

High-Resolution AFM and Simulation of THF Clathrate Hydrate Growth and Structure

Jie Huang

Surfaces and Interfaces at the Nanoscale (SIN), School of Science, Aalto University, Finland



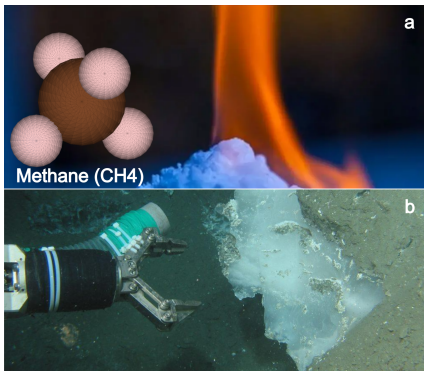
Surfaces and Interfaces
at the Nanoscale (SIN)



Aalto University
School of Science

NCAFM 2026, Innsbruck

Why is natural gas found under the seafloor?

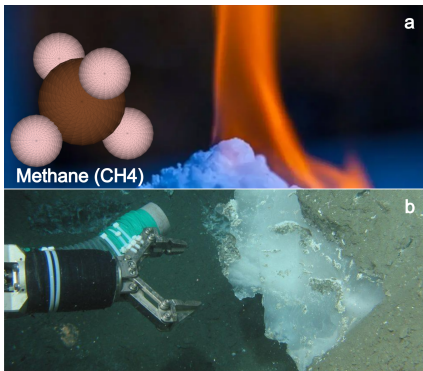


Methane hydrate, natural gas trapped in ice, is found under the seafloor.

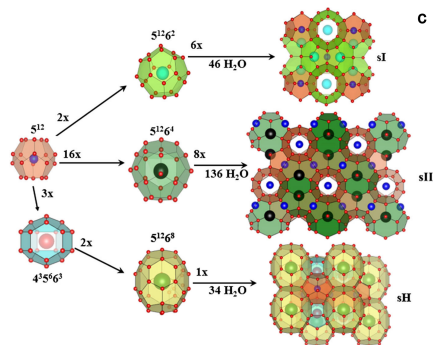
Clathrate hydrates could be an important future energy source.

Image sources: (a) Alamy, via BBC News 2017; (b) JAPAN Forward, 2021; and (c) J. Chem. Phys. 145, 211705 (2016).

Why is natural gas found under the seafloor?



Methane hydrate, natural gas trapped in ice, is found under the seafloor.



Water molecules form cage-like structures, called **clathrate hydrates**, that trap gas molecules.

Clathrate hydrates could be an important future energy source.

Image sources: (a) Alamy, via BBC News 2017; (b) JAPAN Forward, 2021; and (c) J. Chem. Phys. 145, 211705 (2016).

How do clathrate hydrates grow?

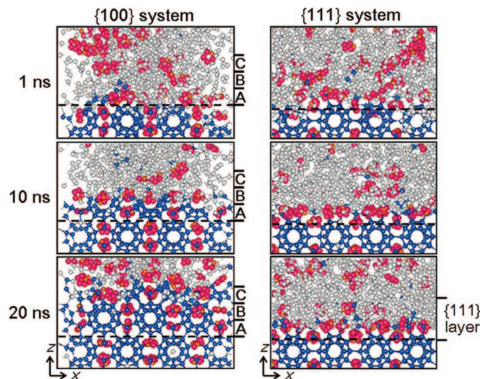
Can AFM show us how clathrate hydrates grow?

Experiment: no atomic-resolution AFM images yet

We need to image while they are growing.

Simulation: the atomic structures behind each AFM image

We need to verify and understand the atomic structures in these stages.

