

Mapping the complete thermodynamic landscape of gas adsorption for a responsive metal-organic framework

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Abstract: To do.

Advanced porous materials are poised for application.

It is often the flexibility of porous adsorbents that enables unparalleled performance in separation applications.

Responsive adsorbents, such as metal-organic frameworks, can significantly change pore structure and volume in response to stimuli.¹

One particularly challenging example is negative gas adsorption (NGA).

To completely describe the thermodynamics of responsive frameworks simulations of a fully flexible solid in presence of adsorbate are necessary. Simulations, within this osmotic ensemble provide access to the grand canonical potential (Ω). This potential completely describes the thermodynamic features of the system with respect to the energies of the framework, the chemical potential of the adsorbed fluid, external pressure and temperature. Atomistic simulations within the osmotic ensemble remain challenging because dynamics must be combined with particle insertion/deletion, which has only been applied to handful of systems.

Analysis of the grand canonical potential are often achieved using analytical descriptions of gas adsorption. This has been particularly insightful the relative stability of two distinct and porous phases. For example, the process of “breathing” can be directly seen for two different porous phases based on the difference in grand canonical potential, Ω (Figure ??a,b).

In the present work we have employed state-of-the-art molecular simulations to produce a detailed picture of the entire landscape of grand canonical potential for changes in pressure, amount adsorbed and cell volume for DUT-49. This complete thermodynamic analysis provides unprecedented insight into the phase stability under adsorption. Our analysis recreates experimental observations, demonstrates the effects of temperature and outlines the kinetic and thermodynamics phases present during NGA.

Our methodology uses grand canonical Monte Carlo moves combined with molecular dynamics trajectories in the $(N, V, \sigma_a = 0, T)$ ensemble, to effectively constraining the volume while allowing the cell shape to fluctuate. Subsequently, adsorption isotherms at each unit cell volume then are used to construct the grand canonical potential as Equation ??.

The resulting potential at different methane gas pressures and cell volumes is displayed in Figure ??c. To obtain ac-

curate integrals of the number of adsorbed particles (third term in Equation ??), a large number of chemical potentials were considered.

This detailed potential landscape contains metastable and equilibrium states that change with increasing gas pressure (Figure ??). The system, at zero gas pressure, begins at equilibrium in the *op* phase (large cell volume) where there is also a metastable *cp* phase (small cell volume). The observed states correspond are in quantitative agreement with in situ studies. Intermediate phases, between the *op* and *cp* phases, are observed by simulation and experiment further highlighting the accuracy of our proposed landscape.

Simulations were completed for three temperatures (90 K, 120 and 150) to provide insight to the thermodynamic trends responsible for the observations of different phases for DUT-49. Particularly, temperature demonstrates a fascinating non-monotonic relationship with amount of gas released during the negative gas adsorption process. The relative grand potential between the *op* and *cp* phases can be directly computed from these simulations, in addition to the energy barrier between these states (Figure ??a). It is observed that the pressure window for stability of the *cp* phase is correlated with temperature, due to the entropic effects of condensing gas to a smaller pore structure. The maximum energy difference is also correlated with temperature. Contrastingly, the minimum barrier height shows a weaker trend with temperature. A temperature of 90 and 120 K shows no energy barrier between the states. We can alternatively consider these trends with respect to the difference in adsorbed amount in the *op* and *cp* phases ((Figure ??b), which represents the magnitude of negative gas adsorption. Interestingly, the *cp* phase can become more favorable than the *op* phase before the crossing point of the individual isotherms, represent by 0. This is especially true for the.

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References

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