

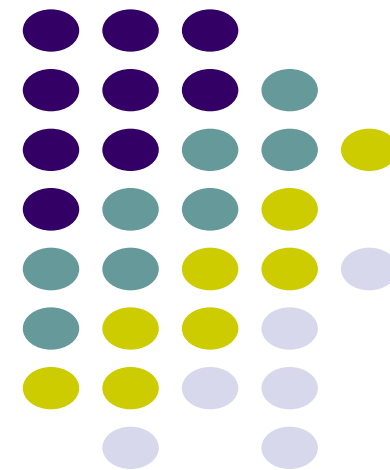
ソフトポーラスクリスタルの 統計物理学

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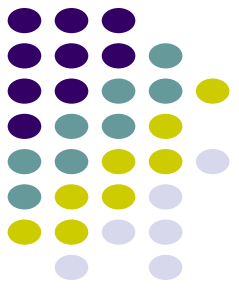
²鳥取大学工学研究科

**K. Mitsumoto and K. Takae,
Proc. Natl. Acad. Sci. 120, e2302561120 (2023);
Phys. Rev. Res. 6, L012029 (2024);
Commun. Phys. 9, 36 (2026).**

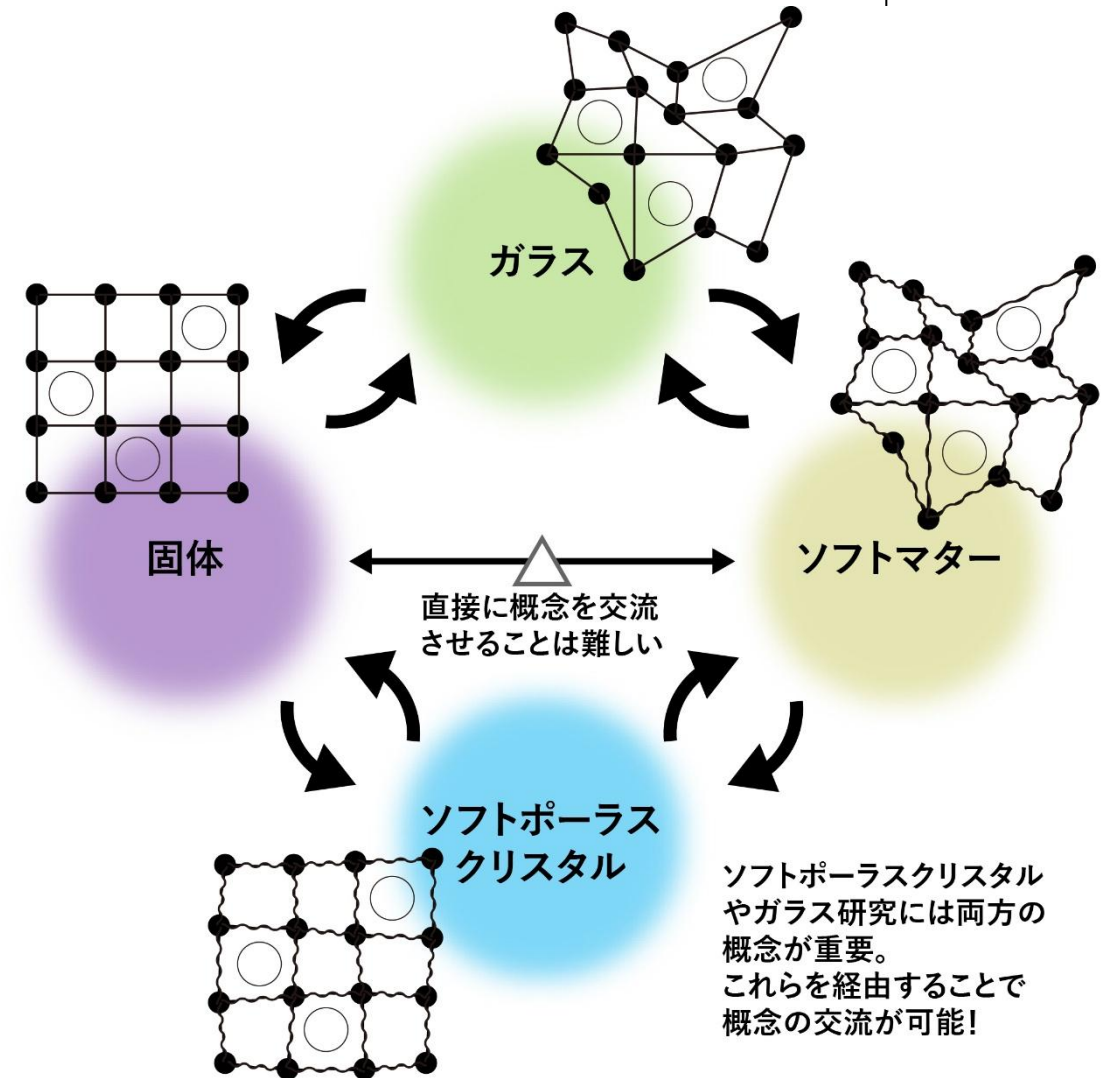


そもそも何をやりたいのか？

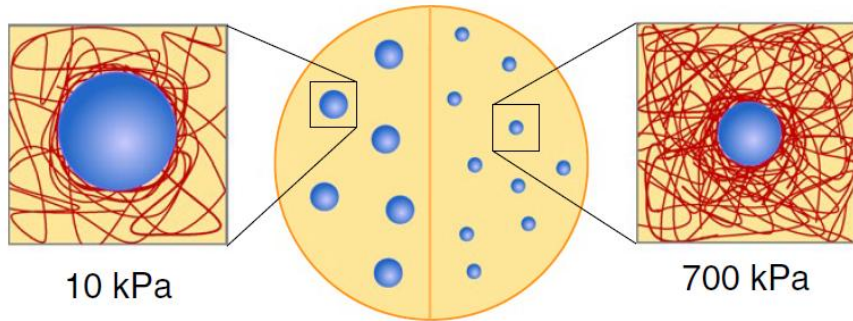
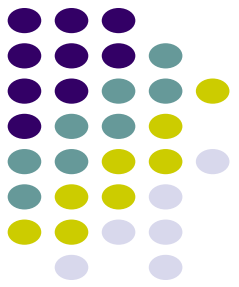
結晶のソフトマター物理学



- 固体物理学（硬く、結晶性を前提）とソフトマター物理学（柔らかく、非晶性を前提）は概念や手法に解離が大きく、直接の交流は難しい
- ソフトポーラスクリスタル（硬さの制御）・ガラス（構造の制御）により両者をなめらかに接続できる可能性？
- 特有の新奇物性も生ずる（ガラスはそこが難しい）

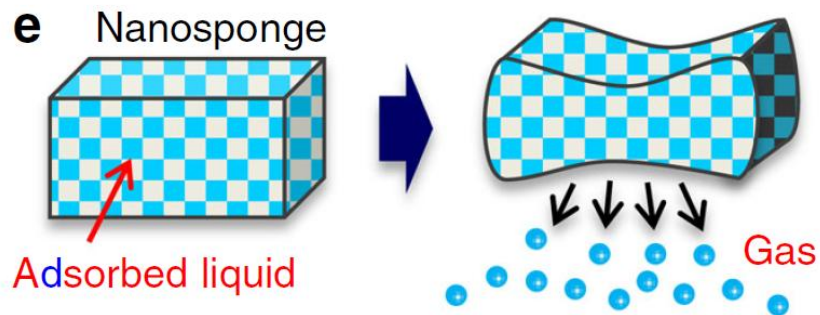


Soft porous matter

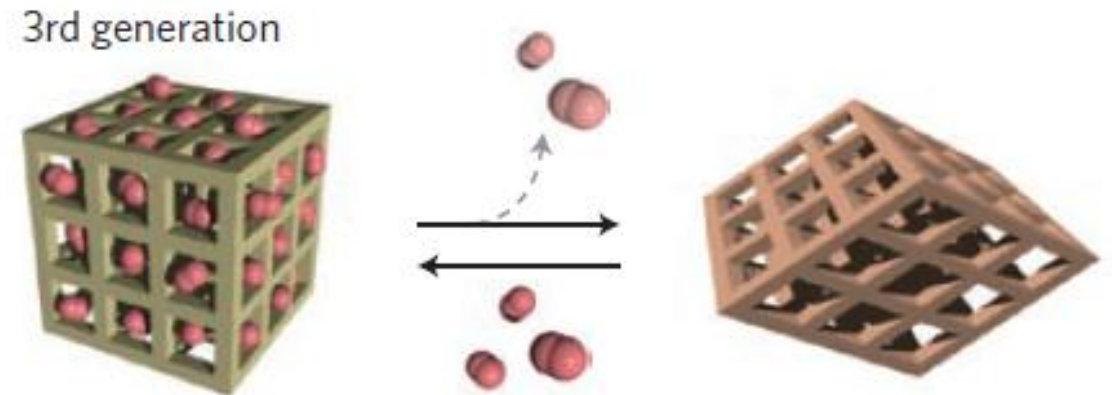


Porous coordination polymer / Metal-organic frameworks (PCP/MOF)
Large pores inside the frameworks, adsorbs small molecules

Porous Polymer networks suppress liquid-liquid phase separation
K.A. Rosowski et al., Nature Phys. 16, 422 (2020).



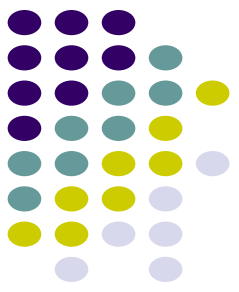
Control gas-liquid phase transition by nanosponges
⇒ application for refrigerator K. Nomura et al., Nature Commun. 10, 2559 (2019).



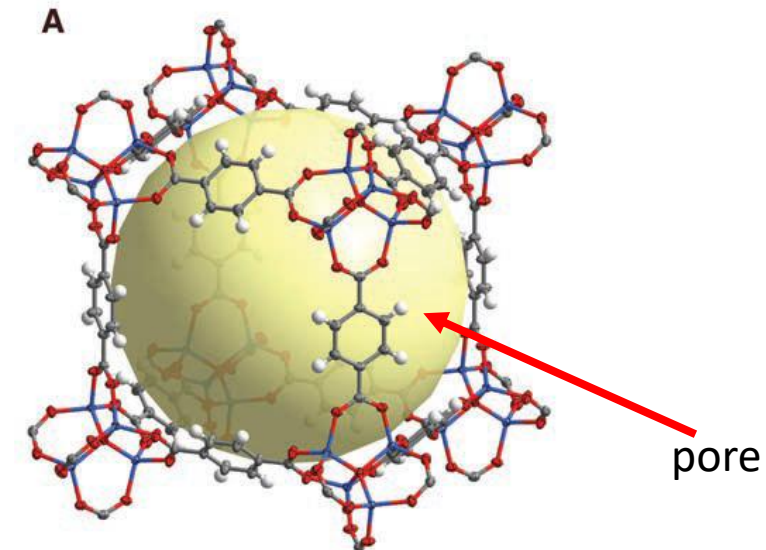
S. Horkie, S. Shimomura, and S. Kitagawa, Nature Chem. 1, 695 (2009).

