A Thermodynamic Characterization of Mechanical, Thermal and Adsorption Properties of Flexible Metal-Organic Frameworks

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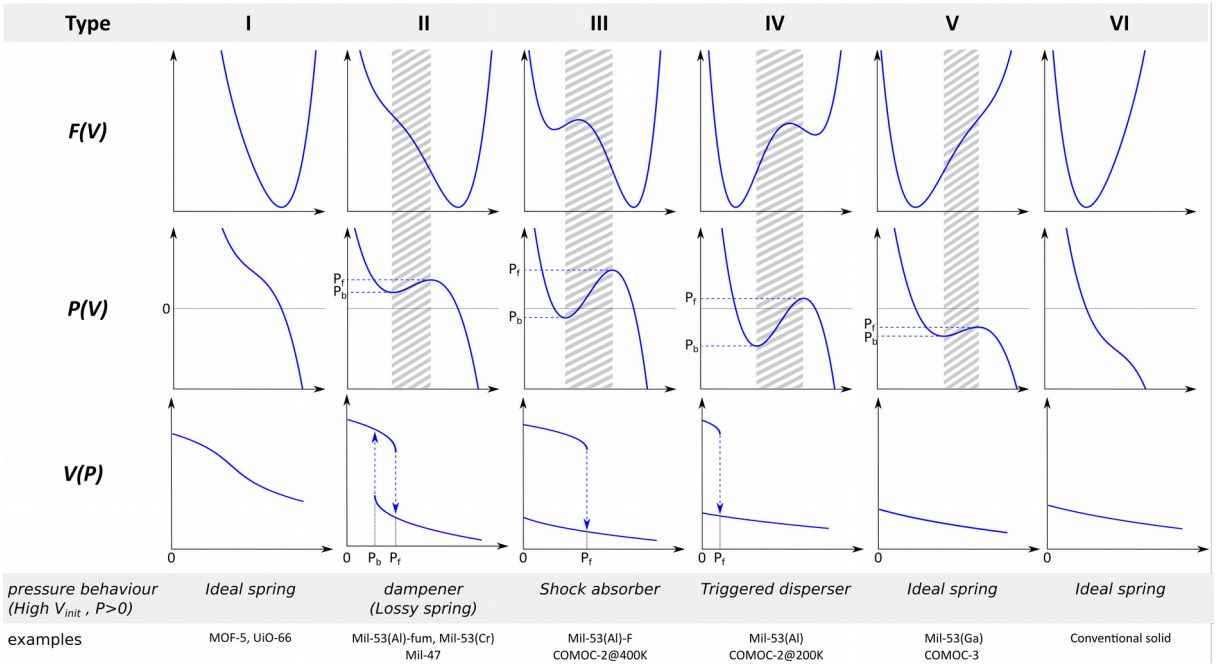
More than 15000 Metal-Organic Frameworks have already been reported and even more have been hypothesized. Most of them display large-scale dynamic behavior [1], eg. negative thermal expansion and negative linear compressibility. Breathing, however, is a specific type of framework flexibility only exhibited by a limited number of MOFs. It can be described as the ability to undergo large structural deformations associated with large changes of the unit cell volume upon external stimuli such as pressure [2,3], temperature [4] and adsorption [5]. These properties are not only fascinating from a fundamental viewpoint, but also highly relevant for emerging technological inventions in various fields such as energy storage and drug delivery.

To investigate such flexibility experimentally, one can use techniques such as mercury-intrusion porosimetry or X-ray diffraction. Although such techniques give crucial insights in breathing mechanisms, they do not allow to reconstruct the full free energy profile (FEP) as function of unit cell volume. From a thermodynamic viewpoint, such a FEP is required to predict the response to any external trigger and characterize the framework flexibility. Here, we apply force fields [6] in advanced molecular dynamics simulations [3] combined with thermodynamic models [5] to construct the FEP and fill the gaps that are not accessible from experiments. As such, we can characterize the mechanical properties of various MOFs, categorize them according to their response to an external pressure (see figure), and describe temperature- and adsorption-induced breathing.



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