New frontiers in modeling adsorption in metal-organic frameworks accounting for flexibility and accurate intermolecular interactions

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Adsorption technology is essential for important technologies such as energy storage, separation, catalysis. Reticular materials like metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs), have been widely explored for adsorption and separation technologies due to their modular design capabilities.[1] Computational simulations are instrumental to screen large sets of MOFs. One can obtain quantitative properties such as the adsorption isotherm, the Henry constant and isosteric heats of adsorption, which can then be compared with experiment. However, modeling also provides a strong vehicle to deduce qualitative features such as preferential adsorption sites or clustering of guests in confined pockets crucial for future design of new materials.[2]

To obtain adsorption isotherms one currently typically relies on grand canonical Monte Carlo simulations (GCMC), which allows to dynamically vary the number of adsorbents at given conditions of temperature and chemical potential. The main drawback of these GCMC simulations for adsorption in framework materials is their assumption of rigid frameworks, making them unsuitable for flexible structures. Furthermore, energy evaluation are typically performed using classical force fields thanks to their computational efficiency. GCMC simulations often require a million number of energy evaluations which is not feasible with quantum mechanical based methods. Adsorption isotherms are extremely sensitive to the level of theory used to describe the intermolecular interactions. Methods giving errors of only 4kJ/mol – known in the field as chemical accuracy – may not reliably predict the true shape of the isotherm.[3] Accurate adsorption simulations require both accurate intermolecular interactions and proper treatment of framework flexibility.

Within this talk, I will show new frontiers to meet these challenges and will highlight the importance of making the adsorption data available for the community. Firstly, we have developed novel methodologies to train accurate machine learning potentials (MLP) to calculate adsorption properties based on very accurate underlying quantum mechanical data.[4,5] It is important to emphasize that, particularly for adsorption, the training process must also include high-energy configurations to ensure that trial moves with high energy can be reliably rejected during Monte Carlo simulations. Second, we have recently developed an alternative sampling procedure as alternative for GCMC simulations, namely the Transition Matrix Monte Carlo (TMMC) method combined with molecular dynamics (MD) trajectories to fully capture framework flexibility.[3] Additional MD simulations furthermore allow to obtain insight into preferential adsorption positions.[2] I will illustrate how these methodological developments have enabled simulation of adsorption properties of realistic MOFs fully accounting for flexibility and for dynamic behavior of the framework. Examples comprise CO_2 adsorption in MOFs with open metal sites (Mg-MOF-74), flexible frameworks (CALF-20),[6] water adsorption in flexible MOFs (MOF-303),[3] olefin/paraffin adsorption in zeolitic imidazole frameworks.[7] Finally, I will highlight how to make the essential adsorption metadata and primary data available in a digital format. In 2021 IUPAC established a task-force for the standardization of adsorption data based on a human readable STAR format, the adsorption information file (AIF).[8] Reporting adsorption data as AIF allows to make all essential primary and metadata findable, accessible, and interoperable, which is essential for reproducibility and future analysis.

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