Common feature: Coupling between molecular adsorption and matrix elasticity

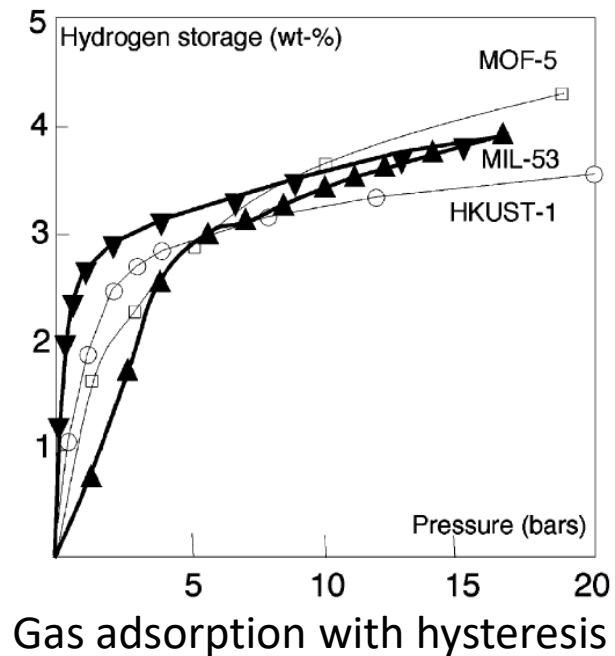
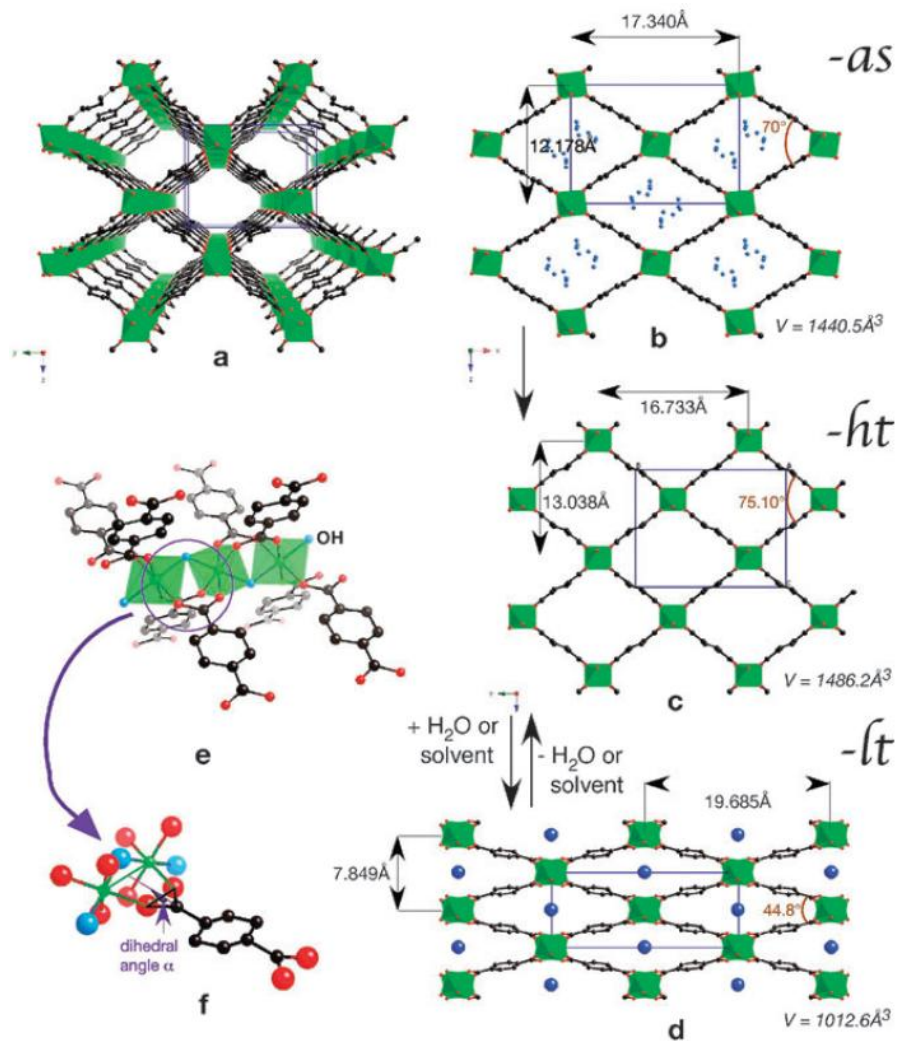
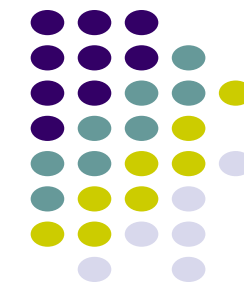
PCP/MOF



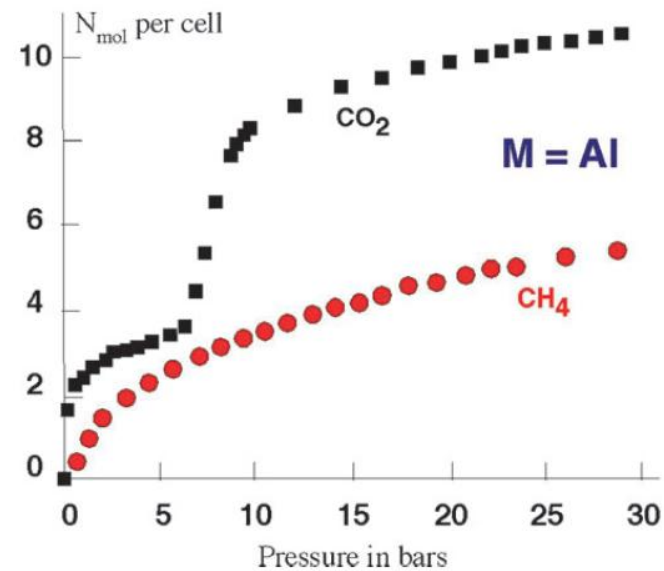
- Porous Coordination Polymer (PCP) or Metal-Organic Frameworks (MOF): Organic molecules coordinate with metallic nodes, forming structures with large internal pores (typically \sim nm).
- **Structure**: Typically Crystalline (cf. some studies on amorphous MOFs)
- **Functionality**: Adsorption/desorption of guest molecules, transport inside MOFs.
Mechanical response: both rigid and flexible materials are synthesized.



Example of MOF: MIL-53 (Matériaux de l'Institut Lavoisier)

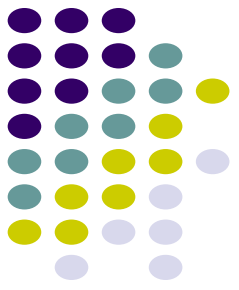


Gas adsorption with hysteresis



Selective gas adsorption

Huge matrix distortion associated with molecular adsorption!



Molecular adsorption in MOFs

- Adsorption of guest molecules changes
 - Crystal size and structure
 - Elastic constants
- Purpose: To reveal the role of these two characteristics (particularly the latter).

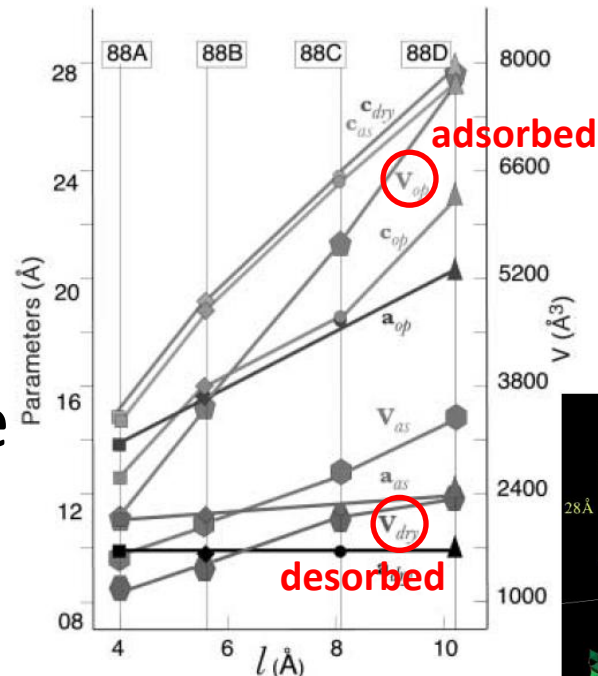


Fig. 2. Evolution of cell parameters and volume of MIL-88 A through D in their different states (synthesized, open, and dry) as a function of the length of the linker.

C. Serre et al., Science **315**, 1828 (2007).

Table 1. Elastic Constants of the ZIF-8 Framework at 300 K for Various Values of CH₄ Loading at 300 K and 0 GPa

CH ₄ /unit cell	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)
0	11.21	7.49	2.75
3	11.26	7.52	2.89
6	11.29	7.55	2.96
11	11.33	7.58	3.18
18	11.38	7.66	4.00

A. U. Ortiz et al., J. Phys. Chem. Lett. **4**, 1861 (2013).

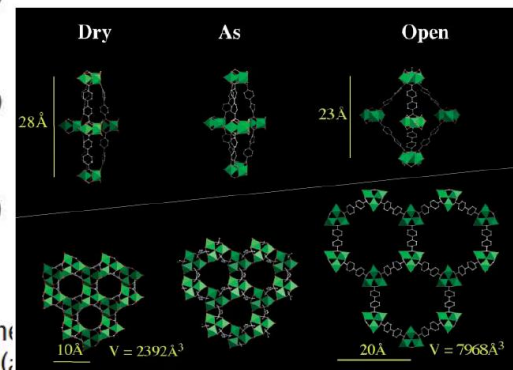


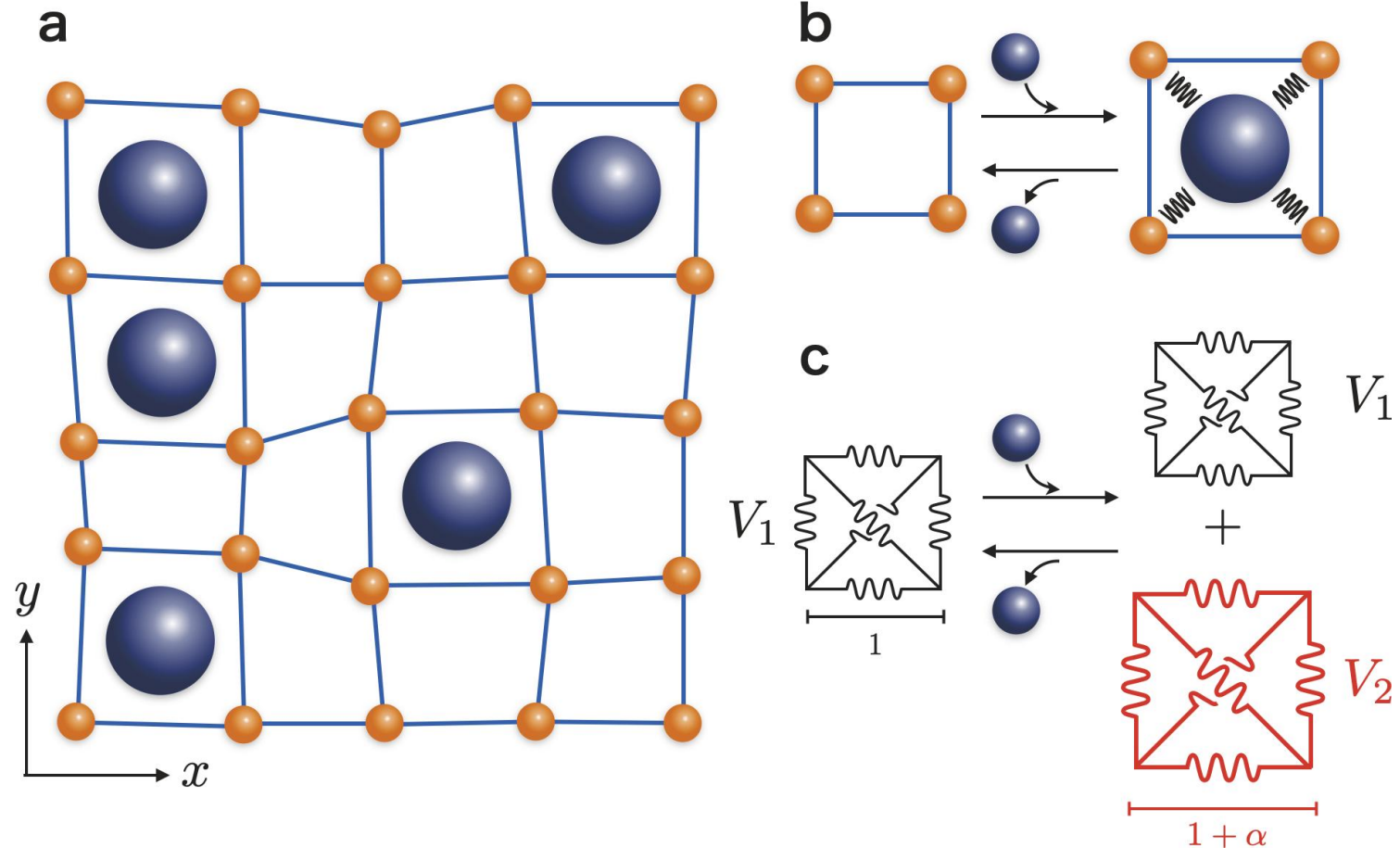
Table 3 Elastic constants (C_{ij}), bulk (B), shear (G), and Young's moduli (Y) in GPa for empty MOF-74-Zn, as well as loaded with H₂, CO₂, CH₄, and H₂O. For the bulk, shear, and Young's moduli only Hill's mean are reported. x , y , and z components of the Young's modulus and B/G are also reported

Prop.	MOF	+H ₂	+CO ₂	+CH ₄	+H ₂ O
C ₁₁	14.84	17.00	19.29	24.16	31.52
C ₃₃	15.34	17.83	19.86	25.96	33.25
C ₄₄	13.03	12.25	12.68	12.75	13.47
C ₁₂	5.60	5.31	4.41	6.07	10.09
C ₁₃	8.64	13.38	14.04	19.84	9.85
C ₁₄	4.89	2.87	3.66	1.74	5.17
B	9.91	13.54	10.05	13.34	17.57
G	4.66	6.48	7.20	6.90	12.04
B/G	2.12	2.09	1.40	1.93	1.46
Y_x	3.44	8.60	1.49	2.19	26.45
Y_y	6.44	9.80	9.87	8.44	33.28
Y_z	3.72	8.10	1.58	2.58	28.99

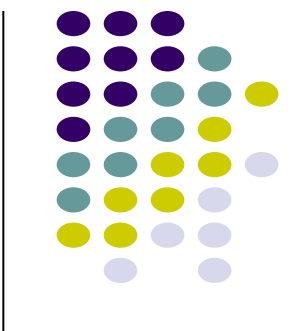
P. Canepa et al., J. Mater. Chem. A **3**, 986 (2015).

