is calculated from:

$$
0 = \sum_j \left( \frac{\partial N_k}{\partial \mu_j} \right)_T \Delta h^\text{ads}_j + T \left( \frac{\partial N_k}{\partial T} \right)_{p,x_i}, k = 1, ..., N_c
$$

with $N_k$ the number of adsorbed molecules of adsorbate $k$, $\mu_k$ the chemical potential, temperature $T$, (bulk) pressure $p$, composition of the bulk phase $x_i$, and the number of components $N_c$. The resulting evaluation of the enthalpy of adsorption is numerically robust and fast relative to the calculation of the density profile itself. Details on the derivation and the calculation of partial derivatives of density profiles are included in the Supplementary Material, Sec. S1C.

The setup of cDFT provides several degrees of freedom (including, for example, the force field for the external potential). Since the goal of this research paper is to show that cDFT calculations can reproduce GCMC predictions, the choice of these parameters is partially given by the parameters used in GCMC. Therefore, in the next section, we present the GCMC data that is used as a benchmark and then define the choice of the degrees of freedom for cDFT.

III. GCMC AND CDFT SETUP

A. GCMC database description

A database containing adsorption isotherms, Henry coefficients, enthalpies of adsorption and zero-loading enthalpies of adsorption was computed with GCMC in the work of Moubarak et al. [26]. This database contains the adsorption properties of N$_2$ and CO$_2$ at 298.15 K for 500 MOFs. For 50 of these MOFs and with both N$_2$ and CO$_2$, the adsorption properties were computed at 4 additional temperatures (323.15 K, 348.15 K, 373.15 K, and 398.15 K). Another database [42] contains adsorption properties of CH$_4$ at 298.15 K for...
1050 MOFs (partially different from the $N_2$ and $CO_2$ set). The adsorption properties were computed for 10 to 30 pressures between the end of the Henry regime and the saturation pressure (see Ref. [26] for more explanation). The enthalpies of adsorption computed with RASPA are corrected to consider non-ideal gas behavior as described in Moubarak et al. [42].

All the details associated with these GCMC simulations are described by Moubarak et al. [26, 42], and here we report the choices most relevant for our study. The GCMC simulations used the Universal Force field (UFF) [43] to describe the framework atoms and the Transferable Potentials for Phase Equilibria (TraPPE) force field [44] to describe the adsorbates. The porous materials’ atomic charges were computed using either the Density Derived Electrostatic and Chemical (DDEC) theory [45], or the extended charge equilibration (EQeq) method [46] for the experimental and in silico structures respectively. Pore blocking, i.e., regions of the porous medium that are inaccessible to the adsorbate molecules, is done with the software Zeo++ [47] using a radius of 1.492 Å for $CH_4$, 1.324 Å for $N_2$, and 1.22 Å for $CO_2$, a number of samples of 100 Å$^{-3}$, and the UFF radii as atomic radius.

To obtain an accurate comparison of computational costs, GCMC simulations for three MOFs with different unit cell sizes were re-run with the three adsorbates considered here ($CH_4$, $N_2$, and $CO_2$) in the same conditions as the database with the same working machine as cDFT calculations (AMD Ryzen Threadripper PRO 3975WX).

B. Deviation metric definition

To compare two adsorption isotherms or two enthalpy of adsorption curves, we compute the mean absolute relative deviation (MARD) between the two curves:

$$MARD = \frac{1}{N_{pressures}} \sum_{i} \frac{|y_{test}^i - y_{ref}^i|}{|y_{ref}^i|},$$

where $N_{pressures}$ is the number of pressures in the two curves (same pressures for both curves), and $y_{test/ref}^i$ is the loading or the enthalpy of adsorption for the test/ref case at pressure $i$. When cDFT and GCMC predictions are compared, the reference is always GCMC. In cases where two cDFT or two GCMC curves are compared, the reference is defined when these comparisons occur. An absolute error was chosen as a non-absolute one would lead to canceling errors if an overestimation and underestimation happens within one comparison.

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TABLE I. Parameters used for cDFT calculations.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic interactions ($V_{\text{Coulomb}}$ in Eq. 1)</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Solid</td>
<td>UFF [43]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluid description for external potential (for $V_{\text{ext}}$ in Eq. 1)</td>
<td>TraPPE [44]</td>
<td>PC-SAFT Non-polar [40]</td>
<td></td>
</tr>
<tr>
<td>Fluid description for Helmholtz functional (for $F$ in Eq. 2)</td>
<td>PC-SAFT Polar [48]</td>
<td>PC-SAFT Non-polar [40]</td>
<td></td>
</tr>
<tr>
<td>Grid density ($\text{Å}^{-1}$)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Additional metrics are shown in the Supplemental Materials to give insights into the question of overestimation and underestimation.

C. Parameters for cDFT

cDFT calculations need the definition of five main degrees of freedom per adsorbate molecule. (see Table III C): 1) the inclusion of Coulombic interactions in the calculation of the external potential, 2) the parameters to describe the MOFs, 3) the description of the fluid for the calculation of the external potential, 4) the description of the fluid in the Helmholtz energy functional, and 5) the grid point density. All these five parameters are summarized in Table III C. Other minor degrees of freedom need to be defined, which are discussed in the Supplementary Materials Sec. S2A.

Coulombic interactions, as described briefly in Sec. II B and more thoroughly in the Supplementary Materials, Sec. S2B, can be included in the calculation of the external potential at the cost of additional computations. As CH$_4$ is known to have negligible Coulombic interactions, these interactions are not included, which corresponds to setting the $V_{\text{Coulomb}}$ term of Eq. 1 to 0. For N$_2$ and CO$_2$, an analysis of the accuracy of adsorption isotherms and enthalpy of adsorption predictions compared with GCMC for 100 MOFs is detailed in...
the Supplementary Materials Sec. S2B. This analysis shows that including the Coulombic interactions for CO\(_2\) makes the cDFT predictions more closely match the GCMC calculations while the effect for N\(_2\) is slightly unfavorable. The observation for N\(_2\) comes from the fact that cDFT predictions slightly overestimate GCMC predictions without the Coulombic interactions. This overestimation increases when adding Coulombic interactions. The initial overestimation without Coulombic interaction might be attributed to PC-SAFT parameters compensating for their limited consideration of Coulombic interactions by enhancing dispersion interactions. Therefore, Coulombic interactions \(V^{\text{Coulomb}}\) are included for the calculations of the external potential when CO\(_2\) is the adsorbate molecule but not for CH\(_4\) and N\(_2\).

The atoms of the MOFs are usually described with the UFF force field [43] or the DREIDING force field [49]. Following the GCMC database discussed in Sec. III, we opt to apply the UFF force field for characterizing the atoms in the MOFs when computing the external potential for cDFT.

The description of the fluid for the external potential depends on the inclusion of the Coulombic interactions: if these interactions are included, the parameters used for describing the adsorbate molecule need to resolve the orientations, which is not the case for PC-SAFT parameters. Therefore, we use the TraPPE force field [44] to describe CO\(_2\) in the calculation of the external potential. For the other adsorbates, we consider two options: the set of non-polar PC-SAFT parameters by Gross and Sadowski [40] and the set of polar PC-SAFT parameters by Gross [48]. The non-polar set of parameters neglects the multipolar term of Eq. 2, whereas it is included for the polar set of parameters. As CH\(_4\) is a non-polar molecule, we use the set of non-polar parameters. For N\(_2\), we want to be consistent in choosing PC-SAFT parameters for calculating the external potential and for the Helmholtz energy functional. In the Supplementary Materials, Sec. S2B, we compare these two sets of parameters and show that the two options produce similar predictions. Therefore, for simplicity, we choose the set of non-polar parameters.

