Cooperative gas adsorption without a phase transition in metal-organic frameworks

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Outline

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Colaborators

Work done in collaboration with Joyjit Kundu[1,2], Jung-Hoon Lee[1,3], Jeffrey B. Neaton[1,3,4], David Prendergast[1], and Stephen Whitelam[1].

1-Molecular Foundry, Lawrence Berkeley National Laboratory.
2-Department of Chemistry, Duke University, Durham.
3-Department of Physics, University of California, Berkeley.
4-Kavli Energy Nanosciences Institute at Berkeley, Berkeley.
(paper at https://arxiv.org/abs/1712.05061)

D. Dhar.

R. Rajesh.

J. Kundu.

CO_2 adsorption

- Technology for CO_2 capture and storage: Metal-organic frameworks (MOF's). Porous materials, tunable molecular properties, large internal surface area.
- Most MOF's: Langmuir type isotherms. Small number of MOF's: step-like adsorption isotherms, more convenient from technological point of view.
- Usually this is attributed to first-order phase transition or a dynamic rearrangement of the framework.
- In some diamine-appended MOF's, ($mmen - M_2$, where M stands for the metal Mg, Mn, Fe, Co, or Zn), no evidence for either, origin of cooperativity unclear.
- Experimental measurements and DFT calculations: at higher partial pressures CO_2 undergoes chemisorption, forming ammonium carbamate chains along the c-axis of MOF.

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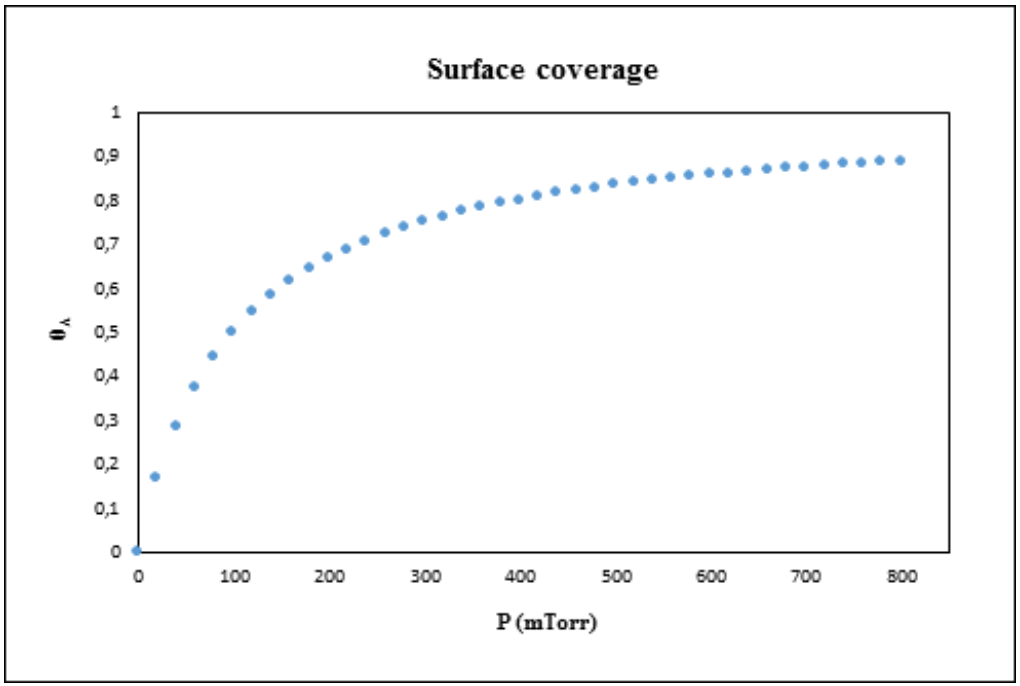
CO_2 adsorption

