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

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Introduction

Model and transfer matrix solution

Comparison with experiments

Conclusion and outlook
Outline

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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$^1$.
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(paper at https://arxiv.org/abs/1712.05061)
**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 $P_0 = 100$ mTorr
Model

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


- Grand-canonical partition function:

\[ Z = \sum_{\{n_1, n_i, n_e\}} K_1^{n_1} K_e^{n_e} K_i^{n_i} \Gamma(n_1, n_i, n_e). \]
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Equilibrium polymerization model

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

\[ K_1 K_e^4 K_i \]
Equilibrium polymerization model

- Edges: with ($\eta = 1$) or without ($\eta = 0$) bond on them.
- Transfer matrix elements: $T_{00} = 1 + K_1$, $T_{01} = T_{10} = K_e$, $T_{11} = K_i$.
- $2 \times 2$ 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 polymerization 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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- Drawback: independent lanes since no transverse bonding (dimers) are present.
- To include dimers: 2-lane (still exactly solvable, $4 \times 4$ transfer matrix) and 6-lane model ($64 \times 64$ transfer matrix).
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Two-lane model. Portion of the lattice and statistical weight:

\[ K_1 K_e^4 K_i K_d \]

Examples of transfer matrix element: 
\[ T_{00,00} = (1 + K_1)^2 + K_d; \]
\[ T_{10,00} = K_e(1 + K_1). \]
The chemical equilibrium constants $K_\alpha$, $\alpha = 1, i, e, \text{and } d$ are of the general form $K_\alpha = g_\alpha W_\alpha$, where $g_\alpha = V_\alpha / \Lambda^3 q_{\text{inter},\alpha}$. $W_\alpha = \exp[\beta(\mu - E_\alpha)]$. To obtain $\mu$ 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 $K_\alpha = r_q \beta PV_\alpha e^{-\beta E_\alpha}$
- 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:
  1. Binding energies taken from experiment - right panel.
  2. Predictive mode: binding energies obtained from DFT calculations - left panel.
- Mg and Mn: 1-lane model (transverse dimers negligible).
- Others: 6-lane model.
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Data
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:

![Graph showing isotherm behavior with different models](image_url)
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 $\xi (\langle \eta_i \eta_{i+\ell} \rangle - \langle \eta_i \rangle^2 \approx e^{-\ell/\xi})$, 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.
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 additional 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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