

# Computational Physics, TFYA90

Modern Techniques in Materials Science  
Part I. Molecular dynamics (MD) and Monte Carlo (MC)

Lecture 1, November 2, 2020

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## *Evaluate* – Changes made to course

The Higher Education Ordinance and the recommendations of the Swedish Higher Education Authority (UKÄ) (Chapter 1, Section 14 of the Higher Education Ordinance; Report 2019:20 from the Higher Education Authority (UKÄ), pp. 51-54.) specify that students are to be informed about the result of the previous year's course evaluation and about any changes that may have been made before the new course instance.

1. How many students took the course last time? **11**
2. How many submitted a course evaluation at the time? **3**
3. The overall grade of the course was **4.5/5**

The students have been satisfied with the content of the course, felt that what they learned was relevant for their education and thought that the task/assignments/evaluation methods were appropriate for the number of credits (see **Evaluate\_2019\_document.pdf** under “course documents” in Lisam).

4. Describe the input that formed the basis for the changes that are now being carried out. This input may be, for example:

Changes have been made on the basis of comments from the previous student evaluation, discussion with colleagues, and with more focus on contextualizing knowledge on applications, discoveries, technologies

5. Changes made:

- Improved use of Lisam. All documents of relevance to this course can be found on Lisam. Lisam is now also the main channel of communication with students
- Course PM uploaded on Lisam
- Deadlines for submitting assignments and content of lectures available in the PM
- Clarified methods for final evaluation (detailed individual feedback on request, unless necessary)



# Course Outline

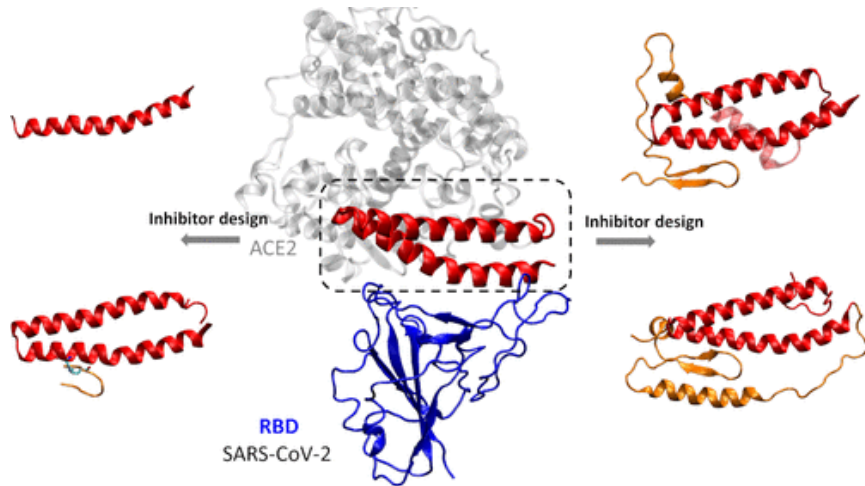
- Scientific Foundation of Computer Simulations
- General Features & Common Techniques
- Molecular Dynamics (MD) Simulations
- Monte Carlo (MC) Simulations
- Applications in Materials Science