For consistency, CH\(_4\) and N\(_2\) are also described with the set of non-polar parameters for the Helmholtz functional calculation. For CO\(_2\), we compare the two sets of parameters in the Supplementary Materials, Sec. S2B, and we show that using the polar set of parameters delivers predictions matching the GCMC data more closely, which is logical as CO\(_2\) has some quadrupole moment.
To numerically minimize the grand potential $\Omega$, the unit cell is discretized into a set of equidistant grid points. The number of grid points is a key parameter for the trade-off between accuracy and speed of computation, as more grid points result in more accurate results but more expensive computations. The density of grid points has been studied to find a compromise between accuracy, computational effort, and convergence (see Supplementary Materials, Sec. S2C). The analysis shows that a grid point density of $2\,\text{Å}^{-1}$ is an appropriate value to have high accuracy while keeping low computational costs. Increasing the grid point density to $2.5\,\text{Å}^{-1}$ results in an average of 0.5\% MARD change for the adsorption isotherms predictions and always less than 5.5\%, which is relatively low. In the interest of computational cost, the grid point density is set to $2\,\text{Å}^{-1}$. However, some enthalpies of adsorption display significant deviations at $2\,\text{Å}^{-1}$ that we attribute to numerical errors (see Supplementary Materials, Sec. S2C). When notable numerical errors arise in the enthalpy of adsorption computed with cDFT (occurring in approximately 7\% of materials), further calculations are conducted at higher grid densities, with an increment of $0.5\,\text{Å}^{-1}$ reaching up to $4\,\text{Å}^{-1}$. Despite these adjustments, some enthalpies of adsorption continue to exhibit notable numerical errors even at a grid density of $4\,\text{Å}^{-1}$. These significant deviations are identified by assessing whether the enthalpy of adsorption varies by more than $10\,\text{kJ}\,\text{mol}^{-1}$ between two consecutive pressures. The computational expenses shown in Sec. IV C include all the examined grid densities.

IV. COMPARISON OF CDFT AND GCMC PREDICTIONS

A. Adsorption isotherms

To validate the cDFT calculations, we compare the predictions of cDFT with GCMC predictions, the state-of-the-art for computing adsorption properties. In Fig. 1, the cumulative curves of the MARDs between adsorption isotherms predicted by cDFT and GCMC are shown for the three adsorbate molecules CH$_4$, N$_2$, and CO$_2$. To offer a comparison with a common practice among the community, the cumulative curves of the MARD of switching from the UFF [43] to the DREIDING force field [49] are also shown. The data is taken for around 700 MOFs for N$_2$ and CO$_2$ from the CRAFTED database calculated by Oliveira et al. [50]. We computed the MARD using UFF as a reference. The data is at 298.15 K, and
FIG. 1. Cumulative curves of the MARDs between cDFT and GCMC computations for adsorption isotherms of three adsorbate molecules CH\textsubscript{4}, N\textsubscript{2}, and CO\textsubscript{2}. The top row of plots serves to illustrate MARD values of 4.2\%, 17\%, and 29\%, offering an intuitive grasp of the meaning of MARD between two adsorption isotherms. As a point-of-comparison, we include MARD comparisons between adsorption isotherms computed using the UFF [43] and DREIDING [49] force fields from another dataset recently published by Oliveira \textit{et al.} [50]. The maximum MARD shown, for clarity, is 100\%. However, for the MARD between using UFF and DREIDING force field for N\textsubscript{2} and CO\textsubscript{2}, there are instances (38/721 and 19/705, respectively) surpassing the 100\% threshold and 1/499 case for the comparison between cDFT and GCMC for CO\textsubscript{2}. All isotherms were calculated at 298.15 K.

the DDEC charges are used. Note that the set of MOFs studied in the CRAFTED database differs from those studied here. Switching from the UFF to the DREIDING forcefields and switching from GCMC calculations to cDFT calculations are two independent decisions and their deviations would be additive. The inclusion of the deviations for switching from UFF to DREIDING offers a comparison with common practice in the community.

For CH\textsubscript{4}, the MARD has a median of 3.9\% and is below 16\% for all materials, which
can be regarded as an almost perfect agreement. As the methods of GCMC and cDFT are intrinsically different, small inherent deviations always occur. CH$_4$ is the case where the underlying molecular model in GCMC and cDFT exhibit the closest agreement because, in both models, CH$_4$ is described as a single Lennard-Jones site without Coulombic interactions. We provide a reference point for the order of magnitude of the MARD between cDFT and GCMC: Gowers et al. [27] compare the adsorption isotherms predicted by five implementations of GCMC (Cassandra [51], DL Monte [52], MuSiC [53], RASPA [54], and Towhee [55]) and show that in the case where no electrostatic interactions are considered, the MARD between the implementations is on average of 3.1 %, and can be up to 5.2 %. Therefore, the median MARD between cDFT and GCMC for CH$_4$ is within the MARD of different implementations of GCMC and thus very accurate. With CH$_4$, cDFT calculations did not converge for 22/1050 MOFs for at least one pressure and were removed from the analysis.

For N$_2$, the MARD has a median of 6.5 % whilst consistently staying under 51 % across all materials. Illustrated in Figure 1, the use of the DREIDING force field [49] as an alternative to UFF [43]—–a common choice for GCMC-based adsorption isotherm computations— yields a median MARD of 24 % with MARD values going up to 588 %. This observation shows that opting for cDFT instead of GCMC when N$_2$ is the adsorbate molecule results in a smaller change of the results. N$_2$ exhibits higher MARD than CH$_4$, possibly because the orientations of N$_2$ molecules can play a role in GCMC that is currently not resolved with cDFT as N$_2$ is not described as a single Lennard-Jones site, contrary to CH$_4$. With N$_2$, 1/500 MOF had at least one pressure where cDFT calculations did not converge and was removed from the analysis.

For CO$_2$, Coulombic interactions are considered. The MARD has a median of 17.5 % and is always below 127 %. For this scenario, switching from UFF force field to DREIDING results in a median MARD of 30 % with MARD values going up to 1339 %. Consequently, the deviations between cDFT and GCMC predictions for CO$_2$ are much lower than uncertainties in the GCMC force field decision. cDFT predictions deviate more with CO$_2$ as the adsorbate molecule than with CH$_4$ or N$_2$. A possible explanation is that the non-consideration of the orientations of CO$_2$ molecules has a greater effect as CO$_2$ exhibits stronger Coulombic interactions than CH$_4$ and N$_2$ or that the Coulombic interactions sampling could be made finer. With CO$_2$, 1/500 MOF had at least one pressure where cDFT calculations did not
converge and was removed from the analysis.

Calculations at temperatures other than 298.15 K show similar deviations between cDFT and GCMC predictions in the available range 323 K to 393 K (see the Supplementary Materials, Sec. S3). Overall, cDFT almost perfectly reproduces adsorption isotherms of GCMC for CH$_4$ and closely matches them for N$_2$ and CO$_2$. As both models are inherently different, deviations are expected, and we show that these deviations are below those observed when switching force fields.

The MARD on the full adsorption isotherms does not give a complete picture of the different regimes observed in an adsorption isotherm: in the Supplementary Materials Sec. S4, more details are given on the behavior at low and high pressure. At low pressure, in the Henry regime, the loading mostly depends on the adsorbate-MOF interactions, whereas at higher pressure, the loading mostly depends on the pore shape of the MOF. In the Supplementary Materials Sec. S4, these different regimes are more detailed. We show, for example, that the Henry coefficients calculated by cDFT deviate from GCMC calculations by less than 10% for 99% of the MOFs for CH$_4$ and is within a factor 2 from GCMC for 95% and 84% of the MOFs for N$_2$ and CO$_2$ respectively. At high pressure, cDFT predictions closely match the loading computed by GCMC for CH$_4$ and N$_2$ with deviations lower than 10% in most cases. However, a small underestimation of the loading at high pressure is observed for CO$_2$.

### B. Enthalpy of adsorption

Fig. 2 displays the results of a similar analysis to Fig. 1, but for the enthalpy of adsorption instead of the loading. Due to its non-stochastic nature, enthalpies of adsorption computed by cDFT display much smaller numerical uncertainties than the ones computed by GCMC. In order to decouple the deviations that come from the numerical uncertainties in GCMC enthalpies of adsorption and the deviations coming from the differences between cDFT and GCMC, we also show the comparison of the zero-loading enthalpies of adsorption. These values can be precisely computed with GCMC and are important as they give the temperature dependence of the Henry coefficient. A comparison of the zero-loading enthalpies of adsorption is shown in Fig. 3.

The deviations between cDFT and GCMC are low for the enthalpy of adsorption (Fig.
FIG. 2. Cumulative curves of the MARD between cDFT and GCMC computations for the enthalpy of adsorption of three adsorbate molecules CH$_4$, N$_2$, and CO$_2$. The top row of plots serves to illustrate MARD values of 2\%, 7.6\%, and 10\%, offering an intuitive grasp of the meaning of MARD between two enthalpies of adsorption curves. The numerical uncertainty of the GCMC calculations is shown. As a reference, we include MARD comparisons between enthalpies of adsorption computed using the UFF [43] and DREIDING [49] force fields, from another dataset recently published by Oliveira et al. [50]. The maximum MARD shown, for clarity, is 40\%. However, for the MARD between using cDFT and GCMC for N$_2$ and CO$_2$, there are instances (1/499 and 5/499 respectively) surpassing the 40\% threshold. All enthalpies of adsorption were calculated at 298.15 K.