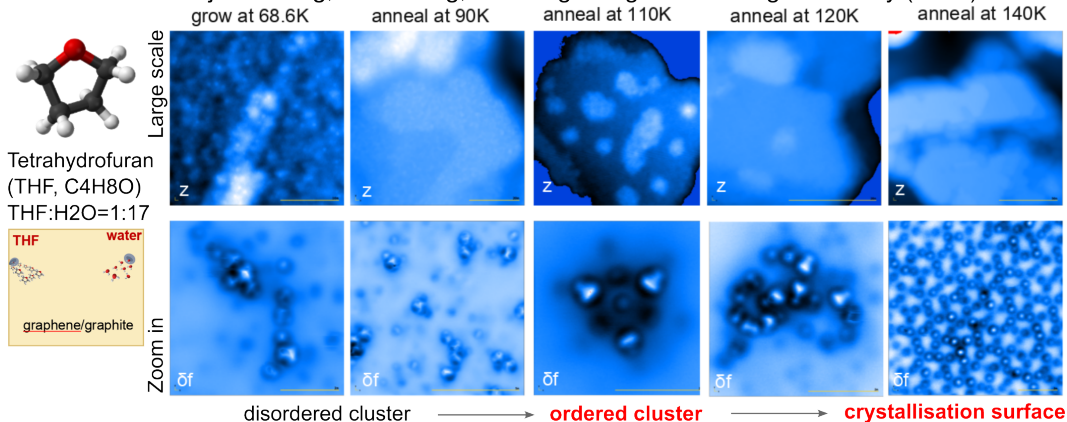


Simulated growth of THF hydrates [1].

[1] J. Phys. Chem. B **113** (2009) 4790–4798.

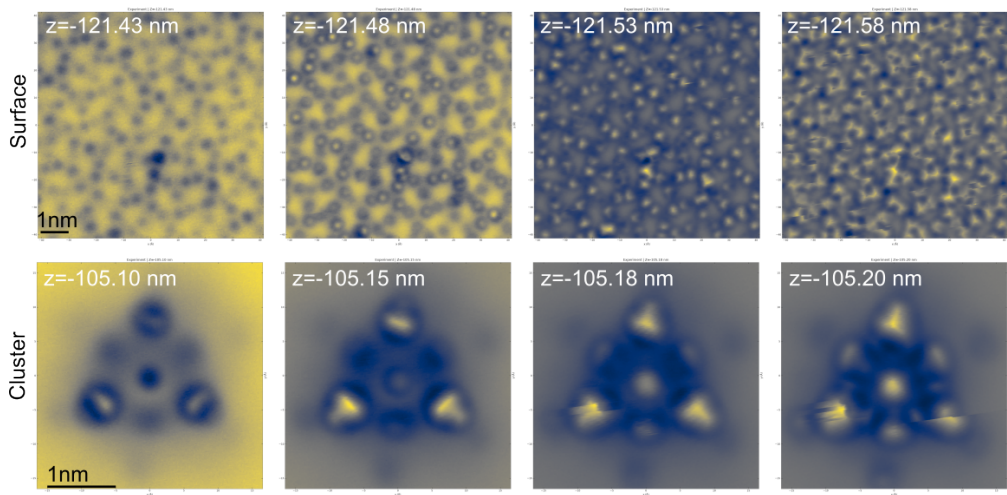
Watching THF hydrate growth with high-resolution AFM

Yuejian Zhang, Jiani Hong, and Ying Jiang from Peking University (2025)



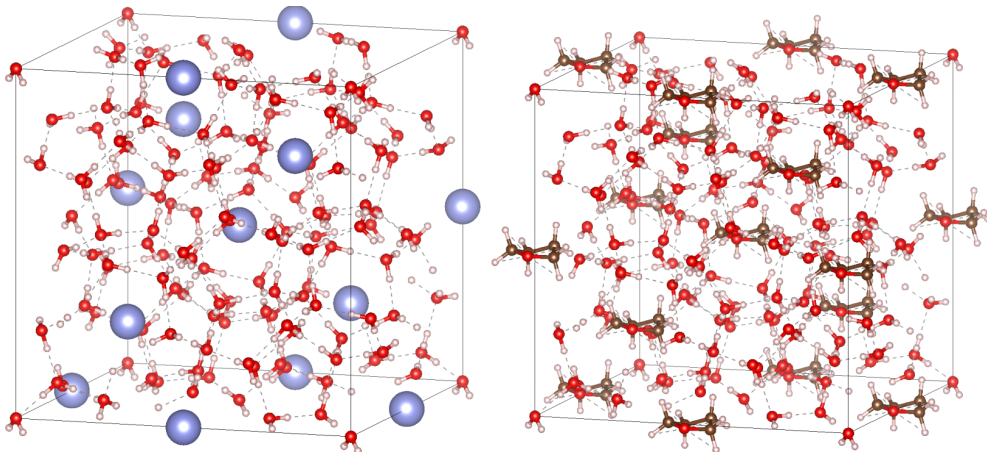
As the hydrate grows, disordered clusters become ordered clusters, and a stable surface forms.

AFM images at different heights for two important stages



What atomic structure lies behind the cluster and the surface structures?