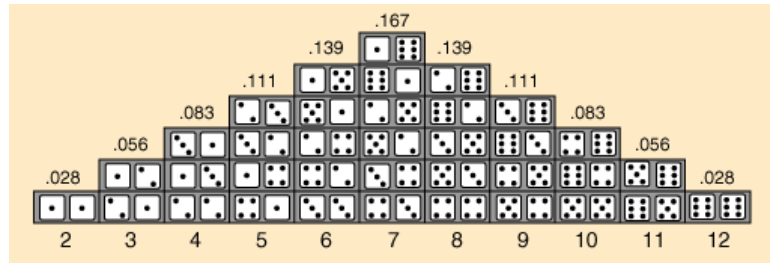
Atomistic simulations

# Examples of applications of atomistic simulations

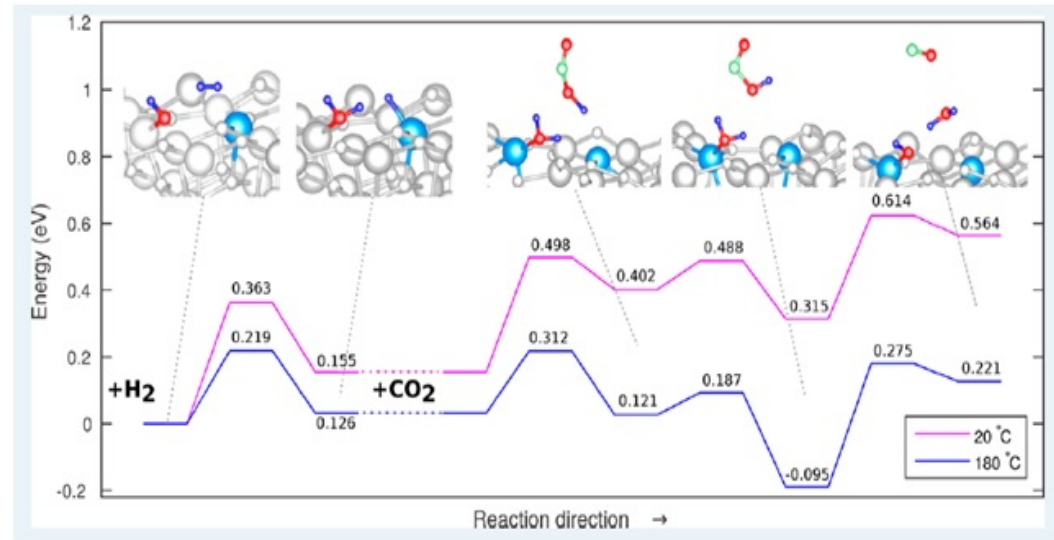
## Proteins folding mechanisms



## Fracture mechanics

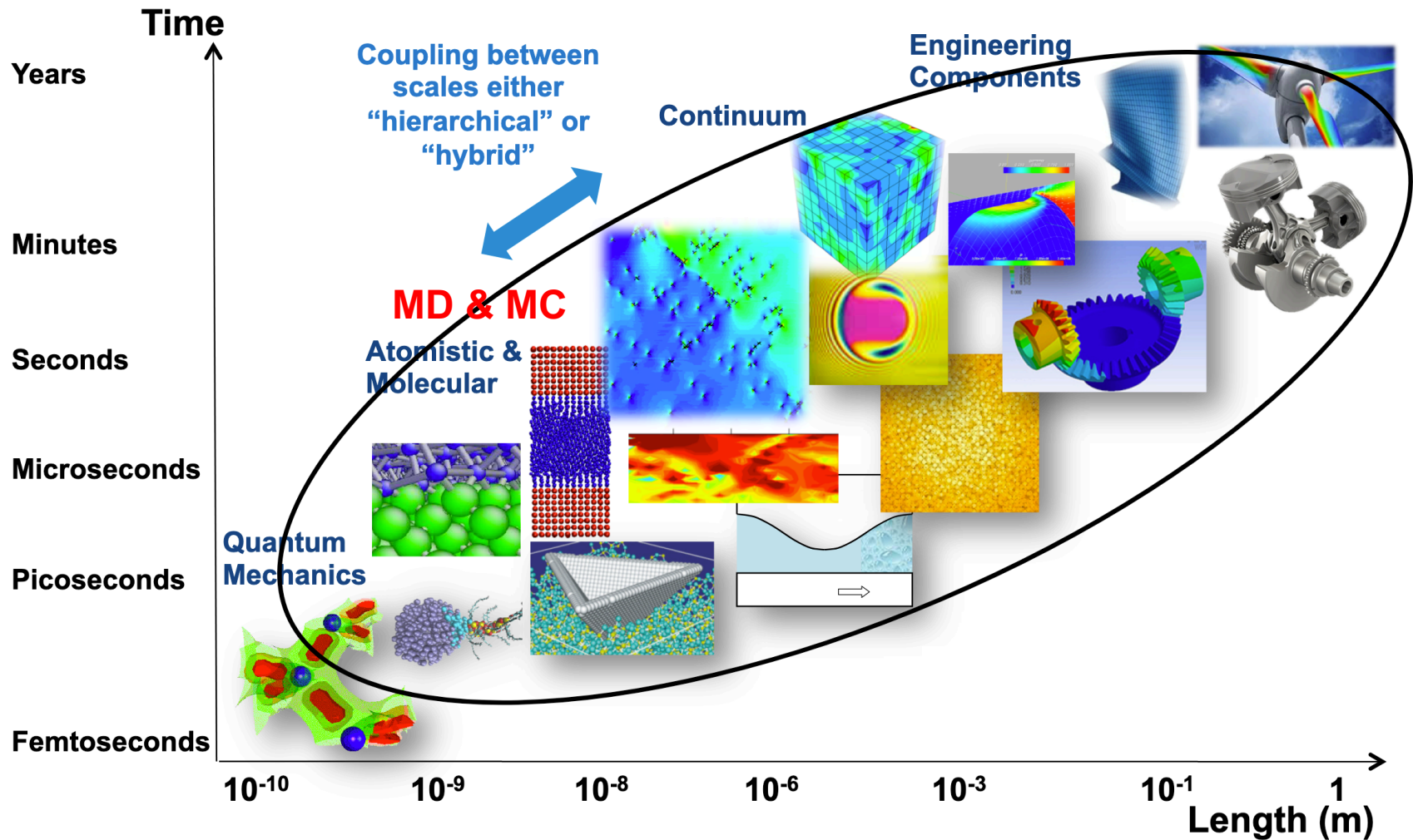


Statistics &  
models for economics



Chemical reactions → catalysis → energy

# Overview of different techniques



# Purpose for part I of the course

- Understand basic principles of molecular dynamics (MD) and Monte Carlo (MC) simulation techniques as well as fundamental concepts of statistical mechanics
- Be able to describe / give examples of typical materials science problems that can be investigated via MD or MC
- Be able to describe and motivate advantages vs disadvantages of these two methods, depending on the problem under consideration
- (Optional/beneficial) basic knowledge of other simulation methods that substitute or complement the predictions of MD and MC
- (Optional/beneficial) be able to describe different variants / current developments of MD and MC techniques

# Introduction on atomistic simulation methods

Basic concepts and fundamentals

# WHY do we need computer simulations ?

- Today, state-of-the-art experimental techniques provide resolutions down to the Ångstrom scale:
  - Electron microscopy (HRTEM, SEM)
  - Scanning Tunnelling Microscopy (STM)
  - Field Ion Microscopy (FIM)
  - Atomic Force Microscopy (AFM)
  - Diffraction techniques (XRD, LEED, RHEED)
- Theoretical models give us a solid understanding of the governing laws in nature and its building blocks:
  - quarks, nucleus, electrons, atoms, elements, galaxies, universe.

Experiments provide detailed information about **initial** and **final** states, but basically **no information** about **transient** processes.

- How are atoms, molecules, or clusters, moving ?

Theory gives us usually equations, describing simple systems. The exact analytical solutions are often unknown.

In materials science, problems involve **many-bodies**, often in **transient states**. Understanding of several physical phenomena requires resolving the motion of atoms at time scales from ps to  $\mu\text{s}$  ( $10^{-12} - 10^{-6}$  s).