The median MARD is 2.4\% for CH$_4$ as the adsorbate molecule, 5.3\% for N$_2$ and 5.2\% for CO$_2$. For N$_2$ and CO$_2$, these MARD values are close to the deviation occurring when switching from UFF to DREIDING force field, whereas the values for CH$_4$ are lower. However, some of the deviations are due to the numerical uncertainties in GCMC calculations. The zero-loading enthalpy of adsorption has a very small numerical uncertainty when calculated with GCMC and allows for more precise comparison. The zero-loading enthalpy of adsorption computed with cDFT matches very closely the one computed with GCMC for CH$_4$ ($R^2 = 0.9987$), and matches reasonably close for N$_2$ and CO$_2$ (respectively, $R^2 = 0.9011$).
FIG. 3. Log-log parity plot for the zero-loading enthalpy of adsorption predicted by cDFT versus by GCMC for the three molecules (CH\textsubscript{4}, N\textsubscript{2}, CO\textsubscript{2}). Each point corresponds to one MOF. The cDFT predictions of the zero-loading enthalpy of adsorption perfectly matches the GCMC results for CH\textsubscript{4} and are in good agreement for N\textsubscript{2} and CO\textsubscript{2}. and \( R^2 = 0.9374 \) (see Fig. 3).

As mentioned in Sec. IIIC, the enthalpies of adsorption computed by cDFT sometimes display unreasonable values attributed to numerical errors (see Supplementary Sec. S3C for more details). These numerical errors can be partially removed by increasing the grid density. In this work, the grid density is increased by 0.5 Å\(^{-1}\) to a maximum 4 Å\(^{-1}\) to avoid these errors. At a grid density of 4 Å\(^{-1}\), still 6/499 materials for CO\textsubscript{2} and 1/499 for N\textsubscript{2} exhibit these large numerical errors at specific pressures. In Fig. 2, the material for N\textsubscript{2} and the 5 materials for CO\textsubscript{2} that exhibit MARD higher than 40\% for the enthalpies of adsorption show large numerical errors at specific pressures.

For the enthalpy of adsorption, the MARD between cDFT and GCMC also does not depend on temperature, as shown in the Supplementary Materials Sec S3.

C. Computational cost comparison

In materials screening, the computational cost of the property estimation method determines the number of materials that can be screened within a specific time. cDFT calculations take a median run time of 6 min per adsorption isotherm, with a minimum of 8 s and a maximum of 40 h (see Fig. 4). The computational time increases exponentially with
FIG. 4. Run time of cDFT and GCMC simulations as a function of the volume of the unit cell. The GCMC adsorption isotherms were re-run for 3 MOFs covering a significant range of unit cell volume, and the precise run time was measured (empty symbols).

The volume of the unit cell as a larger unit cell requires more grid points for a fixed grid point density. When the volume is multiplied by 10, the computational cost multiplies by 33. Computational costs that are particularly high for a given unit cell volume come from the re-calculation of the cDFT predictions at higher grid density when the enthalpies of adsorption exhibit large numerical errors as mentioned in Sec. III C.

For the three MOFs (OLOKEF, WUSSEK, and XAKZAL in the database) where precise computational costs were calculated, GCMC calculations took between 3.4 h and 96 h on one node of an AMD Ryzen Threadripper PRO 3975WX, the same machine used for the cDFT calculations. At an equal volume of the unit cell, cDFT is almost always faster, ranging from 15 000 times faster (small volume unit cell MOF (0.36 nm³) for CO₂) to 42 times faster (large volume unit cell MOF (14 nm³)), resulting in a significant amount of time saved that can allow researchers to screen around 100 times more materials within the same time. Note that for both GCMC and cDFT, the computational cost of computing the enthalpies of adsorption is negligible, once the density profiles have been computed.

V. ASSESSMENT OF CDFT FEATURES AND LIMITATIONS

In this paper, we aim to validate cDFT as a potential tool for adsorption property prediction of porous materials. We demonstrate the generalization of two primary features of cDFT previously mentioned in the literature: its low computational cost and minimal
FIG. 5. Scatter plot of the strongest MOF-CO$_2$ interactions computed with cDFT ((a) and (c)) and the maximal pore size ((b) and (d)) with the ratio of the Henry coefficients computed with cDFT $K_H^{cDFT}$ over the ones computed with GCMC $K_H^{GCMC}$ for N$_2$ ((a) and (b)) and CO$_2$ ((c) and (d)). The y axes are in logarithm scale. Each point corresponds to one MOF.

Numerical uncertainty in the computation of the enthalpy of adsorption. These attributes position cDFT as a relevant tool for efficiently screening materials. The cost-effectiveness facilitates the screening of a large number of materials, while the low numerical uncertainty in enthalpies at high pressure enables robust temperature extrapolation of adsorption isotherms using the Clausius-Clapeyron relation, which is necessary for gradient-based optimization for process optimizations. However, these advantages come with a trade-off in accuracy, stemming from the discretization of adsorbate positions or the exclusion of adsorbate ori-
orientation as a degree of freedom during density profile optimization. Our study reveals that this loss in accuracy is negligible for CH\(_4\) as the adsorbate but becomes more pronounced for N\(_2\) and CO\(_2\). Understanding the materials prone to a larger deviation between cDFT and GCMC is crucial when applying cDFT to specific materials.

In Fig. 5, we present insights into instances where cDFT exhibits significant deviations from GCMC. We employ the ratio of the Henry coefficient calculated using cDFT (K\(_H^{cDFT}\)) to that obtained with GCMC (K\(_H^{GCMC}\)). This ratio is compared to two descriptors: the strongest MOF-CO\(_2\) interactions and the maximal pore size. The strongest MOF-CO\(_2\) interactions are the minimum energy interactions at a grid point between a MOF and CO\(_2\). Strong MOF-CO\(_2\) interactions generally mean strong Coulombic interactions. The maximal pore size is the size of the biggest pore in the MOF structure. The pore size distribution is computed with the Zeo++ software [56]. A small maximal pore size means that all the pores in the MOF are quite small.

For N\(_2\) as the adsorbate in Fig. 5a, stronger interactions between the MOF and CO\(_2\) correspond to underestimation of the Henry coefficients by cDFT. If we consider that strong MOF-CO\(_2\) interactions come from strong Coulombic interactions, the underestimation of the Henry coefficients by cDFT for N\(_2\) could be corrected by the inclusion of the Coulombic interactions for N\(_2\) for the cases where they seem non-negligible. In Fig. 5a, we can also observe that some Henry coefficients are overestimated by cDFT, which are not explained by the strength of the MOF-CO\(_2\) interactions. In Fig. 5b, we can see that the points that are overestimated always occur when the maximal pore size in the MOF is smaller than 5 nm. When the maximal pore size is small, all the pores of the MOF are small. Therefore, small pores in a MOF lead to an overestimation of the Henry coefficients for N\(_2\). A plausible explanation is the following: the orientation of the adsorbate probably plays a larger role when the adsorbate is close to the atoms of the MOF and in smaller pores, the adsorbate is more often close to the MOF atoms. An overestimation may then result from grid points where the external potential calculated with PC-SAFT predicts a grid point where adsorbate molecules are allowed but where no orientation would allow N\(_2\).

In Fig. 5c and 5d, we can observe that similar conclusions can be drawn for CO\(_2\): the Henry coefficient is mispredicted by cDFT for strong MOF-CO\(_2\) interactions and small maximal pore sizes. cDFT underestimates the Henry coefficient for stronger MOF-CO\(_2\) interactions, whereas the Coulombic interactions are included for CO\(_2\). A possible explanation
is that the stronger the Coulombic interactions, the more likely the sampling algorithm for the Coulombic interactions (described in the Supplementary Materials S1B) is to miss the optimal orientation, leading to interactions that are less strong than they should be. Concerning the effect of the small pores, a similar explanation could be given here as for N$_2$ with smaller pores leading to most adsorbate molecules being closer to MOF surfaces where orientations of adsorbates matter more, leading in this case to underestimation of the Henry coefficients. Plots similar to Fig. 5 for the comparison at high pressure are discussed in the Supplementary Materials Sec. S5.