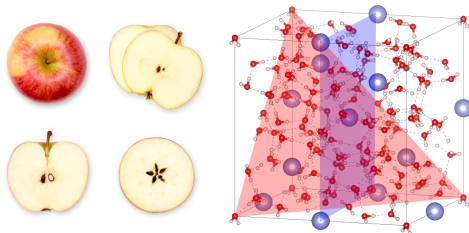
Starting point: the bulk THF hydrate



With the optimised bulk system, we can build different surface structures.

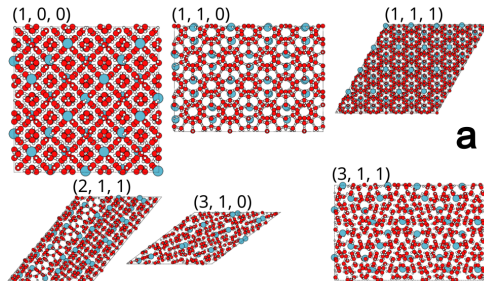
[1] J. Chem. Phys. 138, 124504 (2013)

From bulk to surface: which orientation?



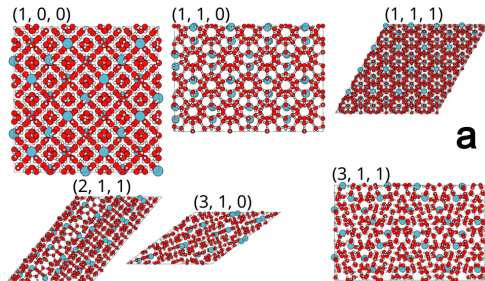
Cutting along different planes gives different surface slabs.

From bulk to surface: which orientation?



(a) Slabs are made by cutting the bulk structure along different planes.

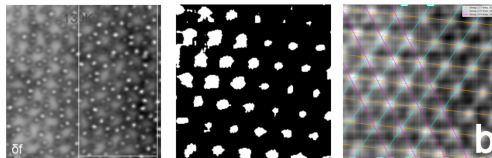
From bulk to surface: which orientation?



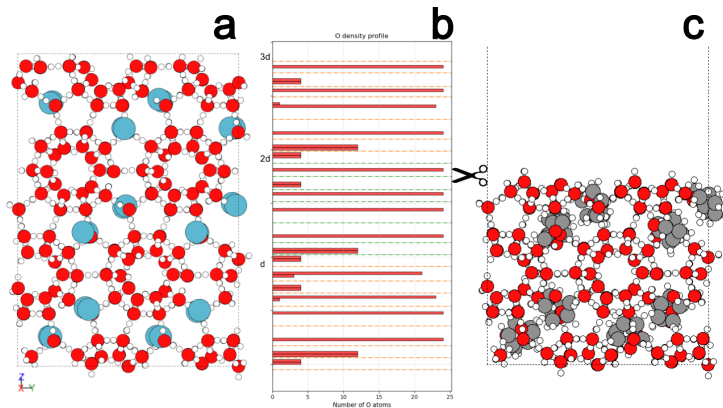
(a) Slabs are made by cutting the bulk structure along different planes.

(b) Analyze the AFM image and compare feature spacing and symmetry with experiment.

Conclusion: the experimental surface is (111).



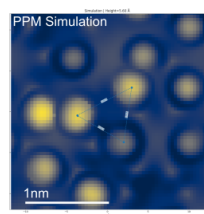
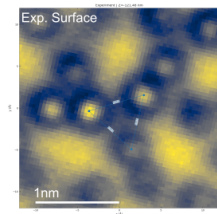
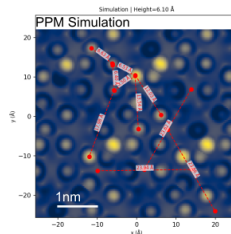
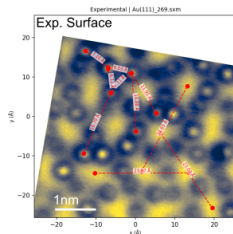
Finding (111) surface terminations



- (a) Cross-section of the (111) slab repeated 3 times.
- (b) The density profile of O atoms along z.
- (c) One termination cut at a specific z value.

