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Comment on “Volume shrinkage of metal organic framework host induced by the dispersive attraction of guest gas molecules”

François-Xavier Coudert,^a Alain H. Fuchs,^a Alexander V. Neimark^b

^a CNRS & Chimie ParisTech, 11 rue Pierre et Marie Curie, 75005 Paris, France

^b Department of Chemical and Biochemical Engineering, Rutgers University, Piscataway, New Jersey 08854, United States

In a recent paper,¹ Joo et al. report from density functional theory calculations that H₂ adsorption in MOF-5 lead to a contraction of the metal–organic framework’s unit cell. The authors contrast that finding with “the intuition that gas adsorption in a confined system (e.g., pores in a material) increases internal pressures and then leads to volumetric expansion”, and describe the contraction as extraordinary. We would like to point out in this comment that adsorption-induced contraction of microporous materials is actually a very generic phenomenon, which has been demonstrated experimentally in a large range of microporous materials and explained theoretically. At the same time, we would like to acknowledge that the authors¹ should be credited for demonstrating this effect on the MOF-5 framework and characterizing its extent (of the order of 1% in volume). This is not atypical, if somewhat large, for inorganic microporous materials like zeolites, but small compared to metal–organic frameworks that show adsorption-induced structural transitions, such as the “breathing” MIL-53 ($\Delta V/V \sim 40\%$).

Nonmonotonic deformation in the course of guest adsorption is the norm, and not the exception, in microporous materials:² these materials contract at low pressure (low loading), and expand at higher gas pressure (higher loading). This behaviour has been observed experimentally and documented dating back to 1940’s³ in zeolites,^{4,5} microporous carbons,^{6,7,8} and metal–organic frameworks.⁹ A good review of experimental measurements can be found in ref. 2.

On the theoretical side, the contraction-expansion behaviour of microporous materials upon guest adsorption has also been well studied, both from the thermodynamic point of view based on the concept of adsorption stress^{10,9} and at the microscopic level using various molecular simulation tools.^{11,12,13} This phenomenon is ubiquitous, and does not depend on the specifics of host–guest interactions, adsorbate distribution within the pores, nor does it require low temperature to observe. At low gas pressure, i.e. at low loading, contraction of the material is driven by the host–guest dispersion attractive interactions (provided the pores of the material are large enough to accommodate the guest). As the gas pressures increases, i.e. at higher loading, the adsorbed phase becomes denser and the host–guest distances diminish

to the point that short-range repulsive interactions come to play and cause the material to expand in order to accommodate additional guest molecules. This is schematized on Fig. 1.

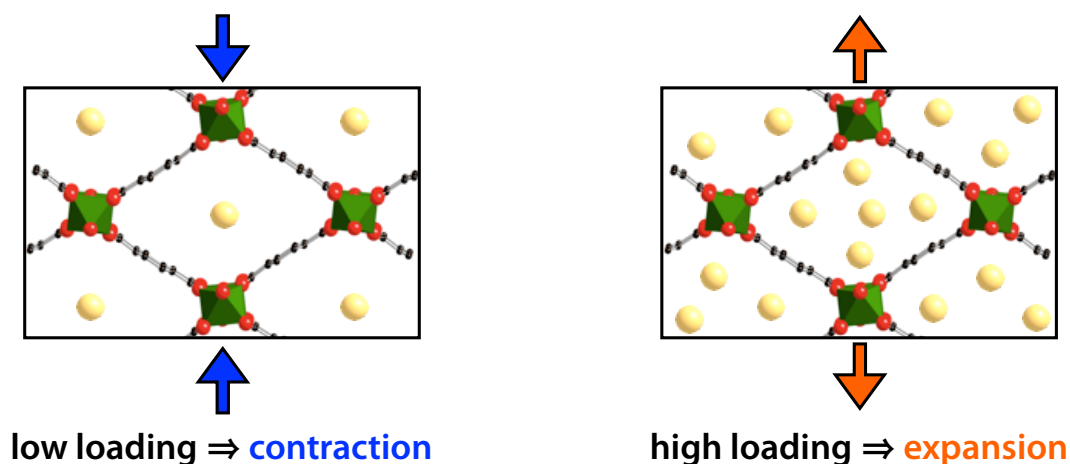


Figure 1. Nonmonotonic adsorption-induced deformation is typical in microporous materials: contraction at low pressure, followed by expansion at higher pressure. This is here schematized using the structure of the highly compliant MIL-53 metal–organic framework.

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