A toy model

- Orange: metallic nodes. They are connected via organic linkers (blue bonds) to form porous crystals.
- Black spheres: guest molecules. Only one sphere can be adsorbed to one site, inducing **local lattice expansion and hardening.**



Mathematical details



- Springs connecting host molecules

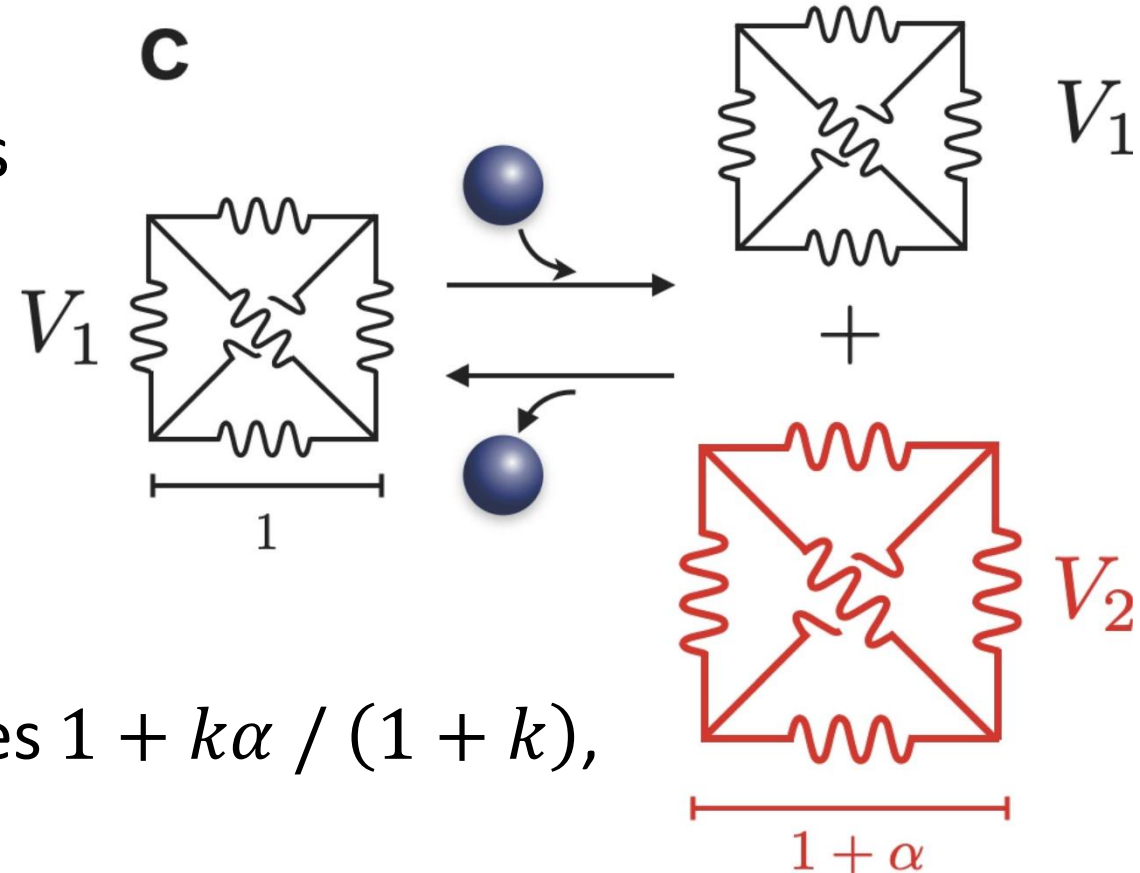
$$V_1 = \frac{1}{4} \sum_{NN} (1 - r_{ij})^2 + \frac{1}{2} \sum_{NNN} (\sqrt{2} - r_{ij})^2$$

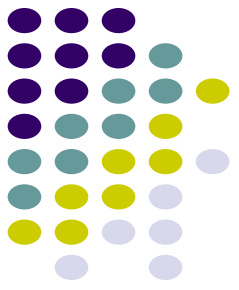
- Additional spring by guest molecules

$$V_2 = \frac{k}{4} \sum_{NN} (1 + \alpha - r_{ij})^2 + \frac{k}{2} \sum_{NNN} (\sqrt{2}(1 + \alpha) - r_{ij})^2$$

$$\mathcal{H} = \sum_{\square=1}^{N_{\square}} [V_1(\mathbf{r}_{i \in \square}) + \sigma_{\square} [V_2(\mathbf{r}_{i \in \square}) - \mu]],$$

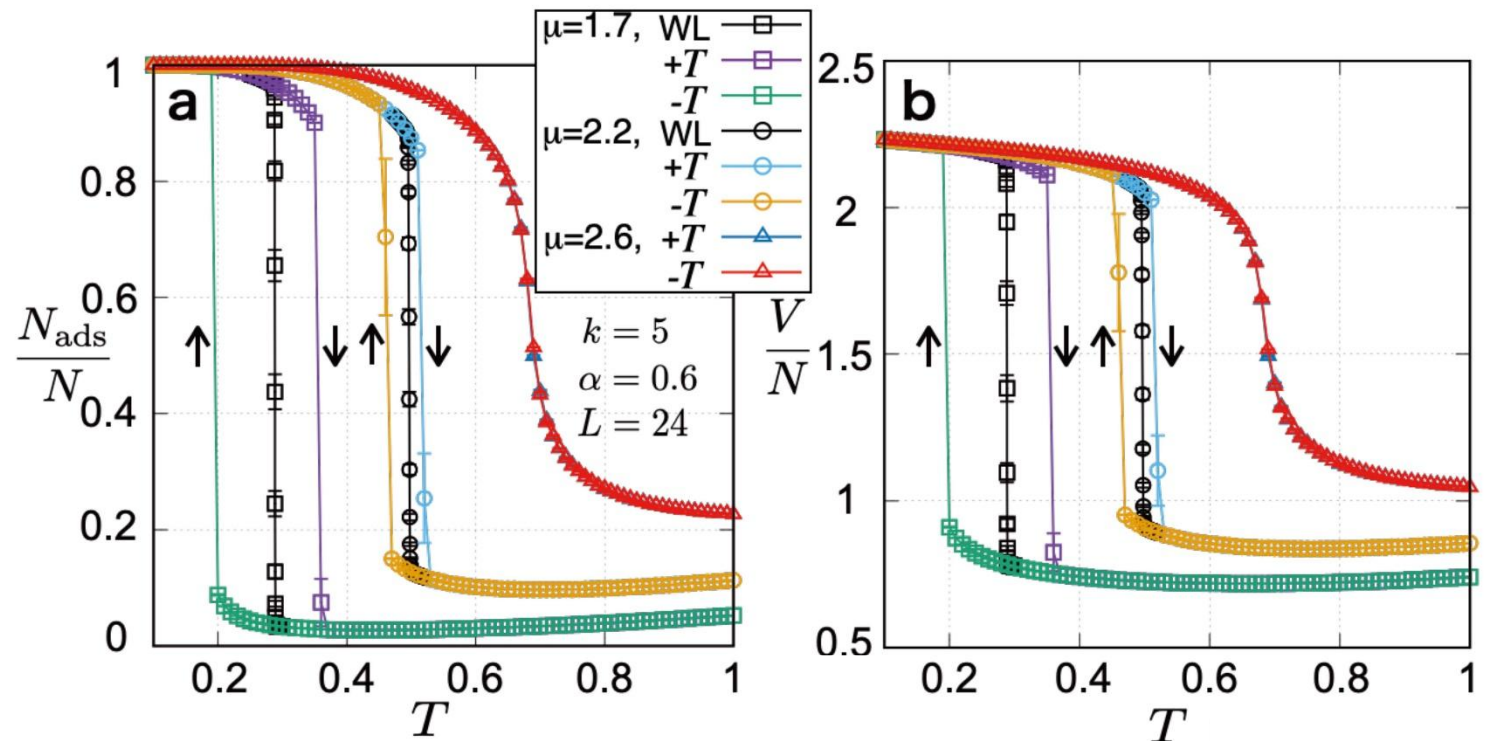
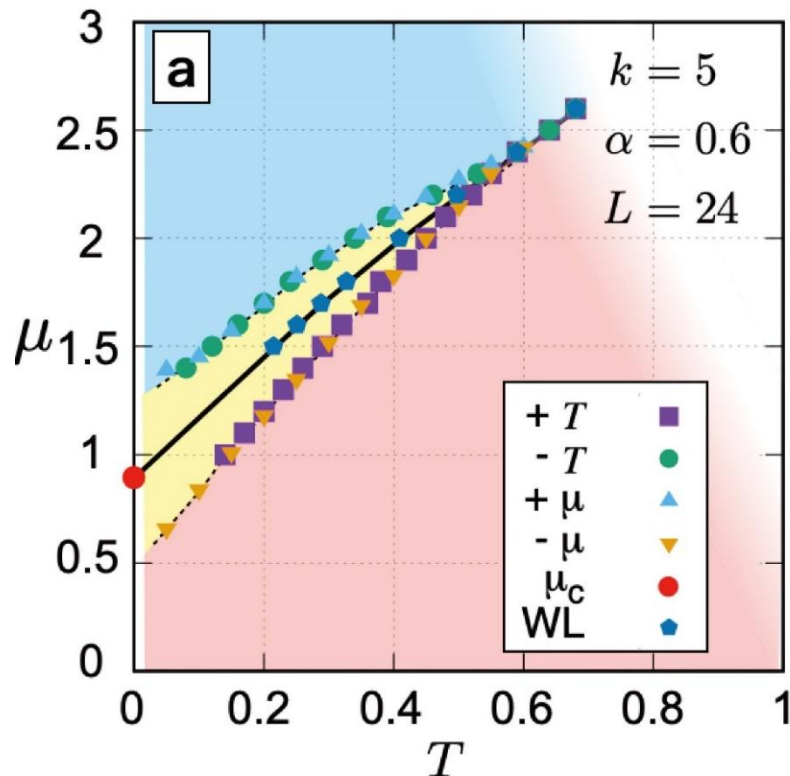
Upon molecular adsorption,
the natural length of the lattice becomes $1 + k\alpha / (1 + k)$,
and the rigidity becomes $1 + k$.

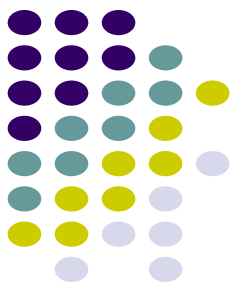




Adsorption-desorption transition occurs

- Phase diagram with respect to temperature T and guest's chemical potential μ : phase transition with hysteresis **without direct interaction between adsorbates!** (WL: equilibrium)

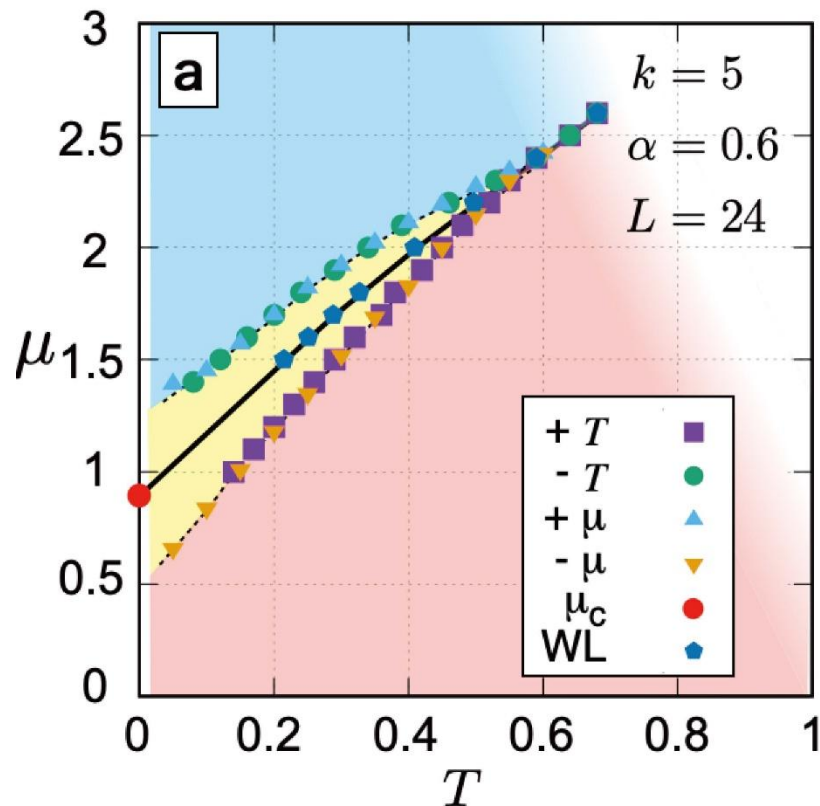




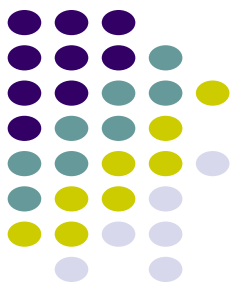
Phase transition is trivial?