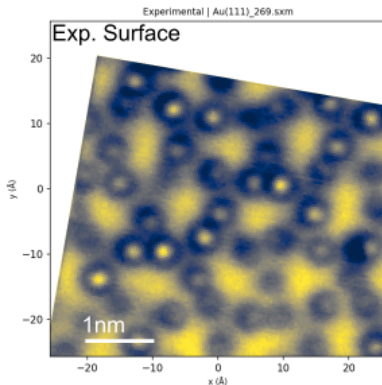
Candidate surface termination

Candidate 1

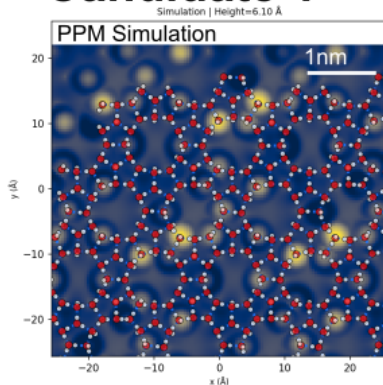


The simulated AFM images closely match the experiment. The spacing between features is the same.

Candidate surface termination



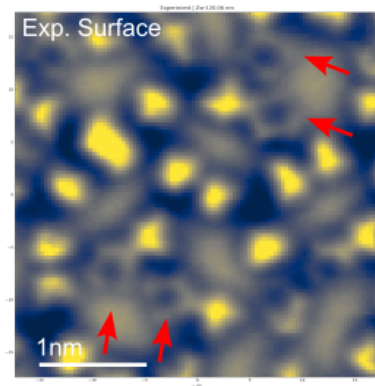
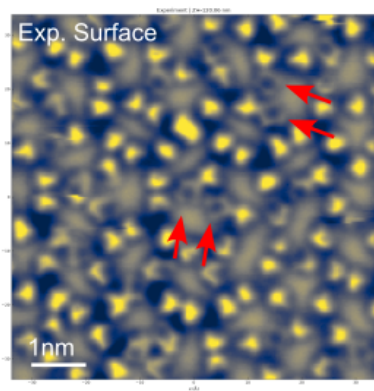
Candidate 1



Upward-pointing free OH bonds appear as the round features. No THF molecules appear in the simulated termination.

PPM: Comput. Phys. Commun. 305, 109341 (2024); Phys. Rev. B 90, 085421 (2014); Phys. Rev. Lett. 113, 226101 (2014).

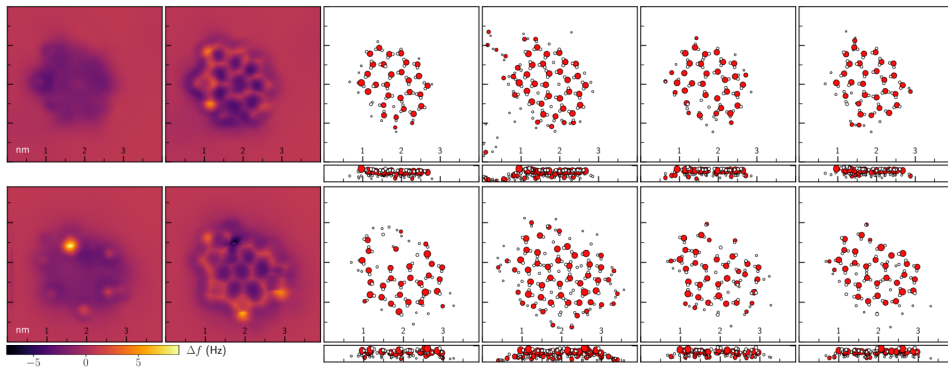
Candidate surface termination



What are the structures of these quadrilateral features? Is it true that there are no THF molecules on top?

Machine-learning structure discovery from AFM images

Input: Exp. AFM $\xrightarrow{\text{ML model}}$ Output: Structure predictions given by different models

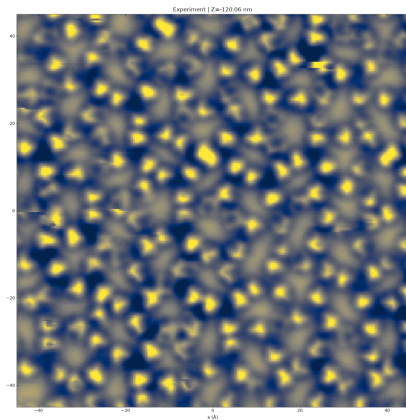


Given height-dependent AFM images to a machine learning model, the corresponding atomic structure can be predicted.

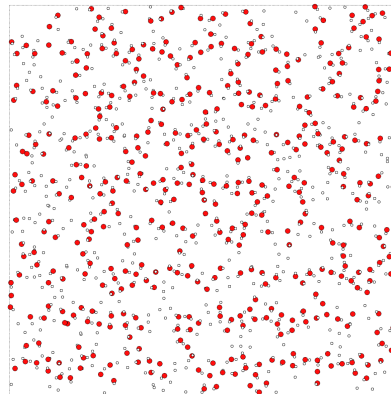
[1] npj Comput. Mater. (2026). DOI: 10.1038/s41524-026-02243-2.