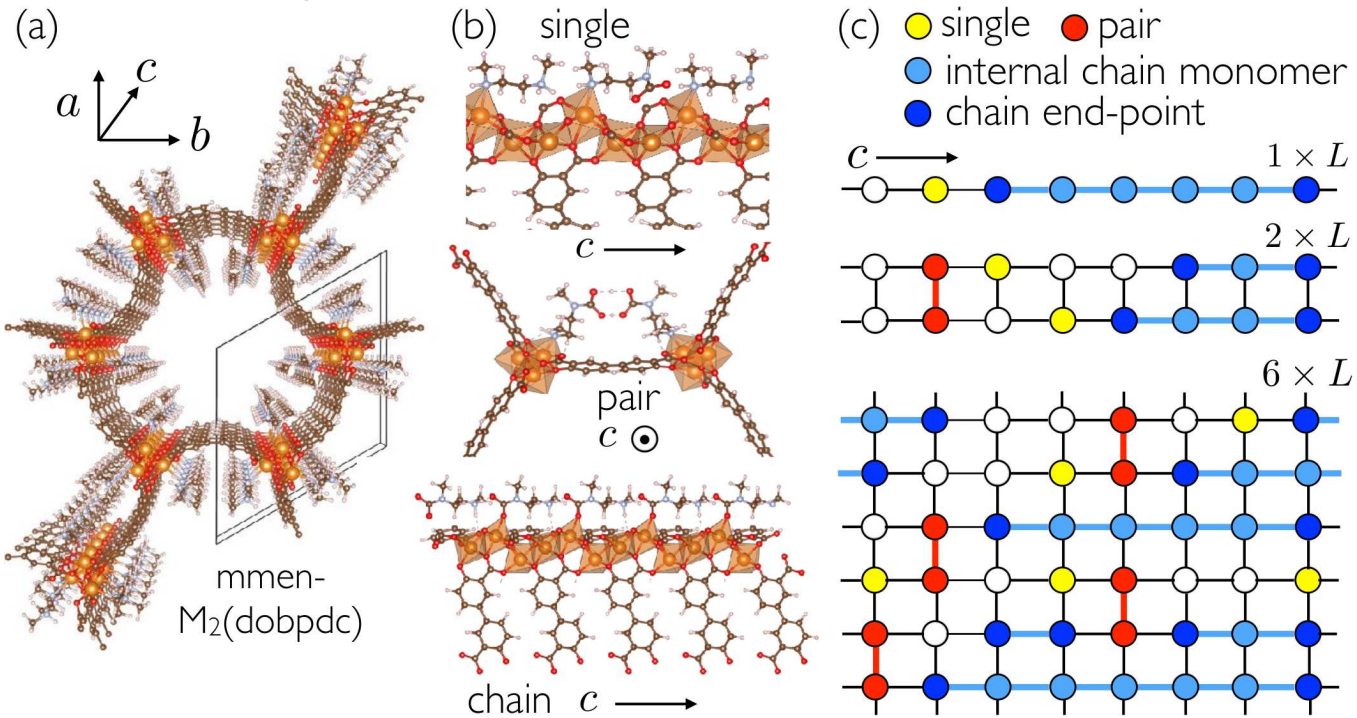
Langmuir adsorption (1918): monomers are adsorbed on substrate, at most one at each site (monolayer). Gas in bulk is ideal. Equilibrium: chemical potentials in bulk and adsorbed phase are the same.



$\Theta_A = \frac{P}{P+P_0(T)}$. Data generated for $P_0 = 100\,\mathrm{mTorr}$

Model

Mapping of system on one dimensional exactly solvable statistical-mechanical model, parametrized by DFT calculations: cooperativity without phase transition.



Equilibrium polymerization model

- P. M. Pfeuty and J. C. Wheeler, Phys. Rev. A **27**, 2178 (1983): equilibrium polymerization in one dimension (polymerization of liquid sulfur). 1-lane model.
- Grand-canonical partition function:

$$\mathcal{Z} = \sum_{\{n_1, n_i, n_e\}} K_1^{n_1} K_e^{n_e} K_i^{n_i} \Gamma(n_1, n_i, n_e).$$

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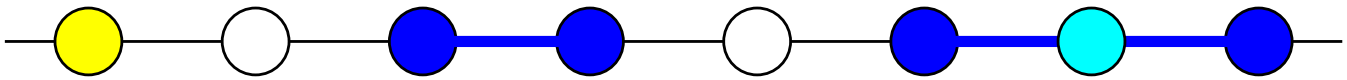
Equilibrium polymerization model

Portion of lattice in a particular configuration and associated statistical weight:



$$\mathbf{K_1 K_e^4 K_i}$$

Equilibrium polymerization model

- Edges: with ($\eta = 1$) or without ($\eta = 0$) bond on them.
- Transfer matrix elements: $T_{00} = 1 + K_1$, $T_{01} = T_{10} = K_e$, $T_{11} = K_i$.
- 2×2 transfer matrix:

$$T = \begin{pmatrix} 1 + K_1 & K_e \\ K_e & K_i \end{pmatrix}.$$

- Perron-Frobenius theorem: no phase transition for $K_e \neq 0$.
- When $K_e, K_i = 0$ (no chains): Langmuir.