- No direct interaction between adsorbates: Adsorption becomes Langmuir isotherm (without phase transitions) if elasticity is absent.

久保演習第5章演習問題29

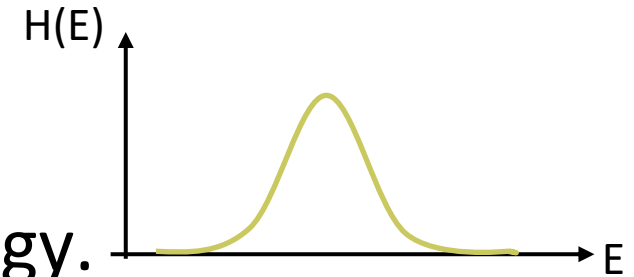


- Effective inter-adsorbate interaction due to the host's elasticity is the origin of the observed phase transition.
- In Landau theory,
$$f = f_{\text{adsorption}}(\phi) + f_{\text{elastic}}(\varepsilon) - \alpha\phi\varepsilon$$
Elimination of the elastic field may result in the occurrence of phase transition.

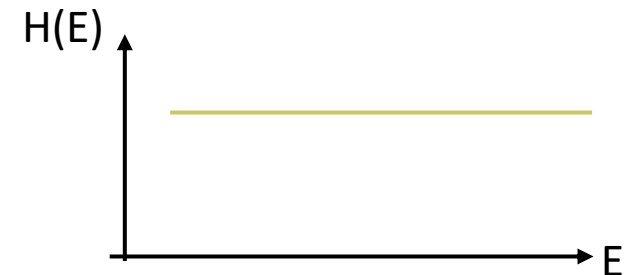


Multicanonical Monte Carlo method

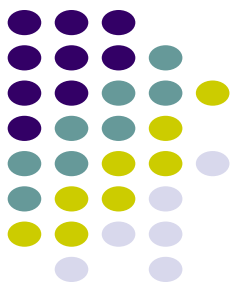
- The probability $P(\mathbf{x})$ of a microscopic state \mathbf{x}
- If $P(\mathbf{x})$ is uniform, the energy histogram $H(E) = \sum_{\{\mathbf{x}|\mathcal{H}(\mathbf{x})=E\}} P(\mathbf{x})$ has peaks:
not efficient sampling to calculate equilibrium energy.



- Multicanonical Monte Carlo: $P(\mathbf{x}) \propto e^{-g(E)}$.
if $g(E) \cong S(E) + \text{const.}$, $H(E)$ becomes uniform.
Then equilibrium energy and thermodynamic potential can be calculated efficiently.



- How to calculate $g(E)$? \Rightarrow Wang-Landau method (in short: tune $g(E)$ until $H(E)$ becomes flat)



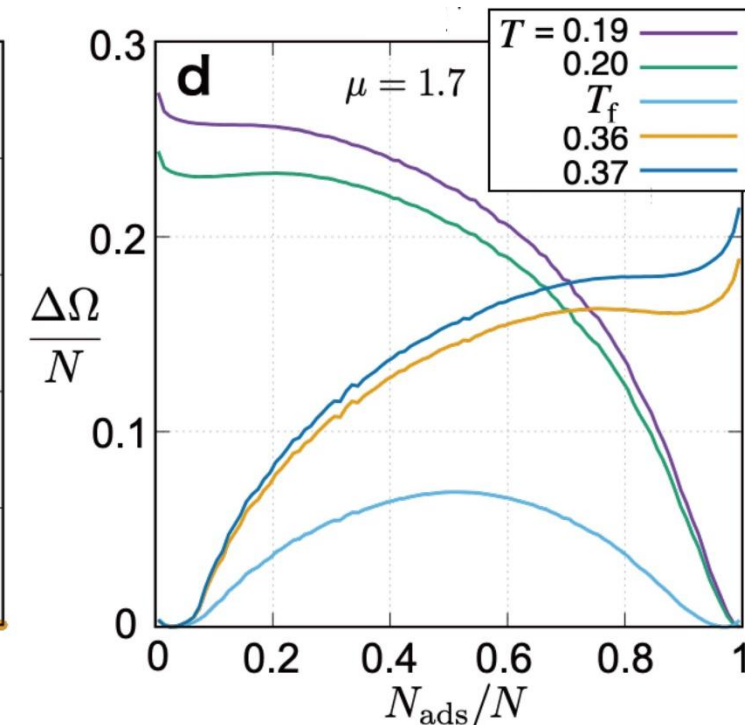
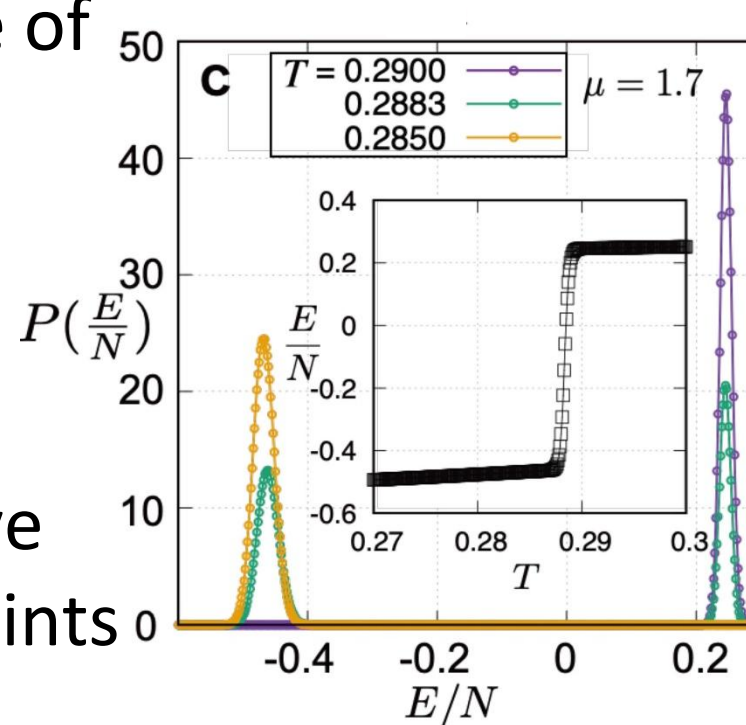
Thermodynamic potential

- Equilibrium phase boundary by multicanonical Monte Carlo.

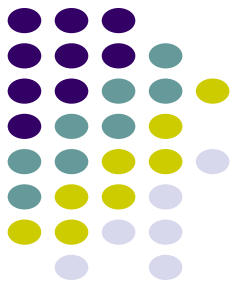
- c: probability distribution of the energy E .

At $T=0.2883$, coexistence of desorbed state (large E) adsorbed state (small E)

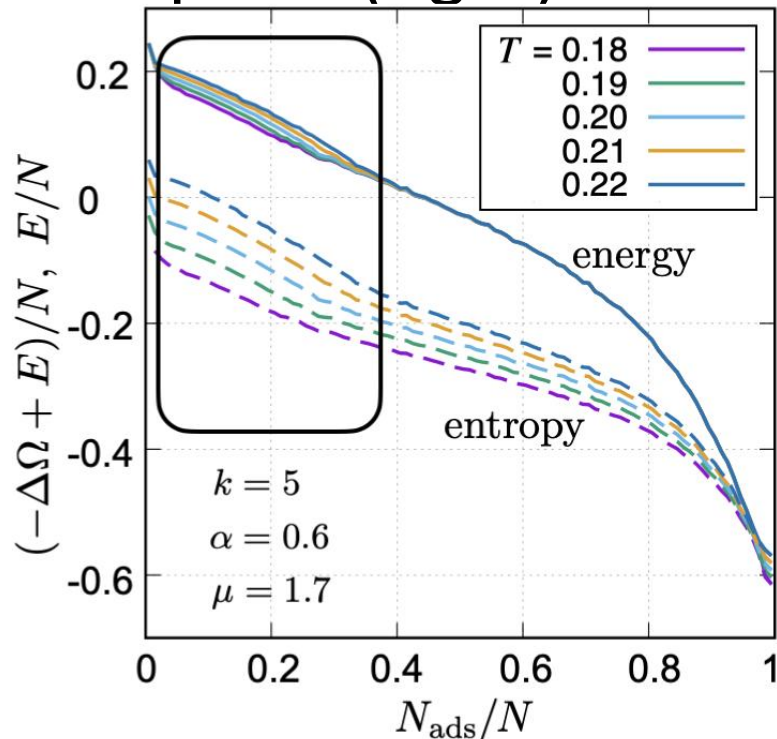
- d: landscape regarding adsorption fraction.
 $T=0.20$ (0.36) is just above (below) the transition points in the hysteresis loop.



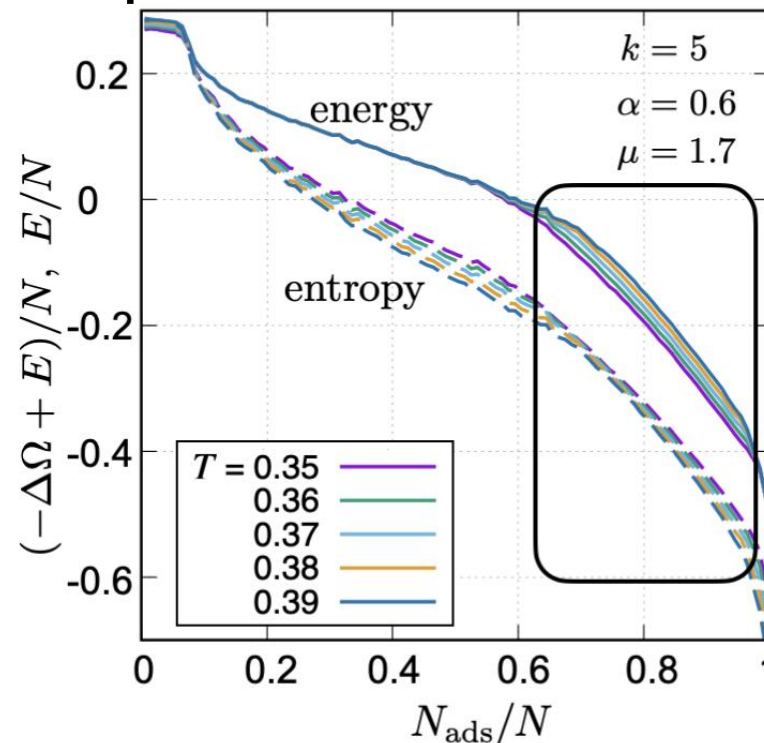
Calculate energy and entropy contributions to the thermodynamic potential



- Decompose thermodynamic potential close to the adsorption (left) and desorption (right) transition points.

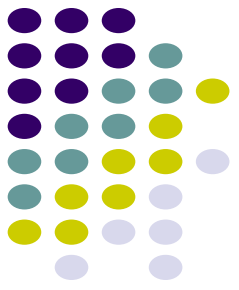


Entropy (broken curves) change is dominant

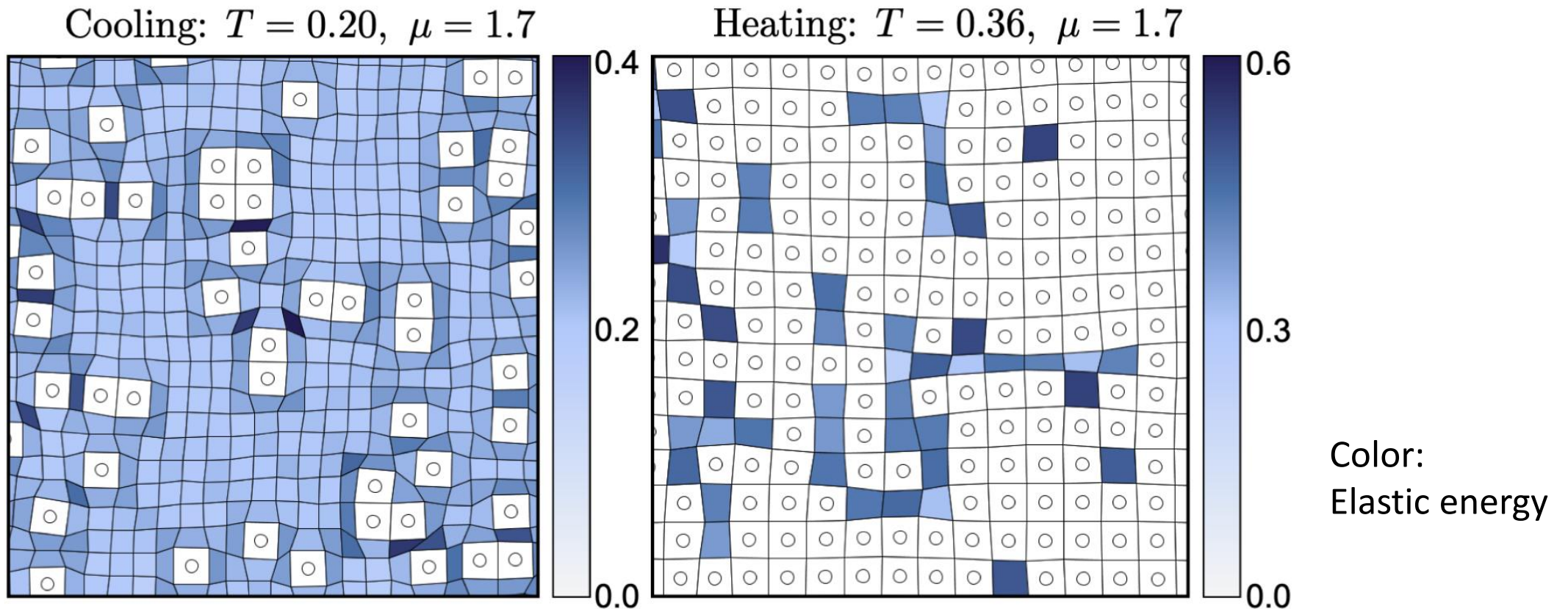


Energy (solid curves) change becomes large (for large N_{ads} region)

