The importance of unit cell fluctuations for free energy profiles of flexible crystals

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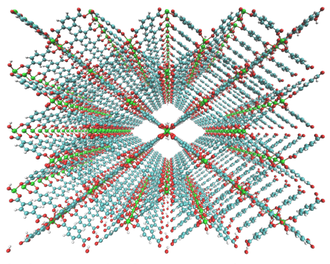
Studied material: MIL-53(Al)



MIL-53 is a metal-organic framework.
It exhibits breathing behaviour:
A transition between a narrow-pore (np) and a large-pore (lp) configuration under adsorption of molecules or other stimuli.

Research question

What is the stability of the structure at 300 K and at a given pressure?
A free energy profile as a function of the volume V is needed.
Three methods exist:
1. Thermodynamic integration
2. Normal mode analysis / Principal component analysis
3. Metadynamics

How to treat the unit cell in simulations?
Is the ensemble important?
What is the most efficient simulation method?

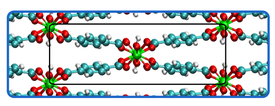
Computational details

We perform molecular dynamics
with a classical force field [1]
using the code Yaff [2].

We apply periodic boundary conditions
to a double unit cell
with a fixed number of particles (152),
a NHC thermostat (300 K) [3],
and a MTTK barostat [4].

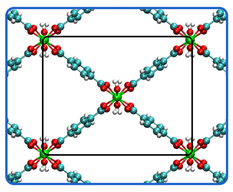
The unit cell at 300K

np



($V_{\mathrm{np}} \approx 793$ Å^3)

lp



($V_{\mathrm{lp}} \approx 1460$ Å^3)

Notation

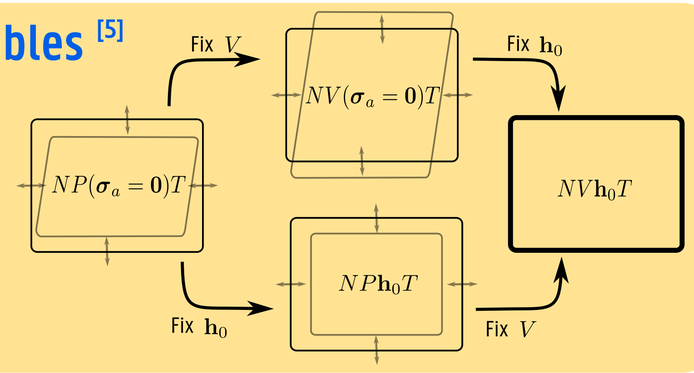
Periodicity $\vec{a}$, $\vec{b}$, $\vec{c}$

Unit cell matrix $\mathbf{h} = \begin{pmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{pmatrix}$

Cell volume $V = \det(\mathbf{h})$

Cell shape $\mathbf{h}_0 = \mathbf{h}/V^{\frac{1}{3}}$

Ensembles [5]



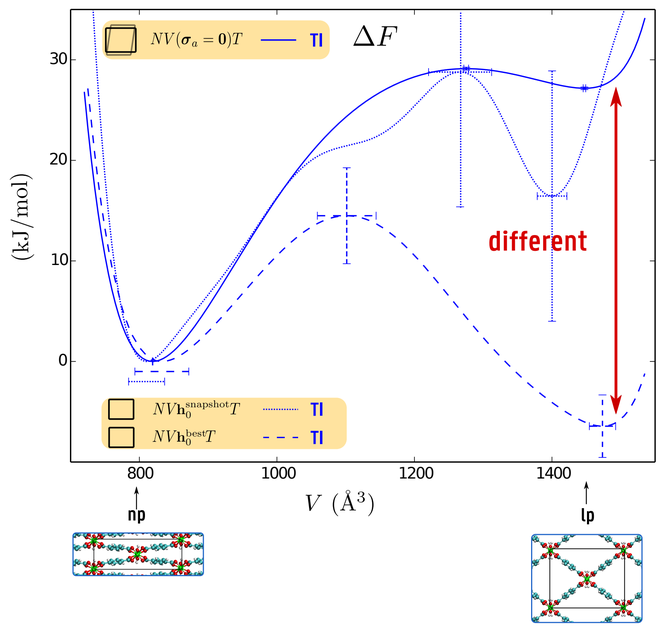
Results

1. Thermodynamic integration (TI) [6]

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

$$\Delta F = F(V) - F(V_{\mathrm{np}}) = -\int_{V_{\mathrm{np}}}^{V} \langle P \rangle_{V'} dV'$$

We tested two ensembles:
- The $NV(\boldsymbol{\sigma}_a = \mathbf{0})T$ ensemble
- The $NV\mathbf{h}_0T$ ensemble, so choose $\mathbf{h}_0$:
  - Snapshots, $\mathbf{h}_0^{\mathrm{snapshot}}$: from $NP(\boldsymbol{\sigma}_a = \mathbf{0})T$
  - Best guess, $\mathbf{h}_0^{\mathrm{best}}$: average of $NV(\boldsymbol{\sigma}_a = \mathbf{0})T$