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Equilibrium polimerization model

- Eigenvalues of transfer matrix:

$$2\lambda_{\pm} = 1 + K_1 + K_i \pm \sqrt{(1 + K_1 - K_i)^2 + 4K_e^2}.$$

- Free energy per site: $f = -k_B T \ln \lambda_+$. Phase transition only in the limit $K_e = 0$.
- In this limit, $\Theta_{A,1} = K_1/(1 + K_1)$, $\Theta_{A,i} = 0$, for $1 + K_1 > K_i$.
- $\Theta_{A,1} = 0$, $\Theta_{A,i} = 1$, for $1 + K_1 < K_i$.

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Equilibrium polimerization model

- Drawback: independent lanes since no transverse bonding (dimers) are present.
- To include dimers: 2-lane (still exactly solvable, 4×4 transfer matrix) and 6-lane model (64×64 transfer matrix).

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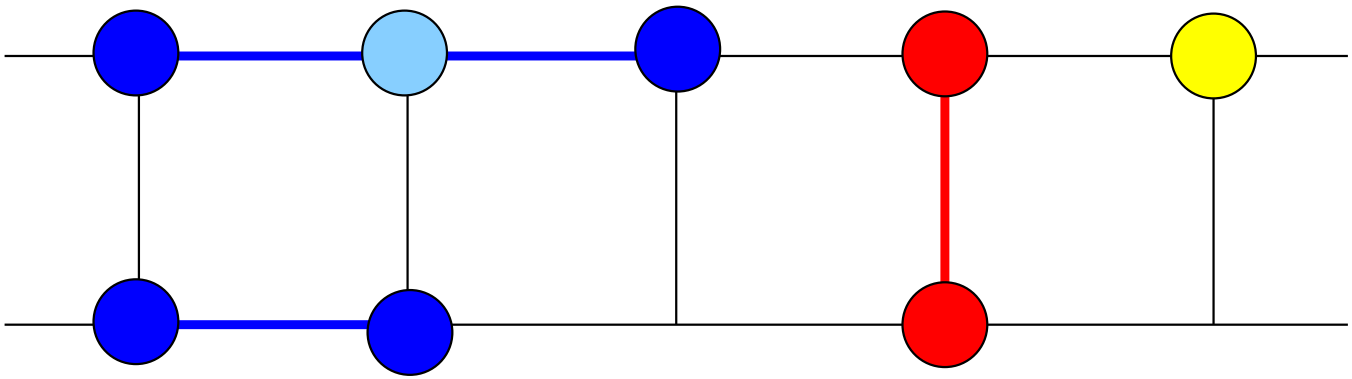
Equilibrium polimerization model

Two-lane model. Portion of the lattice and statistical weight:



$$\mathbf{K_1\,K_e^4K_{\,i}K_d}$$

Examples of transfer matrix element: $T_{00,00} = (1 + K_1)^2 + K_d$; $T_{10,00} = K_e(1 + K_1)$.

Equilibrium polimerization model

The chemical equilibrium constants K_α, $\alpha = 1, i, e,$ and d are of the general form $K_\alpha = g_\alpha W_\alpha$, where $g_\alpha = V_\alpha / \Lambda^3 q_{\mathrm{inter},\alpha}$.
$W_\alpha = \exp[\beta(\mu - E_\alpha)]$. To obtain μ of the CO_2 molecule in the bulk: ideal gas. Contribution of vibrations are important at relevant pressures and temperatures.

Model-experiment

- This leads to $K_\alpha = r_q \beta P V_\alpha e^{-\beta E_\alpha}$
- Even for non-zero K_e, isotherm of adsorbed CO_2 as a function of pressure shows sharp step when $K_i > K_1, K_e$.
- For each metal, two comparisons are made:
- 2- Predictive mode: binding energies obtained from DFT calculations - left panel.
- 1- Binding energies taken from experiment - right panel.
- Mg and Mn: 1-lane model (transverse dimers neglegible). Others: 6-lane model.