The non-inclusion of the orientations in cDFT seems to be one of the main causes of the discrepancies with GCMC. Taking into account the orientations of the molecules is possible for the calculation of the external potential $V_{k \text{ext}}^\text{ext}(r)$ with the method used for CO$_2$ and the calculations of Coulombic interactions. However, as shown in Fig. S2a does not lead to better predictions overall and comes at the cost of computational power. Including the orientations of the molecules during the minimization of the grand potential, where the external potential is fixed, is doable [57] but would require additional efforts to implement and is out-of-the scope of this paper. The discrepancy encountered when Coulombic interactions are strong is also problematic because in applications such as Direct Air Carbon Capture and Storage (DACCs), strong Coulombic interactions may be necessary to capture the diluted CO$_2$. For this case, we can see in Fig. 3, that even if strong Coulombic interactions are mispredicted, the trend is still captured by cDFT. However, if correcting these deviations is necessary, a finer sampling of orientations in the calculation of the external potential could be performed, or GCMC calculations could be run for these particular cases.

In a screening framework, a tradeoff between accuracy and computational cost is necessary and we think that the cDFT framework presented here is an interesting option with a small loss of accuracy and a significant decrease in computational cost. A first preselection could be performed with cDFT and a refined estimation of adsorption properties could be made subsequently with GCMC. However, to study specific adsorption mechanisms of an adsorbate in a porous material (e.g., [58]), GCMC simulations would remain the preferable option as cDFT lacks the resolution to study these mechanisms.
VI. CONCLUSIONS

In this paper, we validate that classical density functional theory (cDFT) is an accurate and efficient method for adsorbent property prediction in the screening of porous materials for a wide range of MOFs with CH$_4$, N$_2$ and CO$_2$ as the adsorbates. For CO$_2$, we introduce the calculations of Coulombic interactions to accurately describe the interactions between the MOF and the guest molecule in the cDFT framework. We show that with this cDFT framework, GCMC calculations of adsorption isotherms of over 500 MOFs can closely be reproduced when CH$_4$ is the adsorbate, and reasonably well when N$_2$ and CO$_2$ are the adsorbates. The enthalpy of adsorption is also well reproduced with the added benefit that cDFT calculations exhibit very low numerical uncertainty. In addition to reproducing GCMC results, cDFT runs between 42 and 15,000 times faster, predominantly depending on the volume of the unit cell of the porous material.

These properties pave the way for cDFT to be used in process optimization, where the loading is often computed using empirical extrapolation models to new conditions of pressures, temperatures, and compositions. cDFT could also be used to design porous materials since the computation time for obtaining adsorption properties is low.

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VIII. SUPPLEMENTARY INFORMATION

The codes developed for this work are available on GitLab:

https://gitlab.ethz.ch/epse/molecular-design-public/paper-3d_dft

A. New feature description

1. Non-orthorhombic cells

The non-orthorhombic unit cell can be defined by the angles $\alpha$, $\beta$, and $\gamma$ between the skewed axes with unit vectors $\vec{e}_u$, $\vec{e}_v$, and $\vec{e}_w$. A point $\mathbf{s} = \left( u \ v \ w \right)^\top$ in the skewed coordinate system can be transformed into Cartesian coordinates using the transform [60]:

$$
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} =
\begin{pmatrix}
  1 & \cos \gamma & \cos \beta \\
  0 & \sin \gamma & \zeta \\
  0 & 0 & \sqrt{1 - \cos^2 \beta - \zeta^2}
\end{pmatrix}
\begin{pmatrix}
  u \\
  v \\
  w
\end{pmatrix}
\quad \text{with} \quad \zeta = \frac{\cos \alpha - \cos \beta \cos \gamma}{\sin \gamma}.
$$

(5)

Here, $u$, $v$, and $w$ are not scaled by the length of the unit cell in the respective direction but use the same metric as the Cartesian coordinates $x$, $y$, and $z$. Fast Fourier transform (FFT) is used to rapidly evaluate a convolution integral of the form:

$$
f \otimes g = \int f(\mathbf{r}')g(\mathbf{r})d\mathbf{r}' = \mathcal{F}^{-1}(\mathcal{F}(f)\mathcal{F}(g)),
$$

(6)

with the Fourier transform

$$
\mathcal{F}(f) = \int f(\mathbf{r})e^{-2\pi i \mathbf{k} \cdot \mathbf{r}}d\mathbf{r},
$$

(7)

and its inverse

$$
\mathcal{F}^{-1}(f) = \int f(\mathbf{k})e^{2\pi i \mathbf{k} \cdot \mathbf{r}}d\mathbf{k}.
$$

(8)

The FFT is crucial for an efficient implementation of cDFT, because it reduces the complexity of the convolution integrals from $\mathcal{O}(n^2)$ to $\mathcal{O}(n \log n)$. However, the frequency values $\mathbf{k}$ at which the transformation is evaluated cannot be chosen arbitrarily. If an FFT is evaluated in the skewed coordinate system $\mathbf{s}$, the resulting $\mathbf{k}_s$ values are also skewed. To calculate a convolution with an analytic weight function, the axes in frequency space must be transformed into a Cartesian coordinate system. This transformation is done by aligning...
the phases $\mathbf{k}_r \cdot \mathbf{r} = \mathbf{r}^\dagger \mathbf{k}_r$ and $\mathbf{k}_s \cdot \mathbf{s} = \mathbf{s}^\dagger \mathbf{k}_s$ of the Fourier transform. Using the coordinate transform in real space $\mathbf{r} = \mathbf{Hs}$ or $\mathbf{r}^\dagger = \mathbf{s}^\dagger \mathbf{H}^\dagger$, the following relation is obtained:

$$\mathbf{s}^\dagger \mathbf{k}_s = \mathbf{r}^\dagger \mathbf{k}_r = \mathbf{s}^\dagger \mathbf{H}^\dagger \mathbf{k}_r \quad \Rightarrow \quad \mathbf{k}_s = \mathbf{H}^\dagger \mathbf{k}_r \quad \Rightarrow \quad \mathbf{k}_r = (\mathbf{H}^\dagger)^{-1} \mathbf{k}_s. \quad (9)$$

The values $\mathbf{k}_s = \left( k_u, k_v, k_w \right)^\dagger$ are determined by the FFT. The values of $\mathbf{k}_r = \left( k_x, k_y, k_z \right)^\dagger$ are then determined from Eqs. (6) and (9) as:

$$k_x = k_u \quad (10)$$
$$k_y = \frac{1}{\sin \gamma} \left( k_v - k_u \cos \gamma \right) \quad (11)$$
$$k_z = \frac{1}{\sqrt{1 - \cos^2 \beta - \zeta^2}} \left( k_u \left( \frac{\zeta \cos \gamma}{\sin \gamma} - \cos \beta \right) - k_v \frac{\zeta}{\sin \gamma} + k_w \right). \quad (12)$$

Integrating in a skewed coordinate system also introduces a constant factor that stems from the Jacobian determinant:

$$d\mathbf{r} = \text{det} (\mathbf{H}) \, d\mathbf{s} \quad \text{with} \quad \text{det} (\mathbf{H}) = \sin \gamma \sqrt{1 - \cos^2 \beta - \zeta^2}. \quad (13)$$

For the calculation of convolution integrals, the constant factor can be ignored because it cancels out during the inverse transform in which:

$$d\mathbf{k}_r = \text{det} \left( (\mathbf{H}^\dagger)^{-1} \right) \, d\mathbf{k}_s = \frac{1}{\text{det} (\mathbf{H})} \, d\mathbf{k}_s. \quad (14)$$

is used. When integrating distributed properties over the unit cell (evaluating a Fourier transform at $\mathbf{k} = \mathbf{0}$), however, the Jacobian determinant must be accounted for.