Machine-learning assisted verification

Input: Height-dependent exp. AFM images

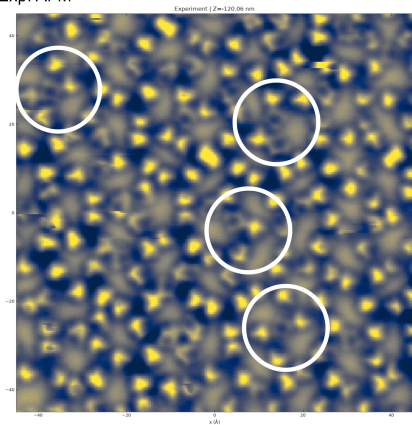


ML output: Structure prediction

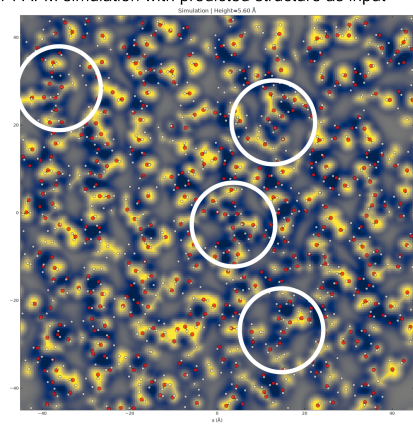


Machine-learning assisted verification

Exp. AFM

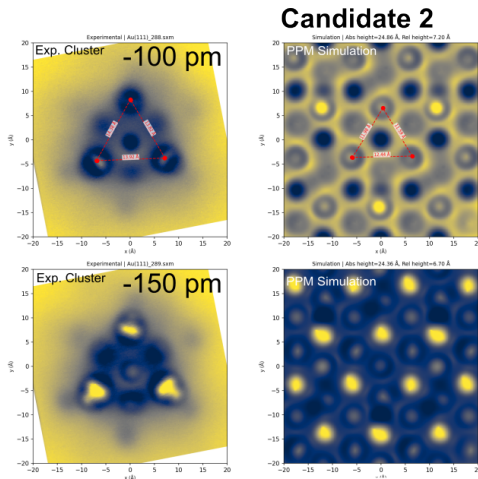


PPAFM simulation with predicted structure as input



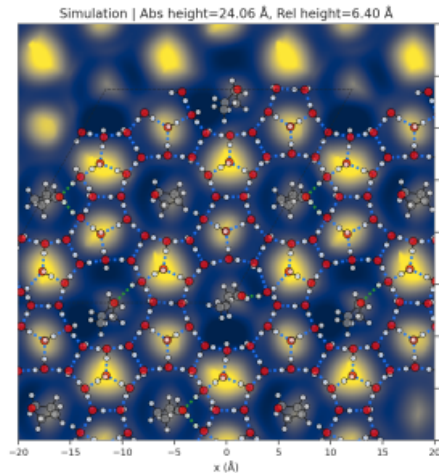
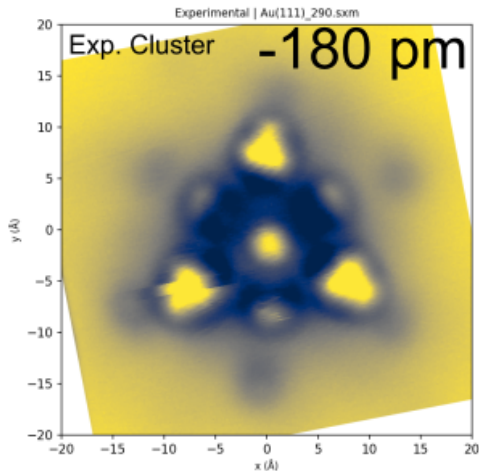
These features come from water molecules. **There is no THF in the top layer of the surface structures.**

Candidate cluster termination



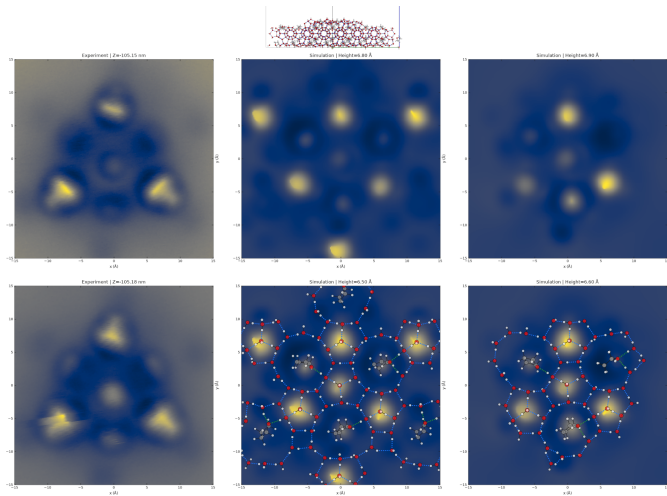
The simulated AFM images look promising, but the spacing between similar features is about 14% smaller than in the experiment.