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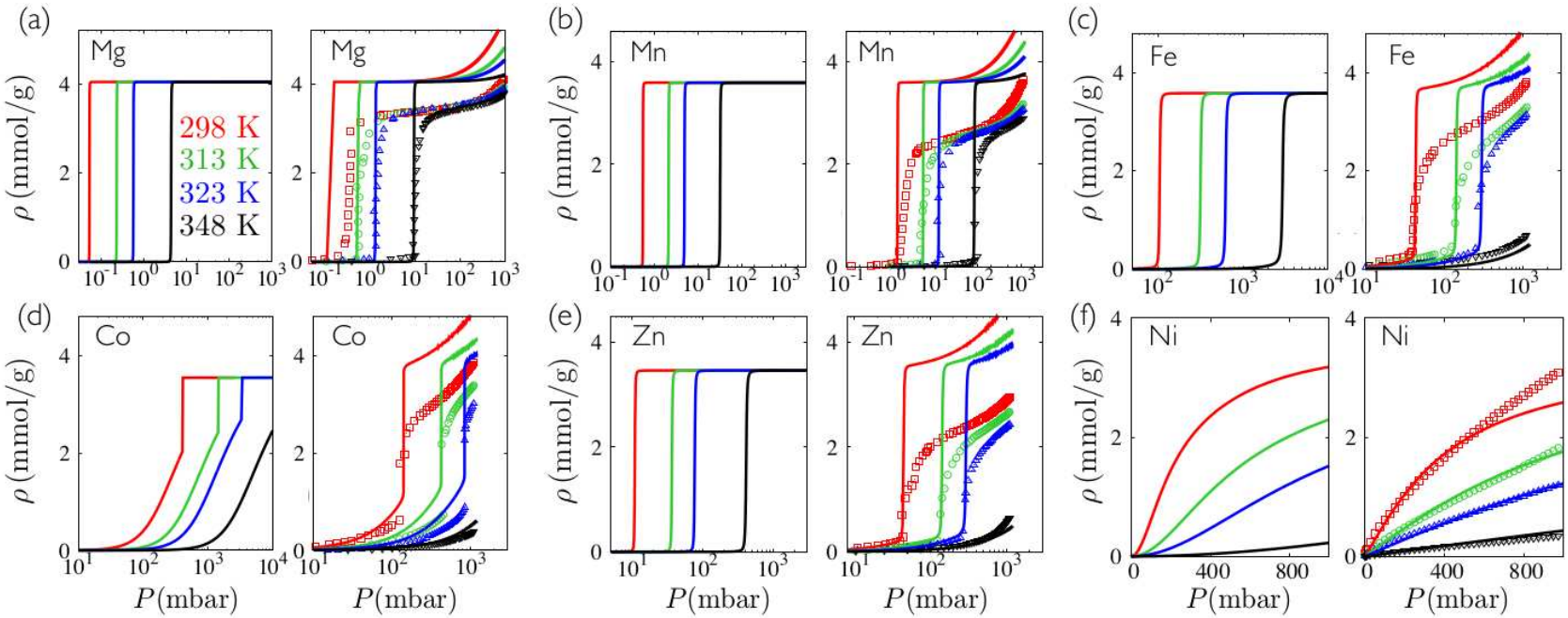
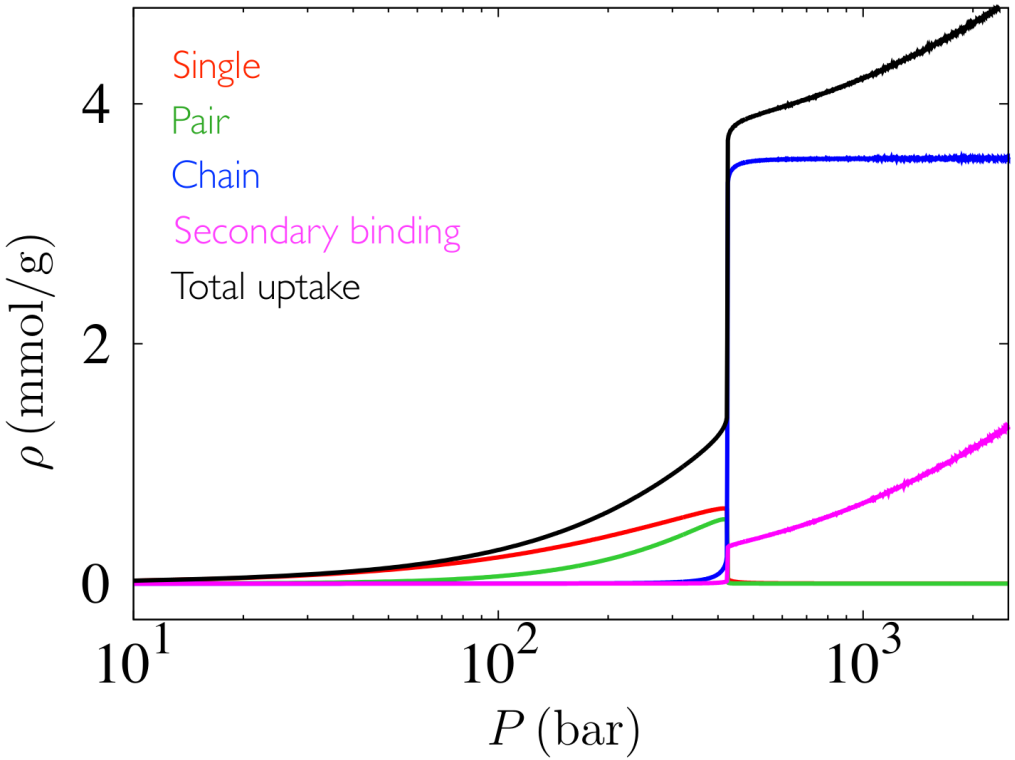
Data