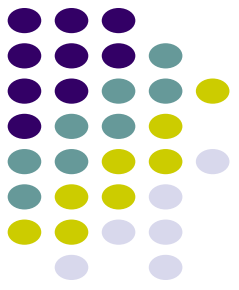
The origin of the hysteresis: Spatial distribution of adsorbed and desorbed sites



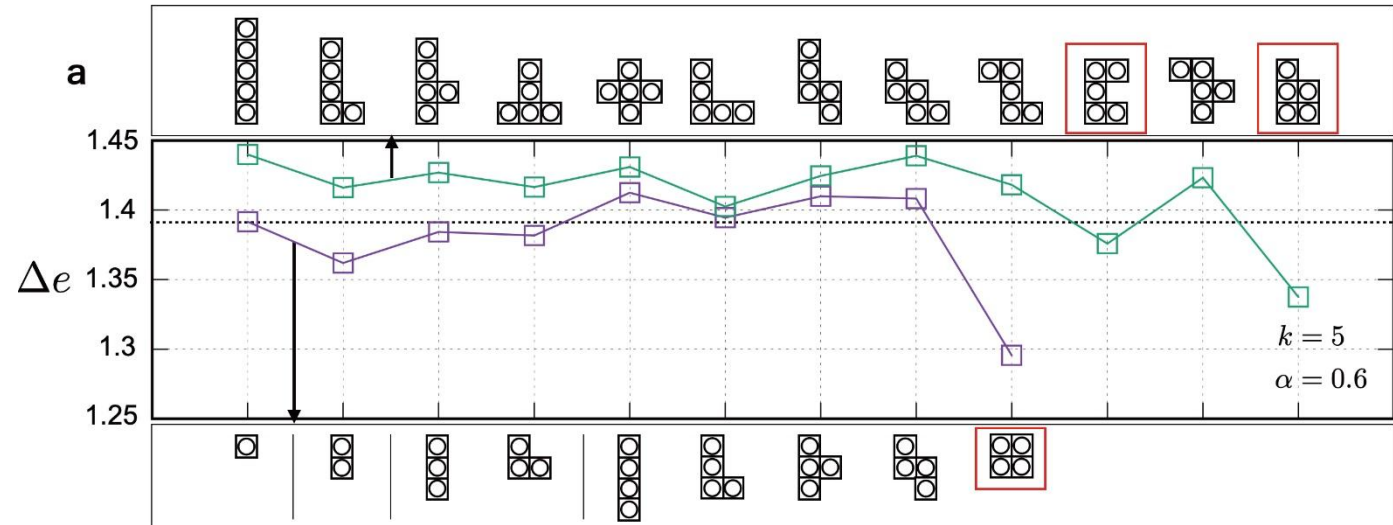
- Adsorbed sites distribute isotropically (left)
- Desorbed sites distribute anisotropically (right: flattened)



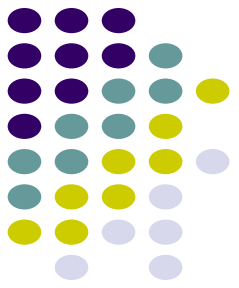
Elastic energy with respect to domain morphology



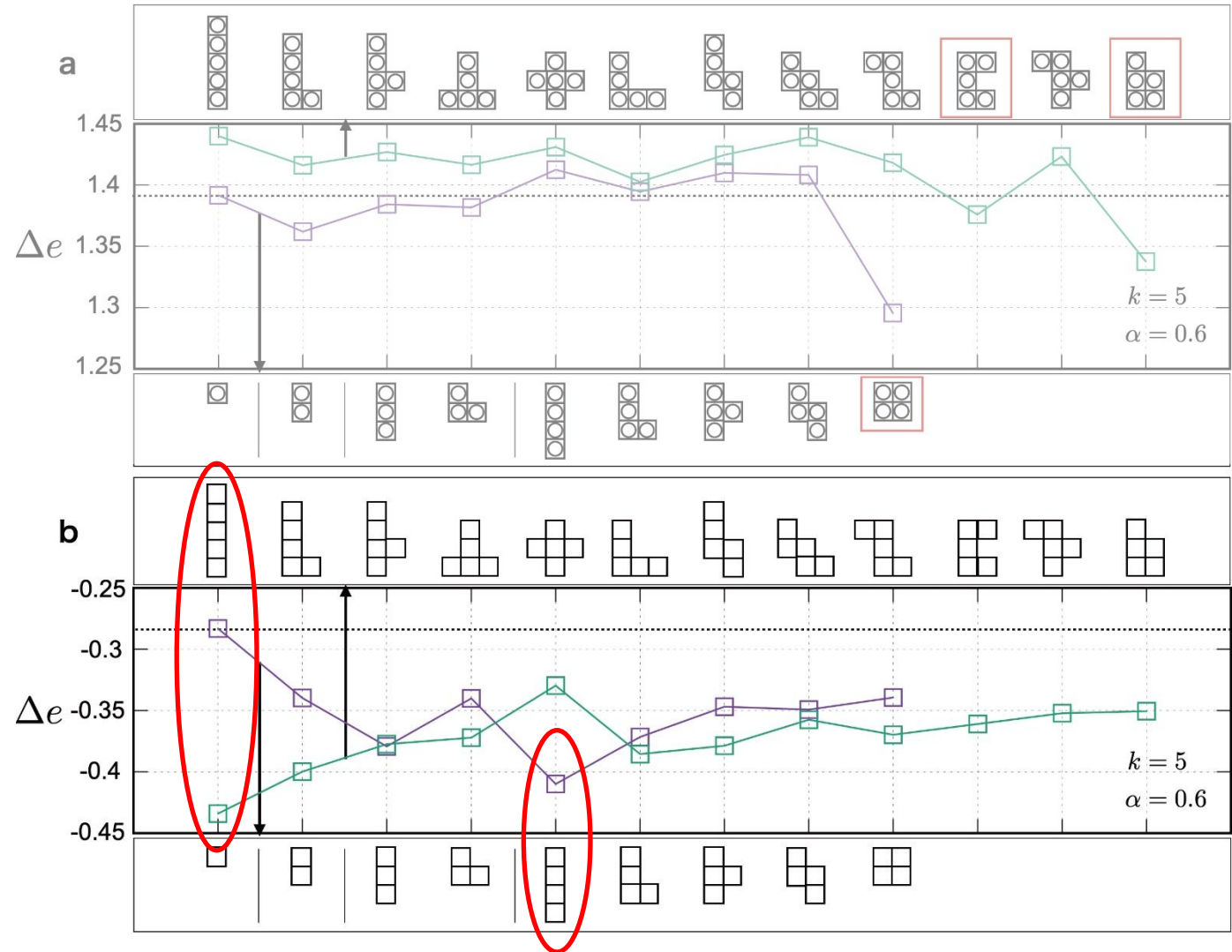
- Elastic energy is asymmetric between adsorbed / desorbed domains
- a: adsorbed domains. Energetic constraint on domain morphology. Only isotropic shapes are favored: Decrease **entropy**.



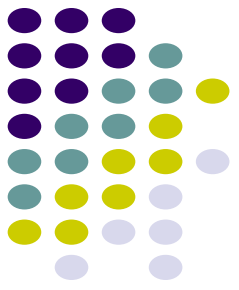
Elastic energy with respect to domain morphology



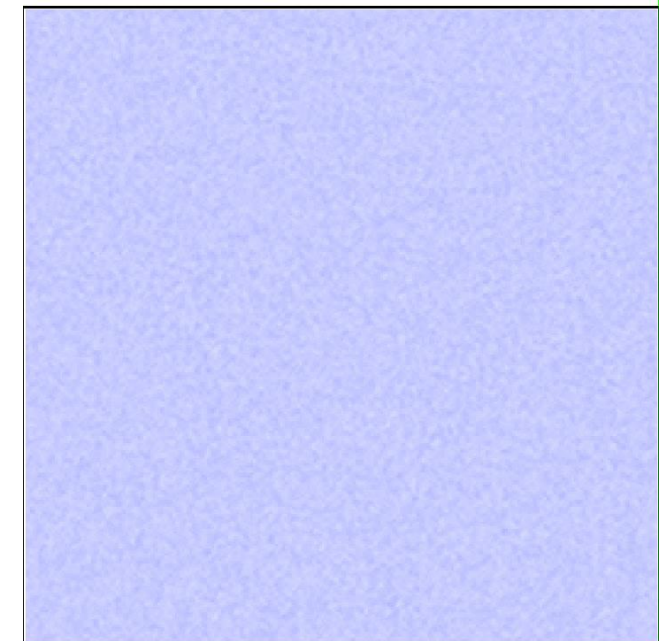
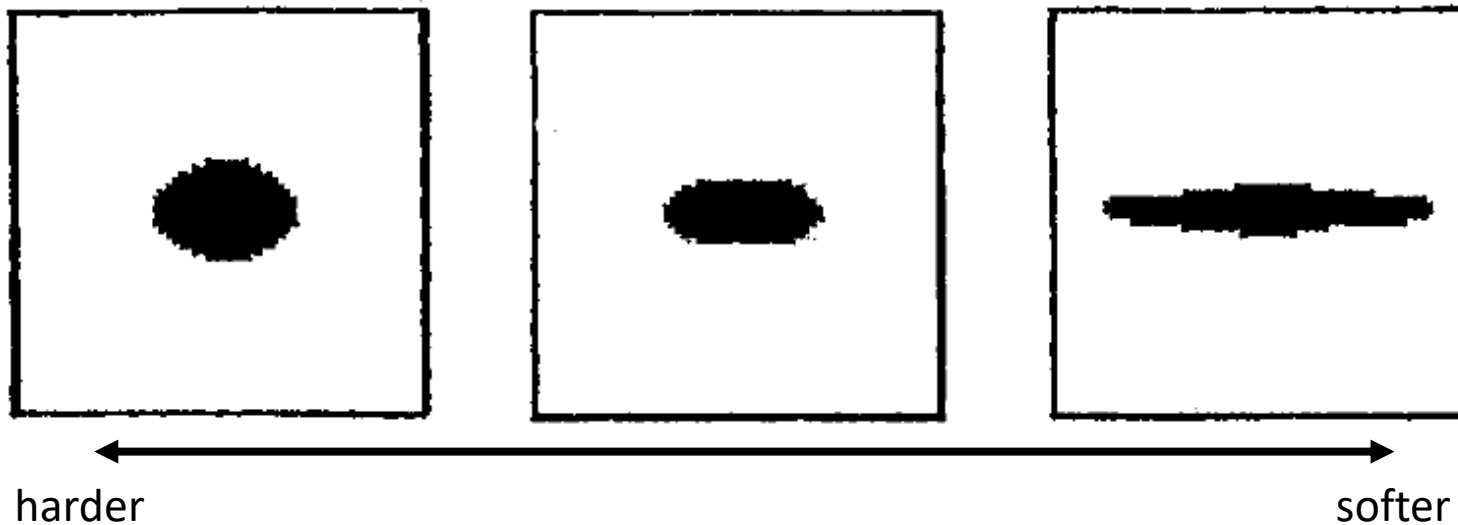
- Elastic energy is asymmetric between adsorbed / desorbed domains
- b: desorbed domains
Flattened domains with larger size are energetically favored, which have larger interfacial area.



The origin of the asymmetry: Elastic heterogeneity (Eshelby's argument)

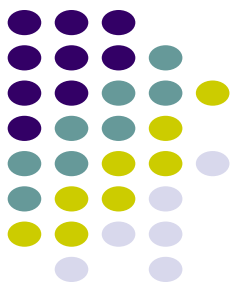


- Popular concept in metallurgy. It can be applied to MOFs!
Softer (harder) precipitate in alloys (shown as black domain) tends to be anisotropic (isotropic) to reduce the elastic energy.