Candidate cluster termination



Free OH bonds pointing upwards correspond to the round features. H-bonds are formed between water molecules and THF molecules. **Where does the 14% spacing mismatch come from?**

Building cluster structure



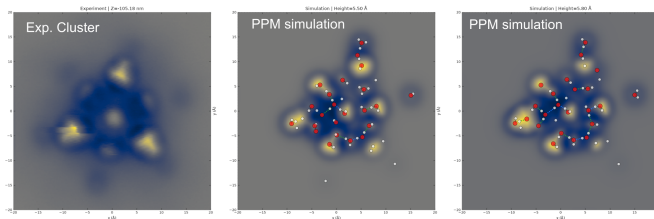
Cluster model

- Build island-like structures by removing surrounding molecules.
- Relax each candidate with DFT, then simulate AFM images.
- Compare feature size and shape with experiment.

**The mismatch dropped from 14% to 11%.
Whether the simulated structure is
correct is still unclear.**

Machine learning assisted verification

Input: Exp. AFM $\xrightarrow{\text{ML models}}$ Output: Structure predictions

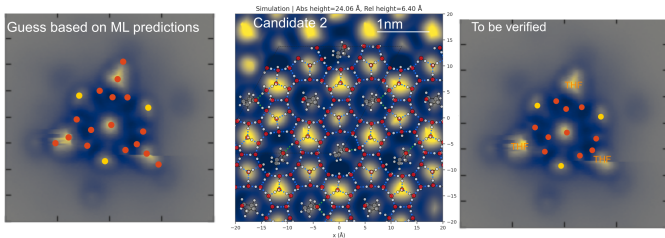


ML-assisted guess

- Structure discovery model trained on the water system.
- Given the 3D AFM images, the atomic structure of the surface structure can be predicted.



Machine learning assisted verification



ML-assisted guess

- Structure discovery model trained on the water system.
- Given the 3D AFM images, the atomic structure of the surface structure can be predicted.
- **The proposed structure is need to be verified.**

Summary

What we have answered?

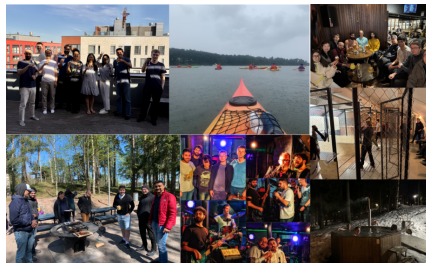
- 1 The surface orientation is (111).
- 2 We've found out the surface structure. There's no THF molecules in the top layer of surface structures.

What we still don't answer?

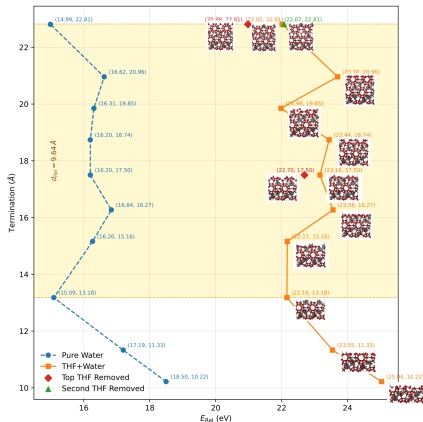
- 1 What is the atomic structure of the cluster?
- 2 Where does the mismatch come from?
- 3 What role do clusters play during the hydrates growth?

Acknowledgements

- Advisor: **Adam S. Foster** (Aalto University, Finland).
- Collaborators: **Yuejian Zhang, Jiani Hong, Ying Jiang** (Peking University, China).
- PPM developers: github.com/Probe-Particle/ppafm
- World Premier International Research Center Initiative (WPI), MEXT, Japan.
- Academy of Finland projects 347319 and 346824.
- Computational resources: Aalto Science-IT Project and CSC.