2. Coulombic interactions in external potential

Here, we describe the algorithm that is used to obtain the external potential at a position $\mathbf{r}$ when Coulombic interactions are considered. The detailed algorithm can be found in the code provided in the GitHub repository given above.
for each MOF atom a do
    dir\_atoms\[a\] = pos\_a - r;
    compute energy adsorbate centered on r pointing to a for Lennard-Jones $E^{LJ}_{r,a}$ and Coulombic $E^{Coul}_{r,a}$ interactions;
end

$dir^{LJ}_1 = dir\_atoms[\text{argsort}(E^{LJ}_{r,a})[0]]$;
$dir^{LJ}_2 = dir\_atoms[\text{argsort}(E^{LJ}_{r,a})[1]]$;
$dir^{LJ} = \text{cross}(dir^{LJ}_1, dir^{LJ}_2)$;

$dir^{Coul}_{pos} = \text{WeightedPCA}(dir\_atoms[\text{where}_a(E^{Coul}_{a,r} > 0)], \text{boltzmann}(E^{Coul}_{a,r}[\text{where}_a(E^{Coul}_{a,r} > 0)]))$;
$dir^{Coul}_{neg} = \text{WeightedPCA}(dir\_atoms[\text{where}_a(E^{Coul}_{a,r} < 0)], \text{boltzmann}(E^{Coul}_{a,r}[\text{where}_a(E^{Coul}_{a,r} < 0)]))$;
frac\_pos = sum(|$E^{Coul}_{a,j}$[\text{where}_a(E^{Coul}_{a,r} > 0)]|)/sum(|$E^{Coul}_{a,r}$|);
frac\_neg = sum(|$E^{Coul}_{a,j}$[\text{where}_a(E^{Coul}_{a,r} < 0)]|)/sum(|$E^{Coul}_{a,r}$|);
proj\_neg\_dir\_on\_pos\_plane = projection(dir\_neg\_Coul, dir\_pos\_Coul);
dir\_Coul = frac\_neg * dir\_neg\_Coul + frac\_pos * proj\_neg\_dir\_on\_pos\_plane;

energies\_temp = zeros(10);
for j in range(10) do
    dir\_temp = j/10 * dir^{LJ} + (1 - j/10) * dir^{Coul};
    compute total energy adsorbate $E_j$ molecule in direction dir\_temp;
    energies\_temp = $E_j$
end

**Algorithm 1:** Algorithm to compute external potential when Coulombic interactions are considered.

For the case where Coulombic interactions are included for CO$_2$, the following method is used: at a position $r$, we search for the orientation of the adsorbate molecule that would give the most favorable interactions. For this purpose, we noticed that the Coulombic interactions between an adsorbate molecule and an atom of the MOF are, in general, larger in magnitude than the Lennard-Jones interactions, except when one atom of the adsorbate
molecule is too close to the atom of the MOF. From this observation, we concluded that the
Lennard-Jones interactions forbid some orientations while the Coulombic interactions push
to a favorable orientation. Therefore, we compute two directions: an approximate optimal
direction for Lennard-Jones interactions which are away from the 'most forbidden directions'
and an approximate optimal direction for Coulombic interactions. We then compute the sum
of Lennard-Jones and Coulombic interactions in 10 directions between the two computed
optimal directions and retain the minimum energy for these 10 calculations.

For the optimal direction for Lennard-Jones interactions, we compute the Lennard-Jones
interaction of the adsorbate molecule pointing toward each of the atoms of the MOFs. The
two highest interactions define the two directions that are the less favorable. We approximate
a non-favorable direction to a favorable plane, meaning that the adsorbate molecule will be
attracted to the plane perpendicular to the non-favorable direction. By taking the cross
product of the two directions that are the less favorable, we obtain the intersection of the
two 'favorable' planes, which is set to be the approximate optimal direction for Lennard-
Jones.

For the optimal direction for Coulombic interactions, we compute the Coulombic inter-
action of the adsorbate molecule pointing toward each of the atoms of the MOFs. The
Boltzmann average of all the favorable orientations is calculated with a weighted Principal
Component Analysis (wPCA). The Boltzmann average of all the unfavorable orientations
is also calculated with a wPCA. The approximated optimal direction for Coulombic inter-
actions is then the weighted average of the favorable direction and the projection of this
favorable direction on the plane perpendicular to the unfavorable direction. The weight of
the favorable and unfavorable directions is the fraction of the total Boltzmann energy of,
respectively, the favorable and unfavorable interactions.

To save computational power, this algorithm is only computed when the position \( \mathbf{r} \) is at a
distance higher than 2 Å\(^{-1} \) from any point of the MOF, since if it is closer than this distance,
the interaction energy at this position would be too high for a molecule to be adsorbed at
this position. For positions at a distance of less than 2 Å\(^{-1} \), a value of 50 kJ mol\(^{-1} \) is given
to the external potential, which is high enough that it does not affect the loading.

To demonstrate the accuracy of our algorithm, we compare the values of the external
potential of 3 MOFs obtained either with our algorithm or by using the Boltzmann average
of the energy sampled every 20\(^\circ \) for the two angles in spherical coordinates (called 'External
FIG. 6. Comparison of the external potential calculated at each grid point with the algorithm proposed here and the full sampling of molecule’s orientations. The adsorbate molecule is always CO$_2$ and the MOFs are MAGVOG02 (a), GUKXIU (b), and BUSQIQ (c). For clarity, only grid points where at least one of the calculations had a value below 35 kJ/mol are shown. A potential above this value means that the grid point is close to an atom of the MOF and the external potential can have very high values.

We observe in Fig. 6 that these computations match reasonably well, while our algorithm is between 30 and 170 times faster for the MOFs considered here. Our algorithm tends to overestimate slightly the external potential, which is logical as it samples less directions for the gas molecule as the full sampling. Therefore,
it can miss directions with strong interactions with the MOF. It should be pointed out that the algorithm presented here has only been tested for linear adsorbates but could show some limitations for non-linear adsorbates. A full sampling approach might be necessary for non-linear adsorbates which would come at the cost of computational power.

3. Enthalpy of adsorption calculation with cDFT

The isosteric enthalpy of adsorption of component $j$ is defined as:

$$\Delta h_{\text{ads}}^j = h_j^b - \left( \frac{\partial U}{\partial N_j} \right)_{T,N_i \neq j}, \quad (15)$$

with the partial molar enthalpy of component $j$ in the bulk phase $h_j^b$, the composition of the bulk phase $x_j$, the internal energy of the fluid in the porous medium $U$, the number of particles in the porous medium $N_j$. The solid material is assumed to be rigid and therefore, the volume of the porous medium is not considered a variable. Using $h_j^b = T s_j^b + \mu_i$ and $dU = T dS + \sum_i \mu_i dN_i$, the chemical potential can be canceled out from the contributions of the bulk phase and the inhomogeneous system, leading to:

$$\Delta h_{\text{ads}}^j = T \left( s_j^b - \left( \frac{\partial S}{\partial N_j} \right)_{T,N_i \neq j} \right). \quad (16)$$

The partial derivative of the entropy $S$ can then be replaced using a Maxwell relation based on the Helmholtz energy $F$ as follows:

$$\left( \frac{\partial S}{\partial N_i} \right)_{T,N_j} = - \left( \frac{\partial^2 F}{\partial T \partial N_i} \right)_{N_k} = - \left( \frac{\partial \mu_i}{\partial T} \right)_{N_k}, \quad (17)$$

which leads to an expression for the enthalpy of adsorption without caloric properties of the adsorbed fluid:

$$\Delta h_{\text{ads}}^i = T \left( s_i^b + \left( \frac{\partial \mu_i}{\partial T} \right)_{N_k} \right). \quad (18)$$

To evaluate the enthalpy of adsorption with classical DFT, which uses temperatures and chemical potentials to define states, the derivative at constant number of particles must be replaced. This is done starting from the total differential of the number of particles:

$$dN_i = \sum_j \left( \frac{\partial N_i}{\partial \mu_j} \right)_T d\mu_j + \left( \frac{\partial N_i}{\partial T} \right)_{\mu_k} dT. \quad (19)$$
Calculating the derivative with respect to $T$ at constant $N_i$ leads to:

$$0 = \sum_j \left( \frac{\partial N_i}{\partial \mu_j} \right)_T \left( \frac{\partial \mu_j}{\partial T} \right)_{N_k} + \left( \frac{\partial N_i}{\partial T} \right)_{\mu_k},$$  \hspace{1cm} (20)

down from which the unknown derivative $\left( \frac{\partial \mu_j}{\partial T} \right)_{N_k}$ can be calculated. In practice, the expression has the disadvantage that $\left( \frac{\partial N_i}{\partial T} \right)_{\mu_k}$ depends on the (sometimes unknown) thermal de Broglie wavelength, which later cancels with $s^b_j$. This can be remedied by calculating the derivative of Eq. (19) with respect to $T$ at constant (bulk) pressure and composition:

$$\left( \frac{\partial N_i}{\partial T} \right)_{p,x} = \sum_j \left( \frac{\partial N_i}{\partial \mu_j} \right)_T \left( \frac{\partial \mu_j}{\partial T} \right)_{p,x} + \left( \frac{\partial N_i}{\partial T} \right)_{\mu_k}. \hspace{1cm} (21)$$