The same phenomenon may occur in MOFs!

Elastic heterogeneity is relevant in experiments?



- The values of k and α are estimated from experiments.

Table 1. Mechanical parameters of three soft porous crystals estimated from experiments and density functional theory: B and V_{cell} represent the bulk modulus and unit cell volume adopted from the literature, where np (cp) and lp (op) represent the narrow (closed) pore and large (open) pores, respectively

Material	np (cp)		lp (op)		np (cp) \rightarrow lp (op)		
	B (GPa)	V_{cell} (\AA^3)	B (GPa)	V_{cell} (\AA^3)	k	α	E_{eff} (10^{-21} J)
MIL-53(Al)	10.7 [*]	939.92 [*]	0.35 [†]	1423.8 [†]	-0.967	-0.0051	0.90
MIL-53(Cr)	4.29 [*] , 10 [‡]	987.2 [*]	2 [‡]	1,486 [§]	-0.53	-0.13	24.1
DUT-49 [§]	5.6	46,070	7.5	96,047	0.34	1.09	8771.7

k and α regarding structural transformations are calculated from B and V_{cell} . E_{eff} is the energy scale of the effective guest-guest interactions due to elastic heterogeneity, estimated from B , V_{cell} , k , and α . We apply $B = 4.29$ for bulk modulus in the np phase of MIL-53(Cr) to evaluate k , α , and E_{eff} .

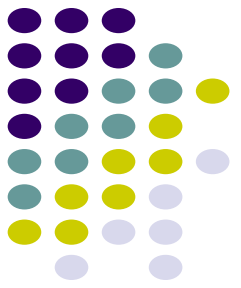
^{*}Taken from ref. 44. B and V_{cell} are determined by fitting experimental data by using the Murnaghan equation of state.

[†]Taken from ref. 45. B and V_{cell} are measured at room temperature.

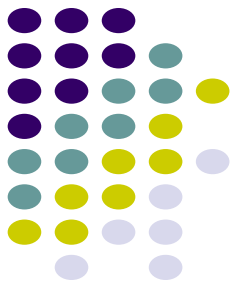
[‡]Taken from ref. 38. B is extracted from mercury intrusion-extrusion, and V_{cell} is determined from crystallography.

[§]Taken from ref. 46. B and V_{cell} are obtained by density functional theory at $T = 0$ (K).

E_{eff} is elasticity-mediated interaction energy estimated from experimental values of B and V_{cell} , which is comparable with (or even larger than) van der Waals and electrostatic energy ($\sim 10^{-21}$ J).

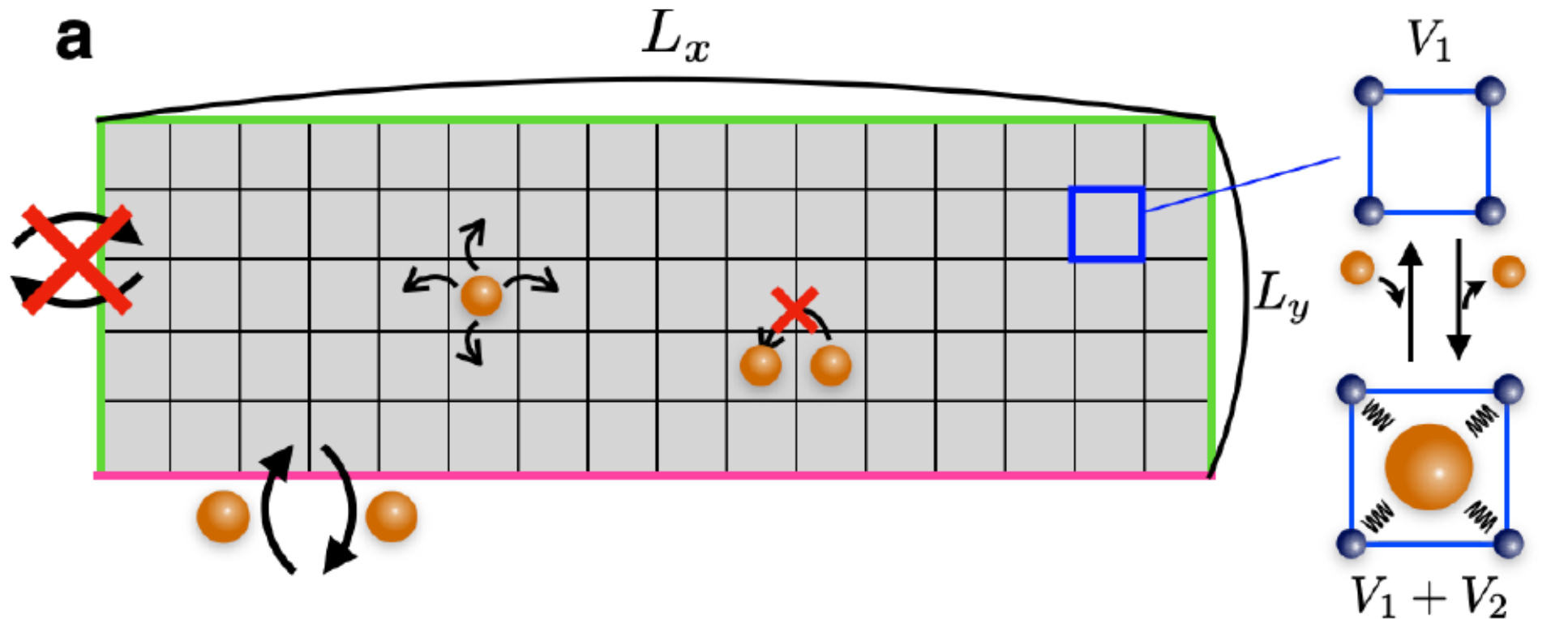


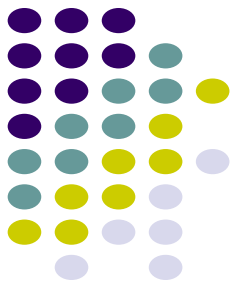
KINETICS



Setup

- Adsorption only from the bottom boundary, diffusion inside.
- Dynamic Monte Carlo: not strict time evolution.





Kinetics!

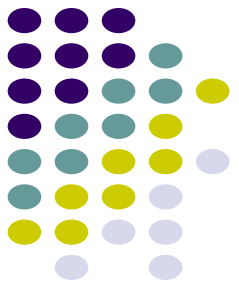
- Adsorption kinetics proceeds heterogeneously!

$t=0$

Boundary: free surfaces without adsorption-desorption

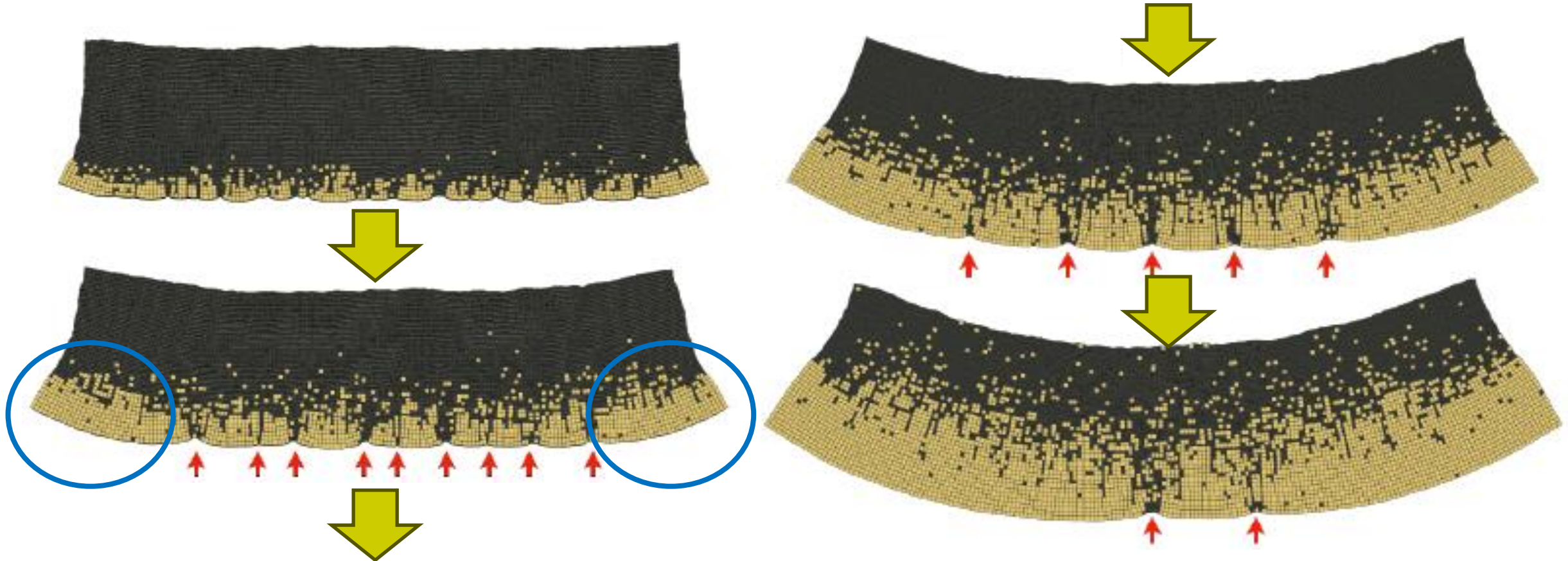


bottom surface: particle entrance and exit can occur



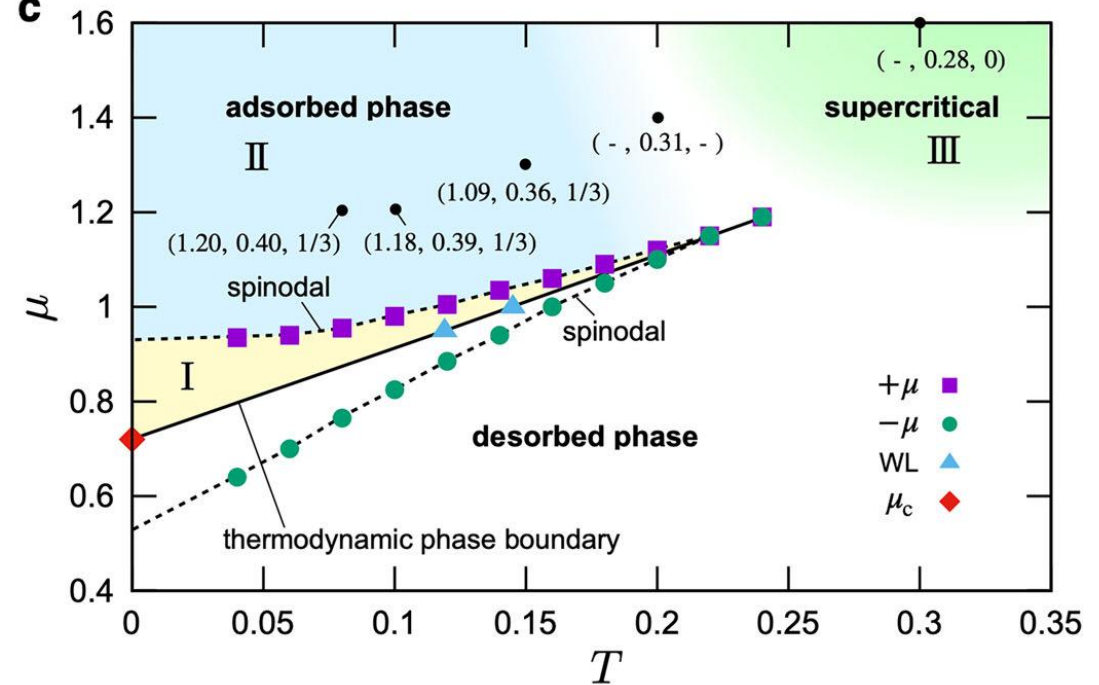
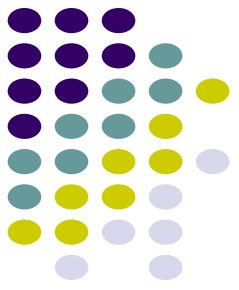
Elastic creasing

- Appearance and coarsening of elastic creases with macroscopic deformation. **universal law: corner effect and dynamic scaling**