Formation energies for different surface structure



Relative energy

$$E_{\text{rel}} = E_{\text{slab}} - (n_{\text{H}_2\text{O}} E_{\text{H}_2\text{O}} + n_{\text{THF}} E_{\text{THF}})$$

where E_{slab} is the DFT energy of the relaxed slab, n_i the number of species i , and $E_{\text{H}_2\text{O}}$, E_{THF} the isolated-molecule reference energies.

Termination	$n_{\text{H}_2\text{O}}$	n_{THF}	E_{rel} (eV)
22.81 Å (top removed)	328	16	20.98
22.81 Å (2nd removed)	328	16	22.07
22.81 Å (with THF)	328	20	22.02
20.96 Å	304	16	23.70
19.85 Å	283	16	21.98
18.74 Å	272	16	23.44
17.50 Å	248	16	23.16
16.27 Å	238	16	23.56
15.16 Å	216	16	22.17

Removing the top-layer THF (**highlighted**) lowers E_{rel} vs. keeping it, and also vs. removing **bulk** THF — losing surface THF is easier, explaining why no THF appears on the surface.

DFT simulations

- Structures were relaxed with periodic DFT (VASP 6.3.2) using the PAW method with PAW-PBE potentials for H, C, and O.
- The optB86b-vdW functional was used to describe dispersion interactions.
- Plane-wave cutoff: 500 eV. Large slab cells (up to ~ 330 H₂O + ~ 20 THF) were sampled at the Γ -point only.
- A Γ -centred $5 \times 5 \times 1$ mesh was used for the bulk reference cells.
- Geometries were optimised with the FIRE algorithm until residual forces < 0.01 eV/Å, with fixed lattice vectors.
- The relaxed structures were used to determine the bulk sll lattice parameter, build (111) surface slabs and island-like cluster models, and simulate high-resolution AFM images with the probe-particle model (ppafm) for direct comparison with experiment.

Classical force-field simulation

- Because the systems are too large for DFT (up to ~ 3000 atoms), structures were also explored with classical molecular dynamics (MD) using GROMACS.
- Water described with the **TIP4P-Ew** model [1]; other molecules (THF) with **OPLS-AA** parameters. The THF topology and charge distribution were generated with the LigParGen server (Jorgensen Lab) [2].
- Lattice-parameter scan of the bulk sII cell ($a = 16.40\text{--}17.10$ Å, $\Delta a = 0.01$ Å) $\rightarrow$ fitted optimum 16.75 Å, in agreement with DFT (16.70 Å).
- (111) surface ($d_{111} = 9.67$ Å) built by repeating the bulk cell $\times 3$ along **c**; terminations cut by the O-density profile. Island-like cluster models (~ 3000 atoms) from expanded cells with surrounding molecules removed.
- Same analysis as DFT: bulk lattice parameter, terminations and cluster structures $\rightarrow$ AFM images via the probe-particle model (ppafm) with point charges, compared with experiment.

[1] J. Chem. Phys. 120, 9665 (2004)

[2] <https://zarbi.chem.yale.edu/ligpargen/>

AFM simulation

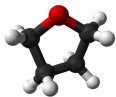
- High-resolution AFM images for a CO-terminated tip were simulated with the **full density-based model** (FDBM), as implemented in the probe-particle model (PPM, ppafm) with GPU acceleration.
- Inputs: atomic structure, electrostatic (Hartree) potential, and electron density, all calculated from DFT with VASP.
- Tip-sample interaction has three contributions:
 - **(i) Short range:** density-overlap model $V_{\text{SR}} = V_0 \int [\rho^{\text{tip}}(\vec{r}) \rho^{\text{sample}}(\vec{r})]^\alpha d\vec{r}$, with $V_0 = 18.0$ and $\alpha = 1.0$ (A_{Pauli} , B_{Pauli} in PPM);
 - **(ii) Electrostatic:** Hartree potential and tip charge density;
 - **(iii) van der Waals:** DFT-D3 scheme with PBE parametrisation.
- For large CFF-relaxed structures (~ 3000 atoms), a simplified PPM with only vdW + point charges enables efficient comparison with experiment.

[1] FDBM: ACS Nano 13, 786 (2019); PPM: Comput. Phys. Commun. 305, 109341 (2024); Phys. Rev. B 90, 085421 (2014); Phys. Rev. Lett. 113, 226101 (2014).