From classical bulk thermodynamics, we know $\left( \frac{\partial \mu_j}{\partial T} \right)_{p,x} = -s^b_j$ and therefore, Eq. (21) can be used in Eq. (20) to give:

$$0 = \sum_j \left( \frac{\partial N_i}{\partial \mu_j} \right)_T \left( s^b_j + \left( \frac{\partial \mu_j}{\partial T} \right)_{N_k} \right) + \left( \frac{\partial N_i}{\partial T} \right)_{p,x_k}. \hspace{1cm} (22)$$

After multiplying with $T$, the expression shown in the main manuscript remains:

$$0 = \sum_j \left( \frac{\partial N_i}{\partial \mu_j} \right)_T \Delta h^\text{ads}_j + T \left( \frac{\partial N_i}{\partial T} \right)_{p,x_k}. \hspace{1cm} (23)$$

Due to $\left( \frac{\partial N_i}{\partial \mu_j} \right)_T = -\left( \frac{\partial^2 \Omega}{\partial \mu \partial \mu_j} \right)_T$, Eq. (23) is a symmetric linear system of equations. The derivatives of the particle numbers are obtained by integrating over the respective derivatives of the density profiles, which are discussed in the following section.

4. Derivatives of density profiles

For converged density properties, equilibrium properties can be calculated as partial derivatives of thermodynamic potentials analogous to classical (bulk) thermodynamics. The density profiles are calculated implicitly from the Euler-Lagrange equation, which can be simplified to:

$$\Omega_{\rho_i}(T, \{\mu_k\}, \{\rho_k(r)\}) = F_{\rho_i}(T, \{\rho_k(r)\}) - \mu_i + V_i^\text{ext}(r) = 0. \hspace{1cm} (24)$$

The derivatives of the density profiles can then be calculated from the total differential of Eq. (24), leading to:
\[
d\Omega_{\rho_i}(r) = \left(\frac{\partial \Omega_{\rho_i}(r)}{\partial T}\right)_{\mu_k, \rho_k} dT + \sum_j \left(\frac{\partial \Omega_{\rho_i}(r)}{\partial \mu_j}\right)_{T=\mu_k, \rho_k} d\mu_j + \int \sum_j \left(\frac{\delta \Omega_{\rho_i}(r)}{\delta \rho_j(r')}\right)_{T=\mu_k, \rho_k} \delta \rho_j(r') dr' = 0.
\]

Using Eq. (24) and the shortened notation for derivatives of functionals in their natural variables, e.g., \( F_T = \left(\frac{\partial F}{\partial T}\right)_{\rho_k} \), the expression can be simplified to:

\[
F_{T\rho_i}(r) dT - d\mu_i + \int \sum_j F_{\rho_i\rho_j}(r, r') \delta \rho_j(r') dr' = 0. \tag{25}
\]

Similar to the Gibbs-Duhem relation for bulk phases, Eq. (25) shows how temperature, chemical potentials, and density profiles in an inhomogeneous system cannot be varied independently. The derivatives of the density profiles with respect to the intensive variables can be directly identified as:

\[
\int \sum_j F_{\rho_i\rho_j}(r, r') \left(\frac{\partial \rho_j(r')}{\partial T}\right)_{\mu_k} dr' = -F_{T\rho_i}(r), \tag{26}
\]

and

\[
\int \sum_j F_{\rho_i\rho_j}(r, r') \left(\frac{\partial \rho_j(r')}{\partial \mu_k}\right)_{T} dr' = \delta_{ik}. \tag{27}
\]

Both of these expressions are implicit (linear) equations for the derivatives. In practice, it is useful to explicitly cancel out the (often unknown) thermal de Broglie wavelength \( \Lambda_i \) from the expression, where it has no influence. This is done by splitting the intrinsic Helmholtz energy into an ideal gas and a residual part:

\[
F = k_B T \int \sum_i m_i \rho_i(r) \left(\ln (\rho_i(r) \Lambda_i^3) - 1\right) dr + \hat{F}^{\text{res}}. \tag{28}
\]

Then, \( F_{\rho_i\rho_j}(r, r') = m_i \frac{k_B T}{\rho_i(r)} \delta_{ij} (r - r') + \hat{F}^{\text{res}}_{\rho_i\rho_j}(r, r') \) and Eq. (27) can be rewritten as:

\[
m_i \frac{k_B T}{\rho_i(r)} \left(\frac{\partial \rho_i(r)}{\partial \mu_k}\right)_{T} + \int \sum_j \hat{F}^{\text{res}}_{\rho_i\rho_j}(r, r') \left(\frac{\partial \rho_j(r')}{\partial \mu_k}\right)_{T} dr' = \delta_{ik}. \tag{29}
\]

In practice, the division by the density should be avoided for numerical reasons and the energetic properties are reduced with the factor \( \beta = \frac{1}{k_B T} \). The final expression is:

\[
m_i \left(\frac{\partial \rho_i(r)}{\partial \beta \mu_k}\right)_{T} + \rho_i(r) \int \sum_j \beta \hat{F}^{\text{res}}_{\rho_i\rho_j}(r, r') \left(\frac{\partial \rho_j(r')}{\partial \beta \mu_k}\right)_{T} dr' = \rho_i(r) \delta_{ik}. \tag{30}
\]

For the temperature derivative, it is more convenient to express Eq. (25) in terms of the pressure of a bulk phase that is in equilibrium with the inhomogeneous system. In the
following, only paths along constant bulk composition are considered. With this constraint, the total differential of the chemical potential simplifies to:

$$d\mu_i = -s_i dT + v_i dp,$$

which can be used in Eq. (25) to give:

$$(F^*_T(r) + s_i) dT + \int \sum_j F^*_{r_ji}(r, r') \delta \rho_j(r') dr' = v_i dp.$$

(31)

It is useful at this point to rewrite the partial molar entropy as:

$$s_i = v_i \left( \frac{\partial p}{\partial T} \right)_{V,Nk} - F^*_T(r) + \int \sum_j \hat{F}^*_{r_ji}(r, r') \delta \rho_j(r') dr'$$

(32)

Then, the intrinsic Helmholtz energy can be split into an ideal gas and a residual part again, and the de Broglie wavelength cancels:

$$m_i k_B \ln \left( \frac{\rho_i(r)}{\rho^b_i} \right) + F^*_{T\rho_i}(r) - F^*_{T\rho_i}^{b,\text{res}} + v_i \left( \frac{\partial p}{\partial T} \right)_{V,Nk} dT + m_i \frac{k_B T}{\rho_i(r)} \delta \rho_i(r) + \int \sum_j \hat{F}^*_{r_ji}(r, r') \delta \rho_j(r') dr' = v_i dp.$$

(33)

Finally, the expressions for the derivatives with respect to pressure:

$$m_i \left( \frac{\partial \rho_i(r)}{\partial \beta p} \right)_{T,x} + \rho_i(r) \int \sum_j \beta \hat{F}^*_{r_ji}(r, r') \left( \frac{\partial \rho_j(r')}{\partial \beta p} \right)_{T,x} dr' = v_i \rho_i(r),$$

(34)

and temperature

$$m_i \left( \frac{\partial \rho_i(r)}{\partial T} \right)_{p,x} + \rho_i(r) \int \sum_j \beta \hat{F}^*_{r_ji}(r, r') \left( \frac{\partial \rho_j(r')}{\partial T} \right)_{p,x} dr' = -\frac{\rho_i(r)}{k_B T} \left( m_i k_B \ln \left( \frac{\rho_i(r)}{\rho^b_i} \right) + F^*_{T\rho_i}(r) - F^*_{T\rho_i}^{b,\text{res}} + v_i \left( \frac{\partial p}{\partial T} \right)_{V,Nk} \right)$$

(35)

follows. All derivatives $X_i$ shown here can be calculated from the same linear equation:

$$m_i X_i + \rho_i(r) \int \sum_j \beta \hat{F}^*_{r_ji}(r, r') X_i dr' = Y_i$$

(36)

by just replacing the right-hand side $Y_i$.

