Molecular Simulation Study of Fluid Adsorption in Compliant Porous Materials

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While it has been observed that porous materials can undergo structural changes upon fluid adsorption, molecular simulations of fluid adsorption often revert to the use rigid frameworks. One of the main reasons for employing this simplifying assumption has to do with the adsorbent forcefield (i.e., interaction parameters for the solid) and its ability to faithfully reproduce the phase behavior of the bare adsorbent, which is often overlooked. Another important reason is that structural changes upon fluid adsorption involve concerted motion of many atoms/molecules, which can be difficult to capture reliably using brute force simulation methods. In this work, we present a relatively simple approach to study fundamental aspects of adsorption in flexible materials using molecular simulation [1]. The approach employs flat-histogram sampling, which has been shown to be an efficient method to calculate adsorptive properties in rigid frameworks [2], and takes as input information about the inherent thermodynamic stability of the adsorbent material. We are able to reproduce well-known, yet non-trivial, "breathing" behavior and uncover its underlying physics. In addition, we will present results exploring the interplay between capillary phase transitions and structural phase transitions.

References

[1] Shen and Siderius, J. Chem. Phys., 140, 244106 (2014).
[2] Siderius and Shen, J. Phys. Chem. C, 117, 5861 (2013).