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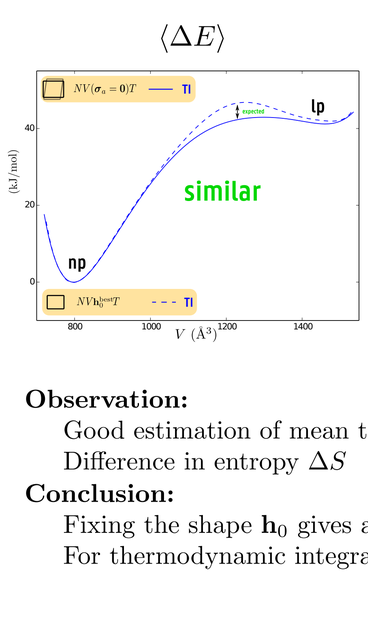

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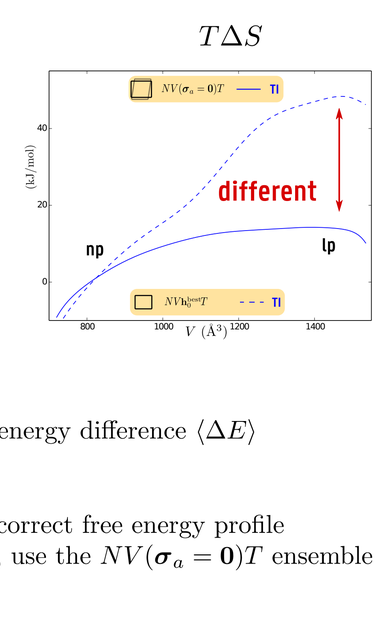


Observation:
Good estimation of mean total energy difference $\langle \Delta E \rangle$
Difference in entropy ΔS

Conclusion:
Fixing the shape $\mathbf{h}_0$ gives an incorrect free energy profile
For thermodynamic integration, use the $NV(\boldsymbol{\sigma}_a = \mathbf{0})T$ ensemble

2. Normal mode analysis (NMA) [7] and principal component analysis (PCA) [8]

Compute the frequencies ν_i in the system, using the classical approximation
NMA: by optimising at constant $\mathbf{h}_0$ (→energy E_0) and by diagonalising the hessian (harmonic approximation)
PCA: by diagonalising the massweighted covariance matrix at 300 K
With these frequencies, calculate the vibrational energy $E_v = 3NRT$ and the vibrational entropy $S_v = R\sum_i (1 - \ln \frac{h\nu_i}{k_B T})$

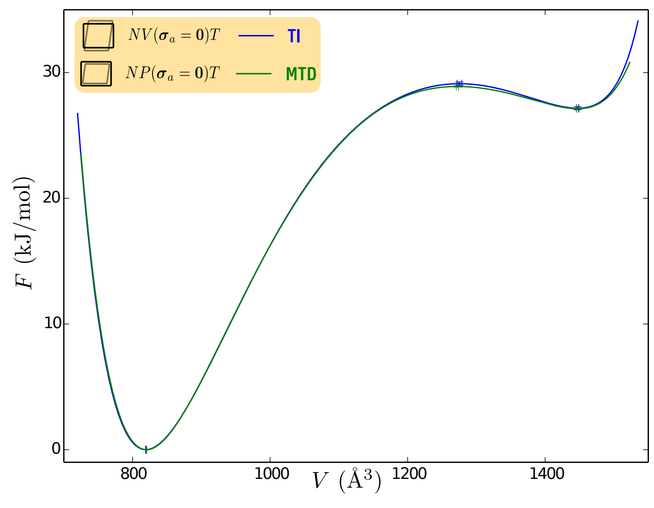
$F_{\mathrm{NMA}} = E_0 + E_v - TS_v$

$F_{\mathrm{PCA}} = \langle E \rangle - TS_v$

Observation:
NMA renders a slightly inaccurate estimate
PCA does not work

3. Metadynamics (MTD) [9]

Add bias potential to the system
Update bias throughout the simulation until convergence
Bias potential gives the free energy profile



Observation:
Metadynamics and thermodynamic integration are equivalent
Here, metadynamics is twice more precise for one fourth of the simulation

Conclusions

For MIL-53(Al), the narrow-pore structure is the most stable at room temperature.
The unit cell shape fluctuations during a molecular dynamics simulation are important for estimating a correct free energy profile.
In thermodynamic integration, fixing the unit cell shape during simulations has a large, incorrect effect on the results. One should always use the correct ensemble. With these simulation parameters, metadynamics renders an equally accurate but more precise free energy profile with an increased computational efficiency.
Normal mode analysis gives a precise but inaccurate estimate of the free energy. Finally, principal component analysis is very inaccurate and inefficient at calculating the free energy.

Prospects

Is the effect of unit cell shape fluctuations equally large for bigger unit cells containing more nuclei?
What happens in other materials?

References

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