**B. Definition of cDFT parameters**

1. **Other parameters to define for cDFT calculations**

Following the setup used for the GCMC simulations, a cutoff of 12 Å is set for the Lennard-Jones interactions, Lorentz-Berthelot combining rules are used for solid-fluid interactions,
TABLE II. Derivatives of the density profile ρ with different variables.

<table>
<thead>
<tr>
<th>derivative</th>
<th>right hand side</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\partial \rho_i(r)}{\partial \beta_{\mu_k}} ) ( T )</td>
<td>( \rho_i(r) \delta_{ik} )</td>
</tr>
<tr>
<td>( \frac{\partial \rho_i(r)}{\partial \beta_{P_k}} ) ( T,x )</td>
<td>( \rho_i(r) v_i )</td>
</tr>
<tr>
<td>( \frac{\partial \rho_i(r)}{\partial T} ) ( p,x )</td>
<td>( -\frac{\rho_i(r)}{k_B T} \left( m_i k_B \ln \left( \frac{\rho_i(r)}{\rho_i^c} \right) + F^{\text{res}}<em>{T \rho_i}(r) - F^{\text{b, res}}</em>{T \rho_i} + v_i \left( \frac{\partial p}{\partial T} \right)_{V,N,k} \right) )</td>
</tr>
</tbody>
</table>

TABLE III. Table with the solver setups used for cDFT. For parameters not explicitly given, the defaults in the software FeOs are used [37].

<table>
<thead>
<tr>
<th>Order</th>
<th>Sequence of algorithms</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Picard Iteration</td>
<td>Damping coeff = 0.01, Max iteration = 50</td>
</tr>
<tr>
<td></td>
<td>Picard Iteration</td>
<td>Damping coeff = 0.1, Tolerance = 1e-5</td>
</tr>
<tr>
<td></td>
<td>Anderson Mixing</td>
<td>Mmax = 10, Tolerance = 1e-8</td>
</tr>
<tr>
<td>2</td>
<td>Newton</td>
<td>Tolerance = 1e-8</td>
</tr>
<tr>
<td>3</td>
<td>Picard line search</td>
<td>Log=True, Max iter = 2000</td>
</tr>
<tr>
<td>4</td>
<td>Picard Iteration</td>
<td>Damping coeff = 0.005, Max iteration = 2000</td>
</tr>
<tr>
<td></td>
<td>Picard Iteration</td>
<td>Damping coeff = 0.01, Tolerance = 1e-5</td>
</tr>
<tr>
<td></td>
<td>Anderson Mixing</td>
<td>Mmax = 10, Tolerance = 1e-8</td>
</tr>
</tbody>
</table>

and tail corrections are included. Ewald summation [61] is used for Coulombic interactions in GCMC, whereas a cutoff of 30 Å is used for cDFT. Four solver setups are considered to minimize the grand potential. These solver setups are used in a hierarchical order, if the previous solver setup failed to converge. These four solver setups are described in Table VIII.B1 and are used in the order they appear in the table. It is possible that the 4 solver setups fail. In this event, these cases are reported and these failures are discussed.

2. Coulombic and PC-SAFT parameters definitions

As discussed in the manuscript, the adsorbate molecules can be described with different parameters, the two most important ones being the inclusion or not of Coulombic interactions and the PC-SAFT parameters used. We consider here two sets of PC-SAFT parameters:
the initial set of PC-SAFT parameters developed in 2001 by Gross and Sadowski [40], which do not include the multipolar term of Eq. 1 in the main manuscript (called here 'PC-SAFT Non-polar'), and the polar set of PC-SAFT parameters developed in 2005 by Gross [48], which include the multipolar term of Eq. 1 in the main manuscript (called here 'PC-SAFT Polar').

As \( \text{CH}_4 \) is not a polar molecule, no Coulombic interactions will be considered. In addition, the non-polarity also means that no polar set of PC-SAFT parameters were developed for \( \text{CH}_4 \). Therefore, \( \text{CH}_4 \) is described with the 'PC-SAFT Non-polar' set of parameters throughout the manuscript [40]. As \( \text{N}_2 \) and \( \text{CO}_2 \) can both have some polarity effects, through a quadrupole moment, the inclusion or not of Coulombic interactions and the choice of PC-SAFT parameters will be studied by comparing the MARD (as defined in the manuscript by Eq. 2) for adsorption isotherms and enthalpy of adsorption, the runtime to get these values, and the number of times the solvers fail. This study is performed on 100 MOFs randomly selected in the database, with the 100 MOFs being the same for \( \text{N}_2 \) and \( \text{CO}_2 \). The results are shown in Fig. 7.

For \( \text{N}_2 \), the set of PC-SAFT parameters does not make a difference for any of the metrics, probably since the quadrupolarity of \( \text{N}_2 \) is negligible, so the non-polar parameters [40] are chosen for simplicity. Adding the Coulombic interactions increases the MARD for the adsorption isotherms and slightly decreases the MARD for the enthalpy of adsorption. The increase in MARD for the adsorption isotherms may be surprising as adding Coulombic interactions should be a more precise description. To understand better what is happening, we show the Mean Relative Deviation (MRD) of the cDFT calculations with the GCMC reference in Fig. 8. This MRD corresponds to the MARD of Eq. 4 without the absolute value at the numerator and can give insights if cDFT is overestimating or underestimating GCMC at the cost of a possible error cancellation. In Fig. 8, we observe that even without Coulombic interactions, cDFT predictions slightly overestimate the loading compared to GCMC calculations. Adding Coulombic interactions, increases the overprediction and make the MARD and MRD worse. The fact that cDFT slightly overpredicts GCMC without Coulombic interactions, may come from the PC-SAFT parameters already containing some Coulombic interactions implicitly by increasing the dispersion term. The reduction of the MARD for the enthalpy of adsorption can be explained by the fact that the external potential calculations match more closely the energies in GCMC as the TraPPE potential is used
FIG. 7. Cumulative plots for the MARD for the adsorption isotherms (left) and the enthalpy of adsorption (middle) and runtime (right) for 4 parameter sets for N$_2$ (a) and CO$_2$ (b). 100 MOFs are used here. For the MARD of the enthalpy of adsorption, some deviations are much higher than 100% and are not shown here for clarity of the visualization. This high deviation will be discussed in Section VII B 3. For N$_2$, all the pressures converged when no Coulombic interactions were used, and only 0.01% of them did not converge when no Coulombic interactions were used. For CO$_2$, all calculations converged and 'PC-SAFT Polar, Coulomb' whereas only 0.01%, 0.01%, and 0.02% of all calculations did not converge for, respectively, the 'PC-SAFT Non-Polar, Coulomb', the 'PC-SAFT Polar, no Coulomb' and 'PC-SAFT Non-polar, No Coulomb' cases.
FIG. 8. Histogram of the MRD of cDFT calculations using GCMC as the reference for the adsorption isotherms of N$_2$ for the four parameters sets. Without the Coulombic interactions, the cDFT calculations overpredicts slightly the GCMC calculations and adding Coulombic interactions increases this overprediction.

to calculate the external potential. As less computation time is needed for the calculation of the external potential, the cases without Coulombic interactions are faster. We choose to use no Coulombic interactions for N$_2$ as it runs faster, converges more often, and gives a reduced MARD for adsorption isotherms, and only slightly greater MARD for enthalpy of adsorption.

We choose to describe CO$_2$ with Coulombic interactions and the 'PC-SAFT polar' set of parameters as this case has reduced MARD for adsorption isotherms and enthalpy of adsorption, and all calculations converged. These observations occur because CO$_2$ can have strong Coulombic interactions that change the adsorption properties. The run time is higher but not unreasonable and this additional computational cost increases the accuracy. The case with Coulombic interactions and 'PC-SAFT polar' set of parameters for CO$_2$ displays 1 MOFs with MARD for the enthalpy of adsorption higher than 100% and these cases will be discussed in Sec. VIIIB3.