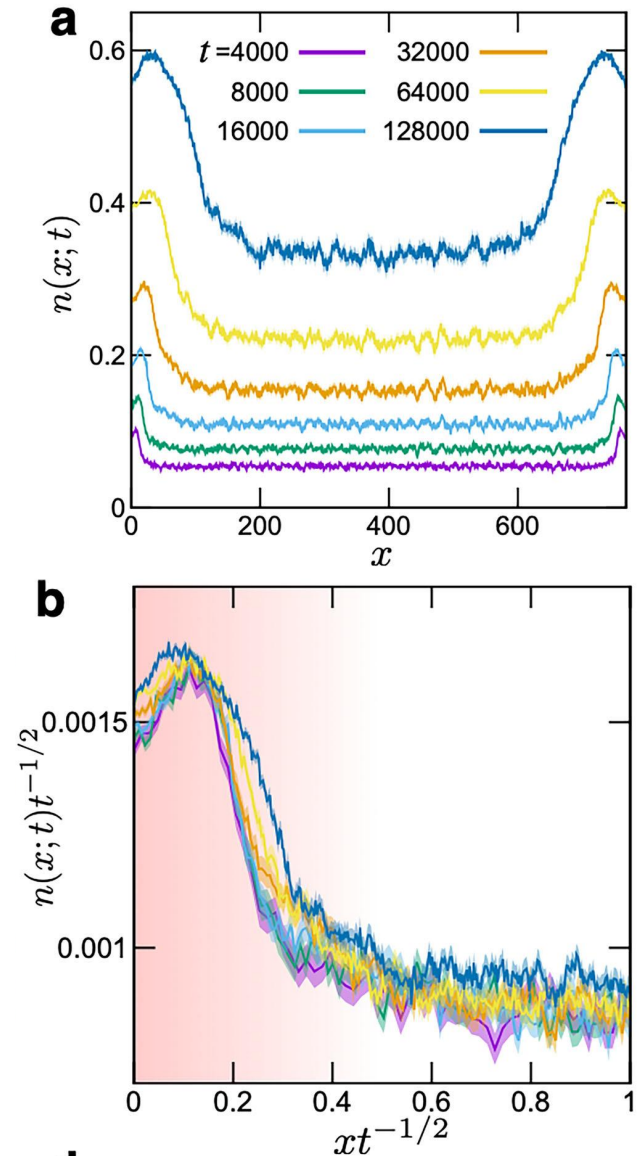
Situation

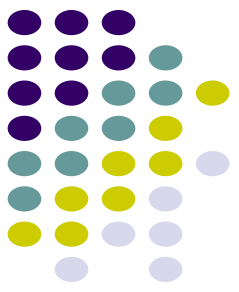
- This growth is in spinodal region (II).
- If the system is inside the metastable region (I), nucleation growth is observed.
- If supercritical (III), characteristic domain growth with elastic creasing does not occur because the adsorption chemical potential and thermal fluctuations are much greater than the elastic energy.



1. Corner effect

- Take sample average: smooth adsorption distribution in (a).
- Adsorption fraction per column $n(x)$.
- b: data collapse by appropriate scaling.
- More adsorption at the corner $n(x) \sim t^{1/2}$, and the corner region is $x/t^{1/2} \sim 0.4$. Hence, the corner contribution $\sim t^1$: faster than the diffusive growth!
- $t^{1/2}$ far from the corner: diffusive growth.





1. Corner effect

- The total adsorption fraction n_{ads} is the sum of corner contribution $\propto t^1$ plus surface contribution $\propto t^{1/2}$:

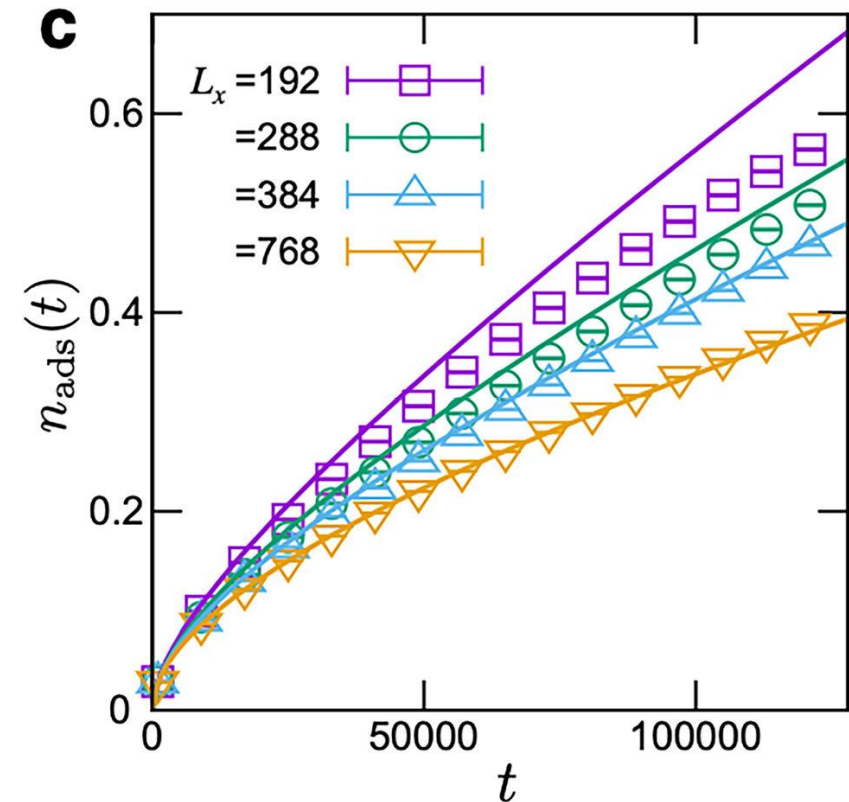
$$n_{\text{ads}} = At^{1/2} + (B/L_x)t.$$

(A, B) : fitting parameter for $L_x = 768$ data

L_x : lateral system length

If particle hopping is diffusive, $n_{\text{ads}} \sim t^{1/2}$

Faster adsorption than diffusion due to elasticity + fast stress relaxation at the corners



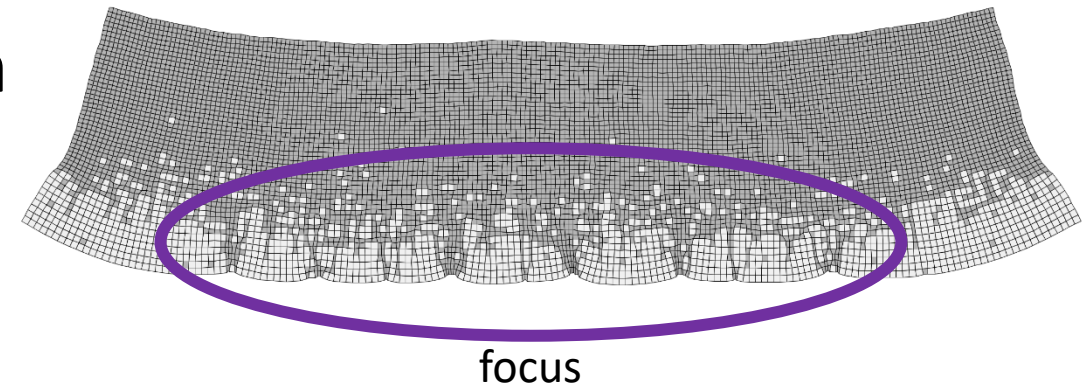
2. Scaling law in surface region

- Universal adsorption kinetics far from corners can be found?
- Hint: scaling laws known in interfacial growth systems*
- Measure spatial correlation function regarding the adsorption distribution $n(x; t)$.

$$n(x; t) = \sum_y \sigma(x, y, t) / L_y$$

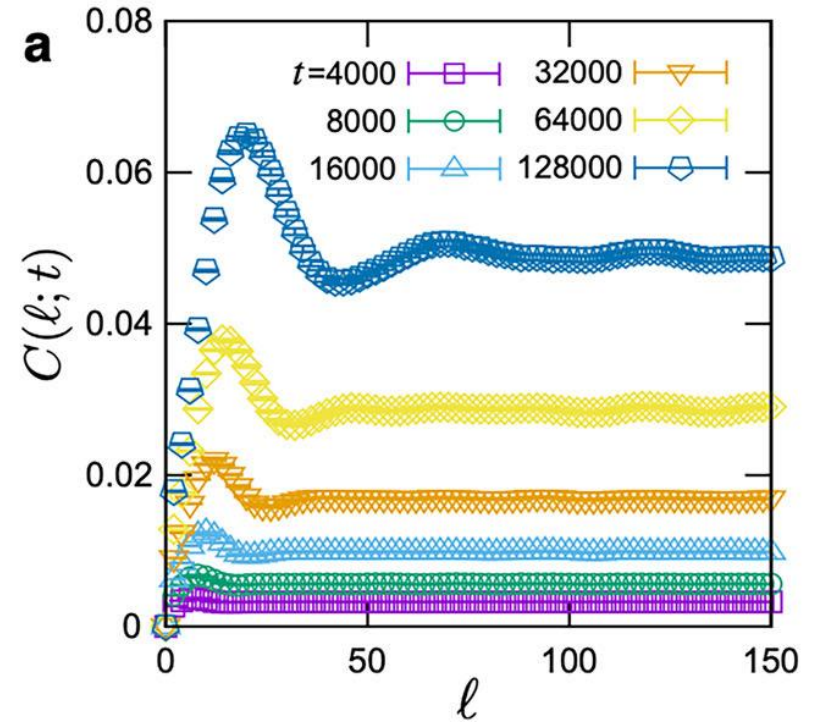
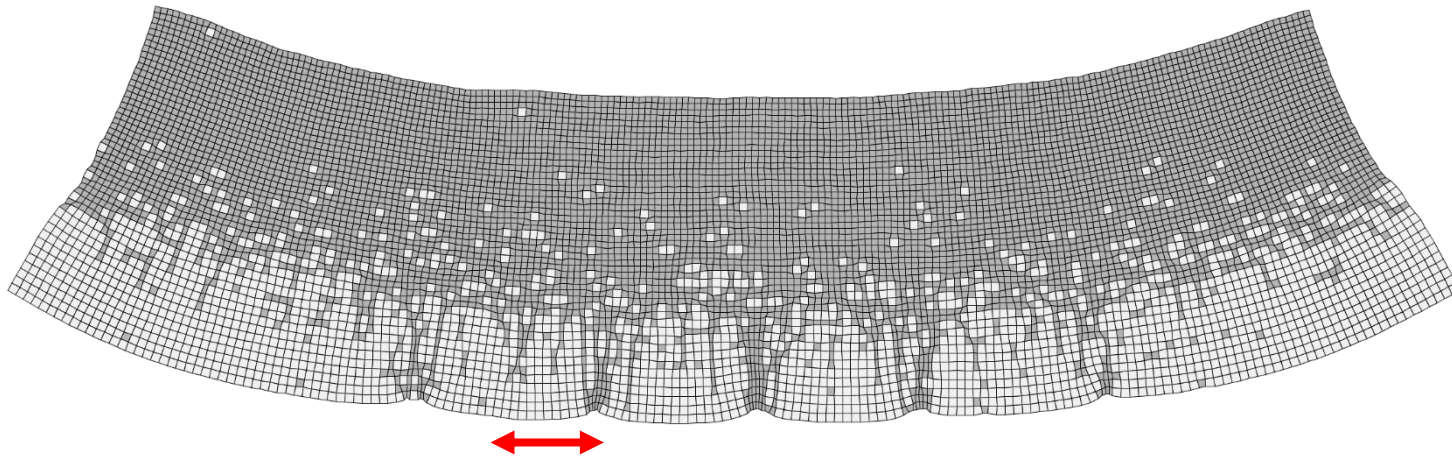
- $C(\ell; t) \propto \sum_x (n(x; t) - n(x + \ell; t))^2$
measure horizontal correlation between adsorption separated by ℓ

* See, e.g., A.-L. Barabási and H.E. Stanley, Fractal Concepts in Surface Growth (Cambridge, 1995).