AFM experiment setup

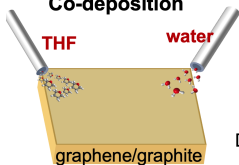
Ideal system: tetrahydrofuran(THF) hydrate

THF molecule Conditions for hydrate formation



- Form around 4.4 ° with THF:H₂O=1:17
- Do not require high pressures
- Binary guest hydrates with gases

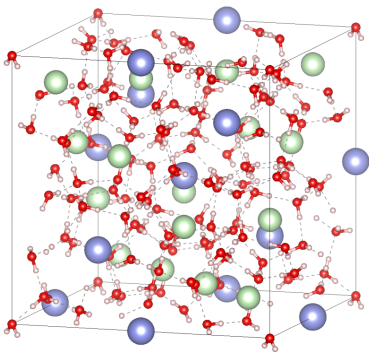
Co-deposition



Deposition temperature: 110K

[1] Yuejian Zhang, Jiani Hong, Prof. Ying Jiang's group, Peking University (2025).

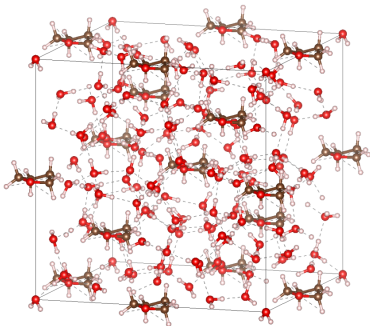
Starting point: the bulk THF hydrate



The sII structure of clathrate hydrates [1]. Green and blue spheres mark the centers of the small and large cages.

[1] J. Chem. Phys. 138, 124504 (2013)

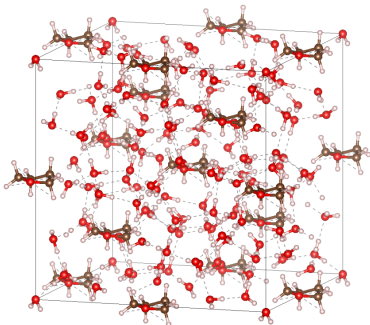
Starting point: the bulk THF hydrate



THF molecules fill the large cages; the small cages stay empty.

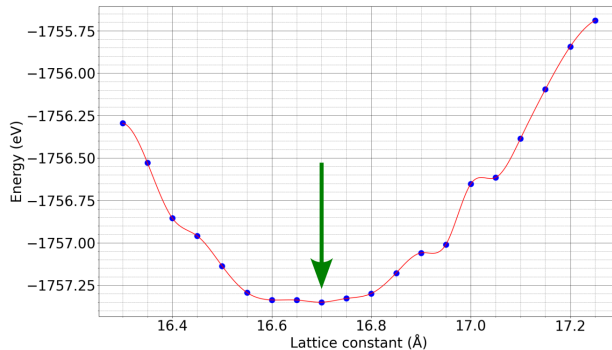
[1] J. Chem. Phys. 138, 124504 (2013)

Starting point: the bulk THF hydrate



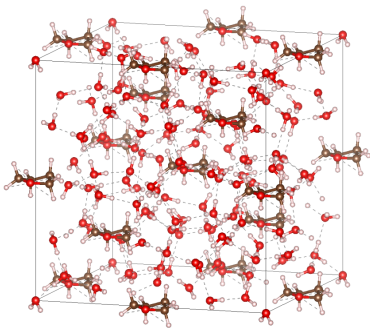
THF molecules fill the large cages; the small cages stay empty.

[1] J. Chem. Phys. 138, 124504 (2013)



DFT energies of relaxed bulk structures with different lattice constants. The optimum lattice constant is 16.7 Å.

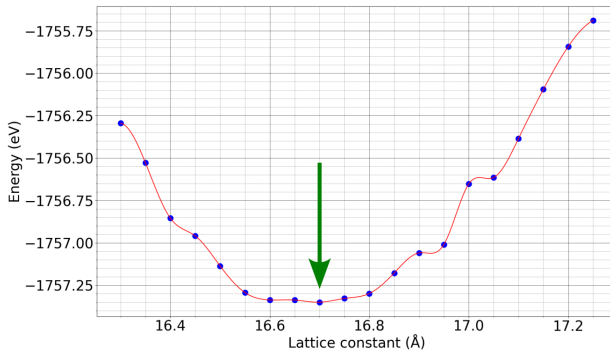
Starting point: the bulk THF hydrate



THF molecules fill the large cages; the small cages stay empty.

With the optimised bulk system, we can build different surface structures.

[1] J. Chem. Phys. 138, 124504 (2013)



DFT energies of relaxed bulk structures with different lattice constants. The optimum lattice constant is 16.7 Å.