**Computer simulations are essential tools** in materials science.

- **overcome** experimental difficulties (time/space resolution).
- **solid** test for theoretical models.
- **bridge** between theory and experiment.
- **yield** realistic predictions: materials science, biology, medicine, engineering, economics etc.

## Computer simulations:

- **do not** replace experiments.
- **are not** as general as pure theoretical treatments.
- **complement** experiments and other theoretical models.

## Advantages:

- **implementation**
- *experimental* inputs
- **reproducibility**
- **visualisation**
- relatively easy & inexpensive.
- easily changeable & varied.
- practically 100 % reproducible.
- offer unique information at atomic level.

## Limitations:

Two main restrictions, based on CPU speed & memory:

- **size** of systems simulated.
- **time scale** of simulations.



## WHAT is a simulation ?

A simulation has some *state* variables –  $\mathbf{S}$ . In classical mechanics,  $\mathbf{S}: (q_i, p_i)$ .

Initial state  $\mathbf{S}_0 \rightarrow$  modified by some *process*  $\rightarrow$  new state  $\mathbf{S}_{n+1} = T(\mathbf{S}_n)$

$T(\mathbf{S})$  = iteration function (deterministic or stochastic).

$n$  = iteration index representing *time* (fictious time).

Goal of simulations is to obtain a set of properties in equilibrium:  $A(\mathbf{S})$ .

-typical examples is internal energy, equilibrium volume, mechanical stress,  
 $E(\mathbf{S})$ ,  $V(\mathbf{S})$ ,  $\sigma(\mathbf{S})$  etc.

Compare with properties measured in real experiments:  $\langle \rangle$  averages over  
large **number** of particles and **time** of measurement.

### QUESTION:

how do we connect microscopic  $(q_i, p_i)$  with macroscopic  $\langle A \rangle$  properties ?

The physical foundation of simulations is **statistical mechanics**.

Real experiments yield  $\langle A \rangle$  as a time average, from measurements made at successive times ( $t_1, t_2, \dots t_M$ ):

$\langle A \rangle = \sum_i A_i P_i$  where  $P_i = n_i/M$  is number of times system is in state  $i$ .

