(P14)

Ab initio parametrized force field for the metal-organic framework MIL-53(Al) to study its framework flexibility

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Thirteen years ago, the group of Yaghi introduced a new class of nanoporous materials known as metal organic frameworks [1] (MOFs) that consist of inorganic moieties connected by organic linkers. Apart from the high porosity, some of these MOFs have another very interesting feature: the framework flexibility. A prototypical example of such a MOF is MIL-53(Al)[2], which is built of long aluminum oxide chains connected to each other by organic linkers. This results in a one-dimensional structure which is the basis of the flexibility: the material can shrink or expand because the rigid linkers can hinge on the oxide chains.

Traditionally, this so-called breathing is induced by the adsorption of guest molecules[2] but in the case of MIL-53(Al), also the empty framework may breathe due to changes in temperature[3] indicating an inherently bistable framework. Ab initio quantum mechanical calculations based on density functional theory (DFT) can be used to model this bistability. This was recently done by Walker et al.[4] revealing that dispersion is responsible for the bistability. Unfortunately, this approach is no longer feasible for large scale molecular dynamics simulations. Force fields provide a much faster alternative in which one approximates the potential energy surface (PES) with a sum of a priori determined analytical functions containing unknown parameters. The purpose of this work is to derive a new force field for MIL-53(Al) from first principles and use this force field to study the bistability of the framework.

Theoretical model

The force field has three main contributions: an electrostatic term based on atomic charges derived with a modified Hirshfeld-I method, a van der Waals (vdW) term with parameters taken from the MM3 model[5] and a valence force field whose parameters were estimated within a new methodology. The training data needed to estimate the charges and valence parameters were generated using DFT calculations on two representative clusters.

Results and discussion

We performed a series of geometry optimizations using the force field to investigate the equilibrium geometry and the energy profile of the breathing mode. The equilibrium geometry predicted by the force field was calculated by means of a full relaxation of the unit cell and all atomic positions. Comparison with the DFT geometry of the clusters showed that the ab initio values of the internal coordinates were very well reproduced. Comparison with the experimental geometry [2] revealed slight deviations on the dimensions of the unit cell. Further investigation indicated that van der Waals interactions are responsible for these discrepancies.

We calculated the energy profile of the breathing mode of the empty framework using a scan over the inter-diagonal angle in the ac-plane of the unit cell – the cell vector b is directed along the oxide chains. To further investigate the importance of the vdW interactions, we repeated the procedure several times but each time, another scale factor is used for the σ and/or ε parameters of the vdW expression relative to the MM3 values. The various energy profiles are shown in Figure 1. Most curves show two local minima: the narrow pore (np) at small inter-diagonal angles, and the large pore (lp) at large inter-diagonal angles. According to Walker et al.[4], the np should be more stable than the lp with an energy difference of 41.59 kJ mol^{-1} per unit cell. The experimental values[2] of the inter-diagonal angle of np (43°) and lp (75°) are indicated on the figure.

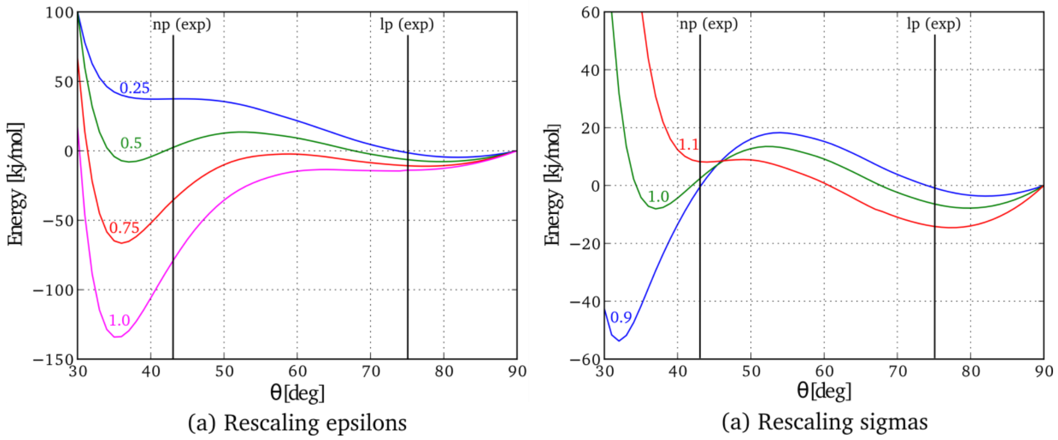

Figure 1. *Energy profiles of the breathing mode after uniformly rescaling (a) the vdW-interaction strength (b) the vdW radii by a factor indicated above each curve. The experimental inter-diagonal angles of lp and np are taken from Ref. 2*

The figure clearly illustrates that the energy profile is very sensitive to changes in the vdW parameters and hence it is crucial to have an accurate set of van der Waals parameters, in order to get a realistic energy profile of the breathing mode. Comparison of the unscaled profile with the experimental data and the results from Walker et al. reveal that the unscaled parameters of the MM3 force field do not result in such a realistic profile. The MM3 force field was developed to describe interactions in small organic molecules, and the parameters are apparently not transferable to high-density organic systems such as the oxide chains of MIL-53(Al).

Conclusions

The force field performs well at reproducing the ab initio geometry due to an accurate parameterization of the covalent and electrostatic interactions. However, to accurately describe the shape of the unit cell and the energy profile of the breathing mode, we need an accurate set of van der Waals parameters specifically for the atoms in MIL-53(Al).

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