Unraveling the breathing in Metal-Organic Frameworks: from force fields to thermodynamic insights

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Metal-organic frameworks (MOFs) are a fascinating class of materials consisting of metal oxides interconnected by organic linkers. The resulting 3D periodic framework has nanosized pores, giving rise to applications such as detection, separation and storage of gasses. A remarkable feature of some MOFs is the inherent flexibility of their framework, allowing it to adapt the shape of its unit cell in response to external stimuli such as pressure[1], temperature, gas adsorption, … This phenomenon is called breathing. Due to the huge number of combinations of inorganic and organic building units, it is impossible to characterize all MOFs experimentally, but a computational screening of large databases of (hypothetical) MOFs provides a valid solution. However, to gain access to thermodynamic macroscopic properties, simulations on a large time and length scale are required, which is not feasible using *ab initio* methods. To tackle this issue, we propose a methodology consisting of multiple steps, which is in first instance applied to the xenon-induced breathing of MIL-53(Al). First, we develop accurate force fields (FF) that mimic *ab initio* input data generated on isolated clusters[2]. More specifically, the FF is constructed to reproduce the *ab initio* equilibrium geometry and Hessian. These FFs can easily be generated with QuickFF[3], a new software package we developed. Next, we use the FFs to perform advanced molecular dynamics and Monte Carlo simulations of the periodic framework that sample the relevant region of phase space to gain access to the free energy of the MOF as function of the unit cell volume and number of guest molecules. Finally, we apply a newly developed thermodynamic model[4,5] that requires input from the molecular simulations. Our model allows to compute the unit cell volume and the number of adsorbed guest molecules under realistic conditions of mechanical pressure and chemical potential.

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