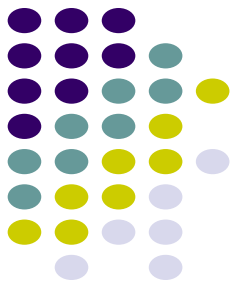


Spatial correlation function

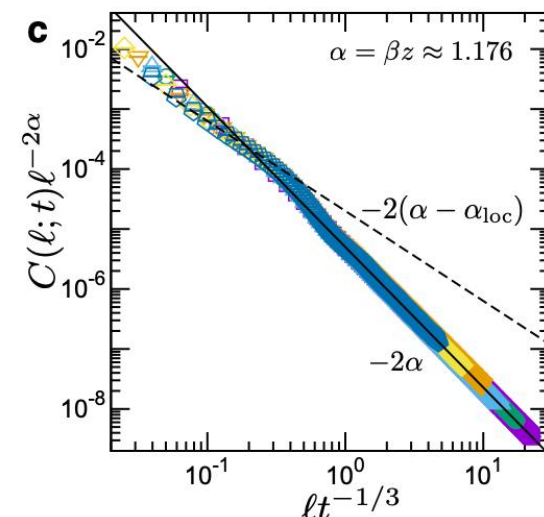
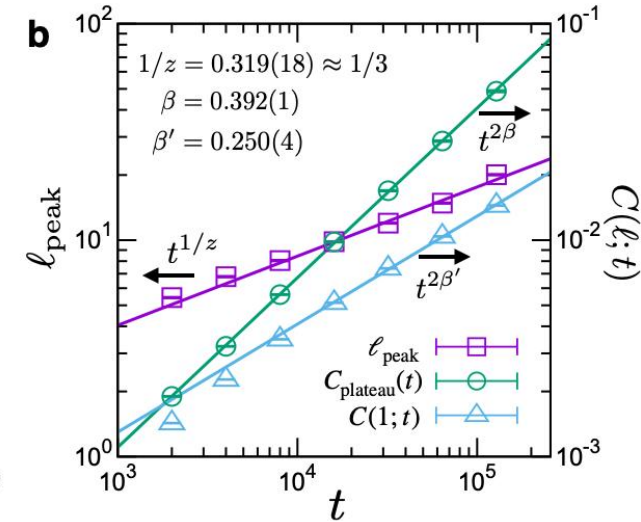
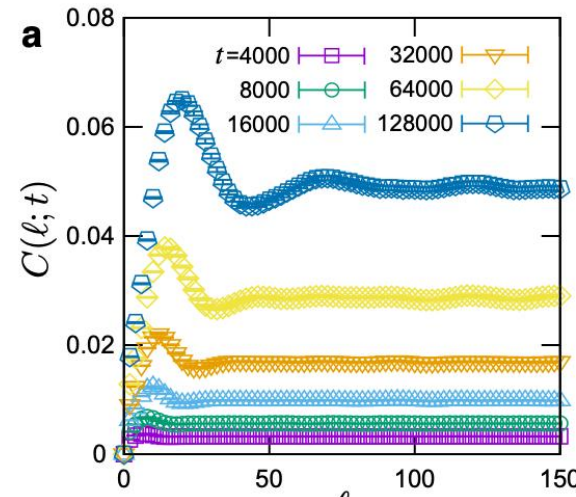
- Correlation function has a peak due to the appearance of elastic creases



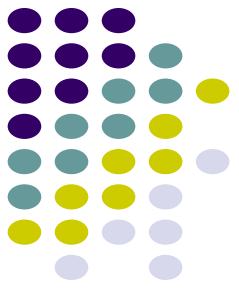
Dynamic scaling of the correlation function



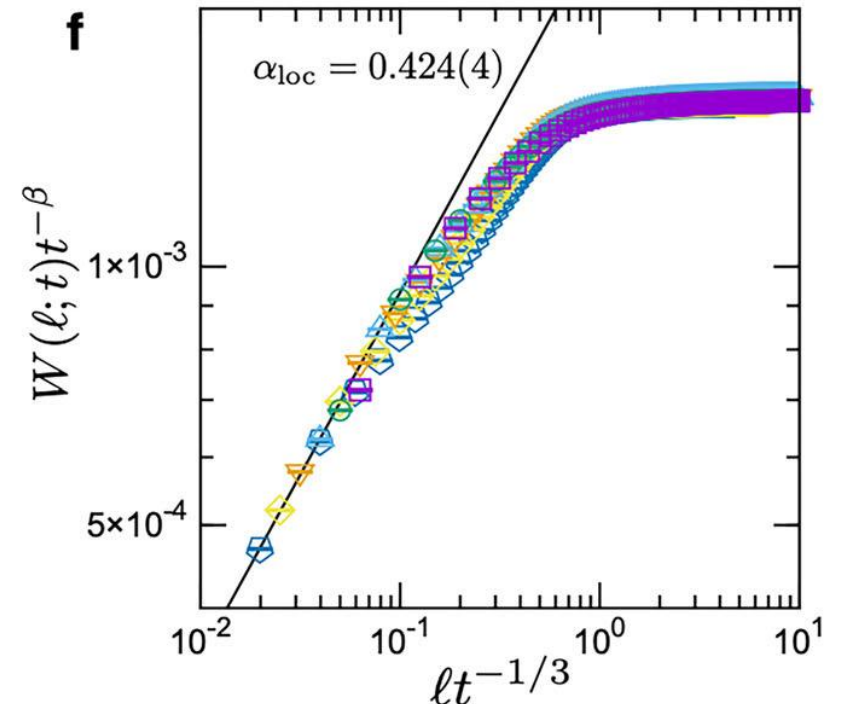
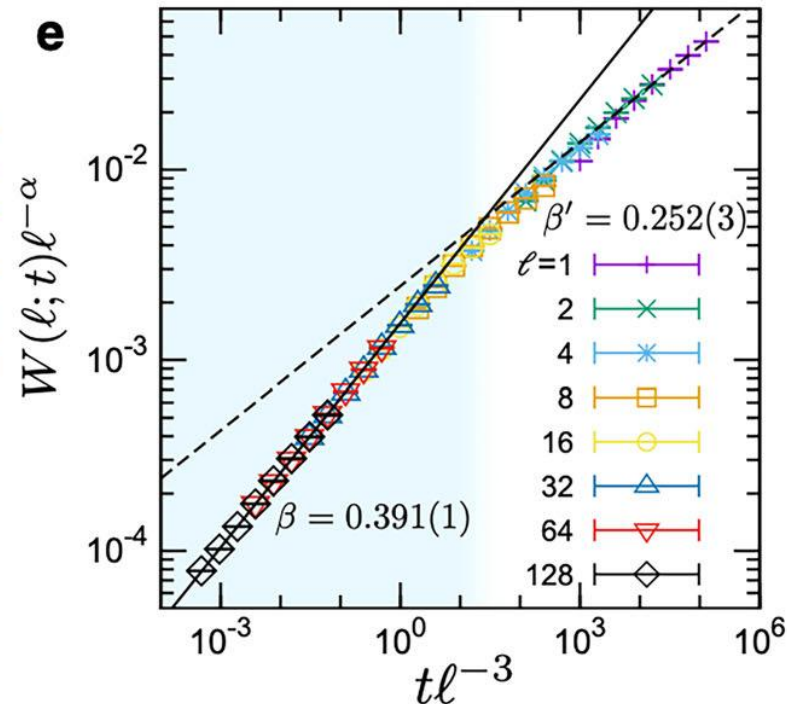
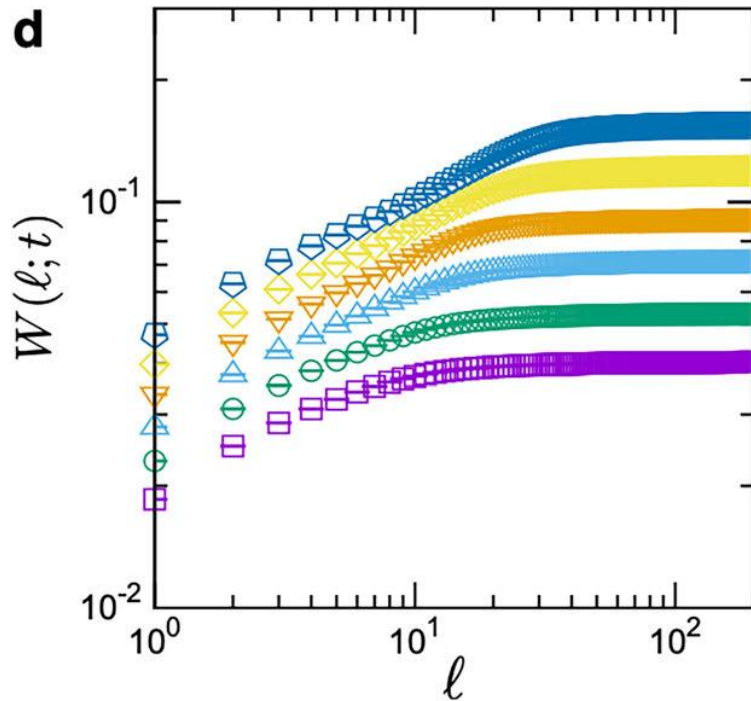
- ℓ_{peak} : $C(\ell)$ becomes maximum
 C_{plateau} : plateau values
- $\ell_{\text{peak}} \sim t^{1/3}$, $C_{\text{plateau}} \sim t^{2\beta} = t^{0.78}$
 and $C(1; t) \sim t^{2\beta'} = t^{0.50}$
- β is growth exponent
 (depends on T and μ).
- β' is anomalous growth exponent.
 This dynamic scaling with scale
 separation is called anomalous scaling.

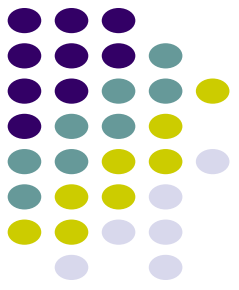


Adsorption deviation



- Adsorption deviation $W \propto \sum_x \sqrt{\langle [n(x; t) - \langle n(x; t) \rangle]^2 \rangle}$
(Surface width in interfacial growth systems)





Scaling exponents

- Scaling exponents are distinct from those in popular models.
- The scale separation in our model is due to the elastic creasing, which results from elastic heterogeneity.

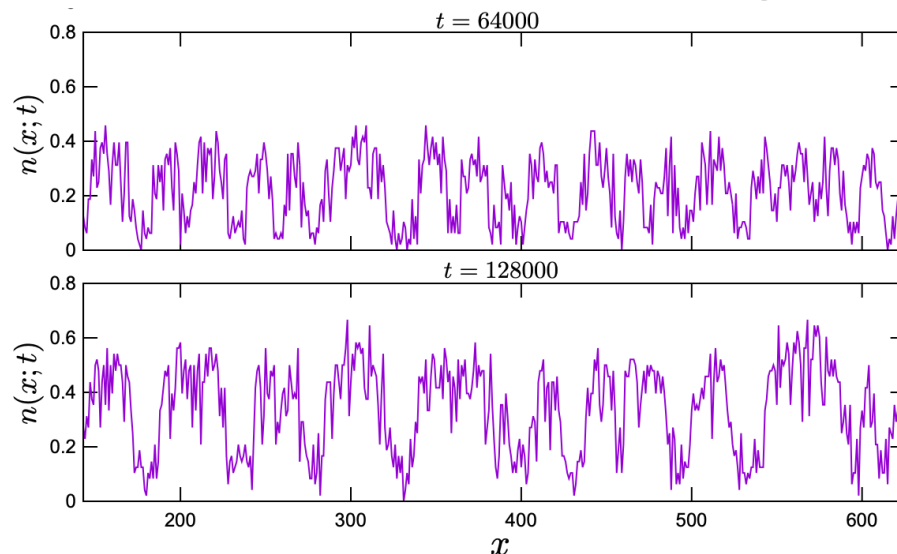
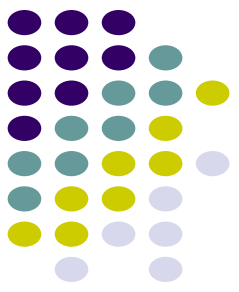


Table 1 | Scaling exponents

	α	β	$1/z$	β'	α_{loc}	α_s
EW	1/2	1/4	1/2	-	-	1/2
KPZ	1/2	1/3	2/3	-	-	1/2
linear MBE	3/2	3/8	1/4	1/8	1	3/2
random diffusion	$\frac{1}{2(1-\rho)}$	$\frac{1}{2(2-\rho)}$	$\frac{1-\rho}{2-\rho}$	$\frac{\rho}{2(2-\rho)}$	1/2	1/2
$T = 0.08,$ $\mu = 1.2$	1.20	0.40	1/3	0.25	0.45	1.20
$T = 0.10,$ $\mu = 1.2$	1.18	0.39	1/3	0.25	0.42	1.18
$T = 0.15,$ $\mu = 1.3$	1.09	0.36	1/3	0.25	0.33	1.09
$T = 0.20,$ $\mu = 1.4$	-	0.31	-	-	-	-
$T = 0.30,$ $\mu = 1.6$	-	0.28	0	-	-	-
$T = 0.50,$ $\mu = 2.0$	-	0.27	0	-	-	-
$T = \infty, \mu = \infty$	-	1/4	0	-	-	-

α : the global roughness exponent, β : the growth exponent, z : the dynamic exponent, β' : the anomalous growth exponent, α_{loc} : the local roughness exponent, α_s : the spectral exponent (Fig. 4 and Supplementary Figs. 12 and 13 for details).

EW, KPZ, and linear MBE stand for (1+1)-dimensional Edwards-Wilkinson, Kardar-Parisi-Zhang, and linear molecular-beam-epitaxy models, respectively^{2,43,51}. ρ in exponents of the random diffusion model is the strength of the disorder given in the probability of the diffusion coefficient $P(D) \sim D^{-\rho}$ for $D < 1$ and $P(D) = 0$ for $D > 1$ ⁴⁸.



Summary

- Molecular adsorption in PCP/MOF induces
 - Lattice deformation
 - Change in elastic constants

When they occur locally, elastic heterogeneity plays a role.

- Elasticity-mediated phase transition and pattern formation.
- Kinetics: corner effect, anomalous dynamic scaling laws due to elastic creases formation.
- トイモデルと現実のMOFとの対応はまだまだ課題。
- 理論もまだまだ不十分... (格子モデル, TDGL, 他の系との比較)