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Thermodynamics of "breathing" of metal-organic frameworks: free energy model for adsorption induced transitions

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CO_2 adsorption in metal-organic frameworks

Metal Organic Frameworks (MOFs) are a new class of porous materials synthesized from metal clusters connected by organic linkers[1]. One of the promising applications of MOFs is carbon capture from fuel gasses, where CO_2 is adsorbed in the pores of the material. In this presentation, we explore framework flexibility as a possible mechanism for selective and reversible CO_2 adsorption by means of Monte Carlo simulations.

Breathing of MOFs

Most MOFs are fairly rigid structures, in the sense that they undergo small changes in volume when external stress is applied. Typical volume changes are of the order of a few percent only. Nevertheless, some MOF materials have an unexpectedly high flexibility and impressively shrink or swell under pressure, temperature or adsorption changes. A well-known example is MIL-53[2], a structure that shows volume changes of over 40%. In an adsorption experiment, the gas pressure is gradually increased while the amount of adsorbed material in the pores is measured. For MIL-53, the measured adsorption isotherm shows interesting features: when MIL-53 is brought into contact with a gas at increasing pressure, the framework's pores constrict, while at even higher pressures, the pores return to their original geometry[3]. The process, referred to as "breathing", is reversible and shows hysteresis. The MOF's flexibility could be exploited to design an efficient pressure swing setup.

The structural changes from an open shape to a closed shape with increasing pressure is contra-intuitive. Our model aims at giving a rational for both transitions.

A mean-field free energy model

We have constructed a mean-field model to gain insight in the thermodynamics of the breathing. The model shows that the behavior is the result of the different factors at play in a (N_{mof},μ,P,T) ensemble. The control parameters in this ensemble are the constant amount of MOF material, the constant gas chemical potential, the constant gas pressure, and the constant temperature.

Various parameters enter in the model: (1) the flexibility of the empty host material, (2) the interaction between the adsorbed molecules and the host material, and (3) the interaction between the particles themselves. The parameters can be obtained from experimental data (i.e. mercury intrusion experiments), from quantum mechanical data (VASP simulation package), and Monte Carlo simulations with a classical force field. The parameters have been derived for CO_2 and CH_4 adsorption in the MIL-53(Cr) material. Interestingly, CO_2 adsorption causes breathing in this material, while CH_4 does not, making this a good test case for the model.

Results and discussion

Once the model parameters had been obtained from the experimental and simulation data, we used our mean-field model to investigate the free energy plot, the phase behavior along the isotherm, the hysteresis, and the phase diagram. The two phases of the material are the large-pore (lp) and narrow-pore (np) structures. The predicted isotherms are displayed in Figure 1. For CO_2, the adsorption and desorption isotherms show two steps. These steps correspond to a transitions lp->np and np->lp. Hysteresis is correctly predicted since the transitions occur at different pressures on the adsorption curve than on the desorption curve. The equilibrium curve is thermodynamically most stable but can in practice not be reached according to the free energy plots (not shown). For CH_4, the structure remains in the lp phase on both the adsorption and desorption curves.

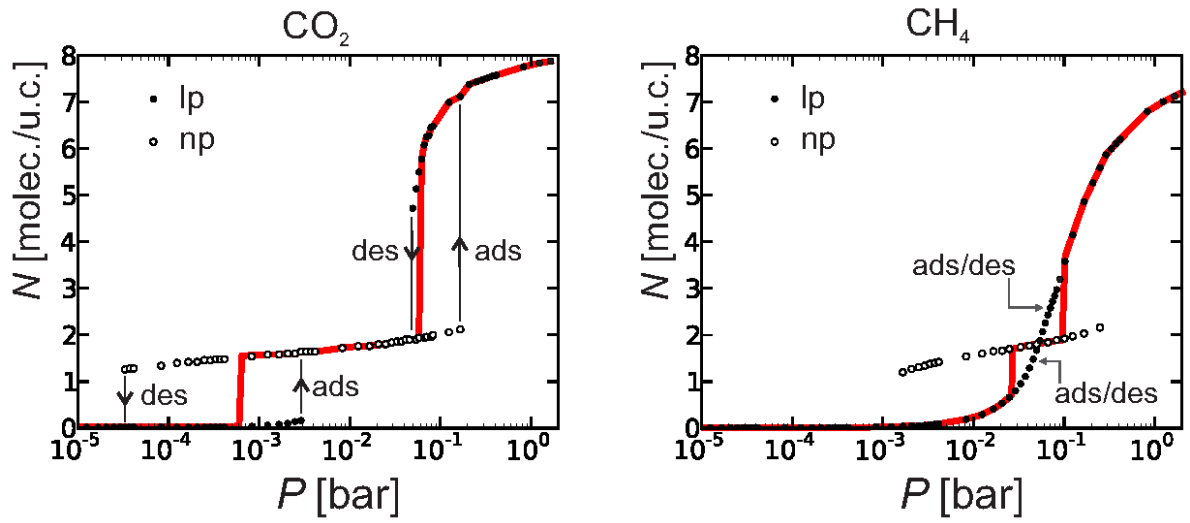

Figure 1. *Predicted equilibrium (red), adsorption (ads) and desorption (des) isotherms for CO_2 and CH_4 .adsorption in MIL-53(Cr). The number of adsorbed particles per unit cell is plotted against the gas pressure in the adsorption chamber. The circles indicate the phase: large-pore (lp) or narrow-pore (np) structure.*

Conclusions

We have proposed a mean-field free energy to describe the thermodynamics of adsorption induced structural transitions of porous media. The parameters in the model have been derived from Monte Carlo simulations and experimental intrusion data. Our model correctly predicts the difference between CO_2 and CH_4 adsorption in MIL-53(Cr). Moreover, the thermodynamic description gives insight in the mechanism of the hysteresis.

The model is general and applicable to other types of materials as well. A possible extension is the prediction of the selectivity, which expresses which component is preferably adsorbed when the MOF is brought in a chamber filled with a specific composition of a gas mixture.

References

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