(a)
Mg
Mg
298 K
313 K
323 K
348 K
(b)
Mn
Mn
(c)
Fe
Fe
(d)
Co
Co
(e)
Zn
Zn
(f)
Ni
Ni
ρ (mmol/g)
P(mbar)

Refinements

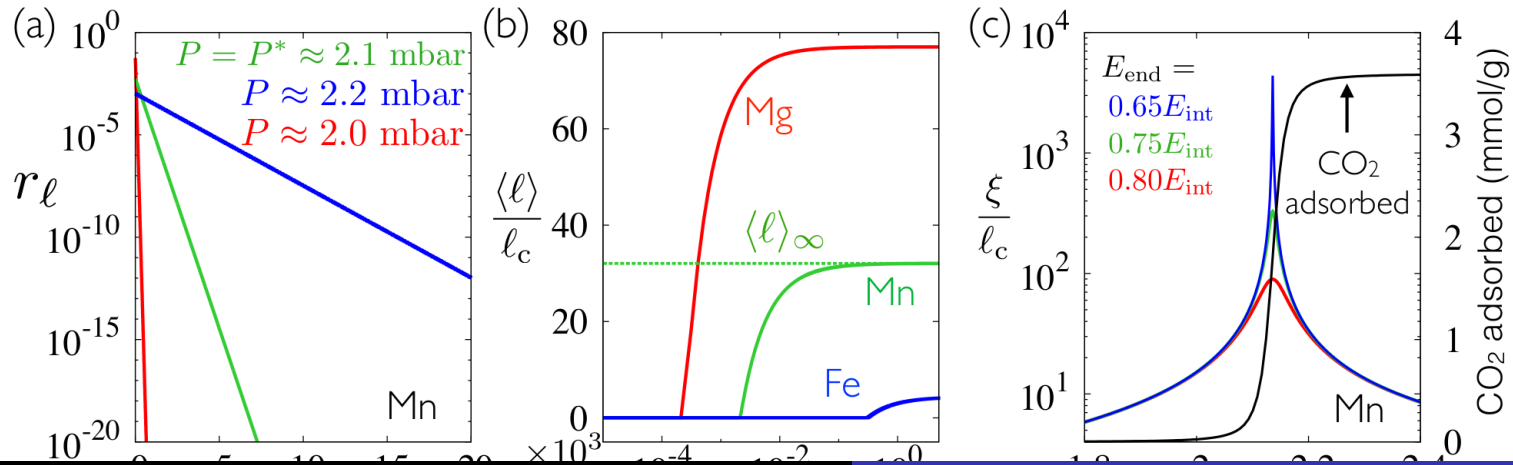
Fine features (rising of isotherm before the step and after the step): introduce secondary binding sites where monomers may adsorb. Densities of different types of adsorbed monomers may be accessible to NMR experiments. Results for Mn, 6-lane model:



Chain length distribution and correlation length

The (exponential) chain length distribution $r_\ell \times \ell$ may be found in the 1-lane model (J. F. Stilck, M. A. Neto, and W. G. Dantas, Physica A **368**, 442 (2006)). Use site dependent statistical weights K_i.

Bond-bond correlation length ξ ($< \eta_i \eta_{i+\ell} > - < \eta_i >^2 \approx e^{-\ell/\xi}$), in units of lattice spacing may also be obtained (Pfeuty & Wheeler)($\xi = 1/\ln(\lambda_1/\lambda_2)$). Results (a,c): Mn at 313 K. (b) Different metals at 313 K.



Conclusion

- No phase transition necessary to explain abrupt rise in isotherm of MOF.
- Model provides understanding for reasons of features of isotherms. Example: increasing K_i/K_e leads to more abrupt isotherms.
- May suggest how to induce cooperativity by introducing aditional binding agents.
- Model with quenched defects may be relevant to compare data in many cases, work in this direction is being done.

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