3. Grid density study

The main parameter of cDFT that defines the trade-off between accuracy and computational cost is the density of grid points: more grid points result in higher accuracy but also
FIG. 9. Study of the effect of a change in grid density on (a) the adsorption isotherms, (b) enthalpy of adsorption, (c) percentage of converged cDFT calculations, and (d) run time of the cDFT calculations. For (a) and (b), the MARD of cDFT with GCMC calculations of the curves (adsorption isotherms or enthalpy of adsorption) between two subsequent values of grid density is shown. A MARD of 0 would mean that no evolution of values is observed when increasing the grid density.

in higher computational cost. To find the best balance, we study the effect of various grid densities (between 1 and 3 Å⁻¹) on the run time of an adsorption isotherm, the accuracy of adsorption isotherm and enthalpy of adsorption predictions, and the percentage of converged optimizations. This study is performed on the same set of 100 MOFs as in Section VIII B 2, with the 3 adsorbate molecules, at 298 K, with the parameters mentioned in Sec. VIII B 2. The objective of this study is to determine the minimum number of grid points required
to effectively prevent any subsequent changes in the outcomes as the grid point density increases. The evolution of the MARD between cDFT and GCMC of two subsequent values of grid points will be computed with Eq. 2 with the reference being the higher grid point density. The results are presented in Fig. 9.

FIG. 10. Examples of enthalpy of adsorption curves where cDFT suddenly displays a substantial error. As these changes are sudden and of significant magnitude, we assume that they are due to numerical errors during the cDFT optimization. Increasing the grid density reduces the probability of these sudden deviations to appear.

For the adsorption isotherms in Fig. 9a, the MARD changes by less than 5.5% from 2 Å⁻¹ to 2.5 Å⁻¹ and by less than 3.2% from 2.5 Å⁻¹ to 3 Å⁻¹. The maximum evolution between 2 Å⁻¹ and 3 Å⁻¹ is 6.2%. This observation makes 2 Å⁻¹ a reasonable density to offer good
accuracy for adsorption isotherms in most cases. For the case of the enthalpy of adsorption in Fig. 9b, there are several systems that show substantial evolutions between 2 Å$^{-1}$ and 2.5 Å$^{-1}$. These cases actually have unreasonable values for the enthalpy of adsorption at specific pressures (see Fig. 10). As these large deviations are sudden and abrupt, we assume that they are due to numerical errors during the optimization phase of cDFT. However, these significant deviations can easily be detected and corrected by increasing the density of grid points in most cases.

Fig. 9c shows the percentage of cDFT simulations that do not converge. At a grid density of 2 Å$^{-1}$, only 0.4% of simulations do not converge. The simulations that do not converge are not equally shared between systems; out of the 300 systems, 297 of them have convergence for all the pressures of the adsorption isotherms. Further studies of optimization computations could help increase the number of convergence cases.

In Fig. 9d, the run times of whole adsorption isotherms at different grid densities are shown. Doubling of the grid density approximately multiply by 10 the computational time. In addition, the run time also depends on the system: the run time is proportional to the MOF unit cell volume as for larger unit cells, more grid points are needed, which increases the computational time.

Overall, a grid density of 2 Å$^{-1}$ was selected because, at this value, the deviation with GCMC does not change by more than 5.5% for the adsorption isotherms, requires a relatively short run time (median time of approximately 5 min), and experiences a low percentage of convergence failure. However, as this grid density may still display substantial numerical errors in the calculations of the enthalpies of adsorption, we set a criterion to detect these substantial numerical errors and re-run the whole isotherm with a grid density 0.5 Å$^{-1}$ higher until a grid density of 4 Å$^{-1}$. At this grid density, the majority of the enthalpies of adsorption display expected behavior, and the cases where it is not the case will be discussed in the manuscript (Sec. 4C). A criterion of a change of less than 10 kJ mol$^{-1}$ of the enthalpy of adsorption between two consecutive pressures was implemented.
C. Additional temperatures

FIG. 11. MARD for the adsorption isotherms of CO$_2$ and N$_2$ at four temperatures. No significant effect of temperature can be observed on the deviation of the cDFT calculations of the adsorption isotherms compared with the ones computed with GCMC.
FIG. 12. MARD for the enthalpy of adsorption of CO$_2$ and N$_2$ at four temperatures. No significant effect of temperature can be observed on the deviation of the cDFT calculations of the enthalpies of adsorption compared with the ones computed with GCMC. For CO$_2$ and N$_2$ respectively, 6/200 and 1/195 cases have MARD higher than 50%.

D. Henry coefficients and high pressure regime

FIG. 13. Log-log parity plot for the Henry coefficients predicted by cDFT $K_{H}^{cDFT}$ versus by GCMC $K_{H}^{GCMC}$ for the three molecules (CH$_4$, N$_2$, CO$_2$). Each point corresponds to one MOF. The cDFT predictions of the Henry coefficient perfectly matches the GCMC results for CH$_4$ and are in good agreement for N$_2$ and CO$_2$.

Henry coefficients computed by cDFT $K_{H}^{cDFT}$ are compared with the ones obtained with
FIG. 14. Histogram of the maximum loading MRD predicted by cDFT versus by GCMC for the three molecules (CH$_4$, N$_2$, CO$_2$). The cDFT predictions of high pressure regime perfectly matches the GCMC results for CH$_4$ and are in good agreement for N$_2$ and CO$_2$.

GCMC $K_{H}^{GCMC}$. In this case, the deviation metric is the ratio of the Henry coefficients $K_{H}^{cDFT}/K_{H}^{GCMC}$. Fig. 13 compares of the Henry coefficients calculated with cDFT with the ones computed with GCMC. For CH$_4$, cDFT Henry coefficients almost perfectly match the ones from GCMC with 97% of the Henry coefficients deviating by less than 10%. For N$_2$ and CO$_2$, cDFT calculations differ a bit more, with respectively 5% and 16% of the Henry coefficients deviating by more than a factor of 2. These deviations should, however, be compared to the large range of values that Henry coefficients can display, as they span 4 orders of magnitude for N$_2$ and 6 orders of magnitude for CO$_2$.

The Henry regime is dominated by the MOF-adsorbate interactions, whereas the high-pressure regime is dominated by the pore geometry of the MOF. In order to check if the cDFT predictions follow the same behavior as GCMC at high pressure, we define a 'Maximum loading MRD', which is the same as the MARD for adsorption isotherms defined in Eq. 4 of the main manuscript, but only considering the points at the highest five pressures and without taking absolute values. We do not take absolute values here so we can know if the maximum loading is overestimated or underestimated. As this behavior is unlikely to change in the high-pressure regime, error cancellation does not occur. In Fig. 14, we can see that even at high pressure, the cDFT loading predictions match very closely the GCMC
calculations, with all the deviations within 10%. For $\text{N}_2$, the cDFT predictions are good too, with 91% of the maximum loading MRD with 15%. For $\text{CO}_2$, it can be observed that cDFT tends to underestimate the loading at high pressure by a median value of -11%, which is still reasonable.

E. High-pressure regime predictor of deviation between cDFT and GCMC

![Image](https://example.com/image1.png)

![Image](https://example.com/image2.png)

![Image](https://example.com/image3.png)

![Image](https://example.com/image4.png)

FIG. 15. Scatter plot of the strongest MOF-$\text{CO}_2$ interactions computed with cDFT ((a) and (c)) and the maximal pore size ((b) and (d)) with the maximum loading MRD between cDFT and GCMC for $\text{N}_2$ ((a) and (b)) and $\text{CO}_2$ ((c) and (d)). The y axes are in logarithm scale. Each point corresponds to one MOF.
In Fig. 15, similar plots to Fig. 4 of the main manuscript are shown, but here for the maximum loading MRD, showing the trends for the high-pressure regime. From Fig. 15a, it also seems that including Coulombic interactions for N$_2$ would be beneficial for the few materials where the maximum loading MRD is underestimated. However, the maximal pore size does not seem to play an important role here. For CO$_2$, no clear trend of the maximum loading MRD with the strongest MOF-CO$_2$ interactions calculated with cDFT can be observed in Fig. 15c. A possible explanation is that over the whole MOF, the Coulombic interactions are, on average, correctly calculated and at high pressures, the adsorbates are loaded over the whole MOF. In contrast, in the Henry regime, only a few grid points would exhibit a significant loading and the deviation of cDFT would depend on how accurately the Coulombic interactions were calculated at these few points. However, a decreasing trend of the maximum loading MRD with the maximum pore size is observed, similar to the one observed in Fig. 4c of the main manuscript.

IX. REFERENCES


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FIG. 16. Table Of Content Graphic