Gibbs introduced the artifice of large number of replicas of a system (*ensemble*) and replaced  $\langle A_{\text{time}} \rangle$  with  $\langle A_{\text{ens}} \rangle$  :

$$\langle A_{\text{time}} \rangle = \langle A_{\text{ens}} \rangle$$

The equality holds only if the system is **ERGODIC**.

**Ergodicity** is the *fundamental* assumption of classical statistical mechanics.

The **ergodic hypothesis** is also the basis of **computer simulations**.

## WHAT is Ergodicity?

- after a certain time, the system loses memory of its initial state.
- systems, no matter how prepared, relax after reasonable time towards statistical equilibrium (all macroscopic variables are constant in time).
- time average over a typical trajectory equals the ensemble average.

**Note: not all systems are ERGODIC!**

Any computer simulation starts with a **statistical ensemble**

microcanonical	-----	constant <b>N, V, E</b>
canonical	-----	constant <b>N, V, T</b>
isothermal-isobaric	-----	constant <b>N, P, T</b>
grand canonical	-----	constant <b><math>\mu</math>, V, T</b>

Often, one should include some contact with a thermal bath (NVT or NPT sampling).

All simulation algorithms can sample each ensemble distribution.

**Molecular dynamics (MD)** - no randomness (*deterministic*)  $\rightarrow \langle A \rangle_{\text{time}}$

**Monte Carlo (MC)** - unbiased random walk (*stochastic*)  $\rightarrow \langle A \rangle_{\text{ens}}$

**MD approach  $\Rightarrow \langle A \rangle_{\text{time}} \sim \langle A \rangle_{\text{ens}} \Leftarrow$  MC approach**

## General features & common techniques

We concentrate on Monte Carlo (MC) and Molecular Dynamics (MD) methods.

Classical system with  $N$  particles  $\rightarrow (q_i, p_i), i = 1, 2, \dots, N \equiv$  classical phase space.

In the classical limit:  $(q_i, p_i) \Leftrightarrow H(q_i, p_i) = K(p_i) + V(q_i)$

**H – the hamiltonian is the basic input in any simulation.**

$q_i \equiv r_i$  – cartesian coordinates;  $p_i$  – conjugate momenta

**Kinetic Energy:**  $K = \sum_{i=1}^N \sum_{\alpha} p_{i\alpha}^2 / 2m_i; \quad \alpha = x, y, z$

**Potential Energy:**  $V = \sum_i v_1(r_i) + \sum_i \sum_{j>i} v_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j} v_3(r_i, r_j, r_k) + \dots$

$\parallel$                        $\parallel$                        $\parallel$   
Ext. field              Pair potential              3-body term

# Semi-empirical interaction potentials

- Mathematical models that are the most important ingredient in *classical* MD (CMD) and Monte Carlo (MC) simulations.
- Results, accuracy of predictions depend massively of interaction quality.<sup>1</sup> The mathematical model needs to be carefully parameterized to reproduce known system properties. Parameter-optimization itself can be done via MC methods (e.g., Metropolis Algorithm with simulated annealing).<sup>2</sup>
- Important current developments of interatomic potentials based on machine-learning techniques<sup>3</sup>
- Alternatively, MD<sup>4,5</sup> or MC<sup>6</sup> simulations based on computationally-heavier *ab initio* calculations of forces and energies

<sup>1</sup> Almyras et al., *Semi-empirical force-field model for the Ti1-xAlxN (0 ≤ x ≤ 1) system*, Materials 12, 215 (2019)

<sup>2</sup> Kirkpatrick, Gelatt, Vecchi, Optimization by Simulated Annealing, Science 220, pp. 671-680 (1983)

<sup>3</sup> A. V. Shapeev, *Moment Tensor Potentials: A Class of Systematically Improvable Interatomic Potentials* Multiscale Modeling & Simulation 14, 1153 (2016)

<sup>4</sup> Born-Oppenheimer molecular dynamics

<sup>5</sup> R. Car and M. Parrinello *Unified Approach for Molecular Dynamics and Density-Functional Theory* Phys. Rev. Lett. 55, 2471 (1985)

<sup>6</sup> Quantum Monte Carlo methods

# Semi-empirical interaction potentials

Most general formulation for potential energy of a classical system depending on the coordinates of the atoms:

$$E_{\text{total}} = \sum_{i < j} \Phi_2(r_i, r_j) + \sum_{i < j < k} \Phi_3(r_i, r_j, r_k) + \dots + \sum_{i < j < k < \dots < n} \Phi_n(r_i, r_j, r_k, \dots, r_n) + \dots$$

where  $n = 2, 3, 4 \dots$  and  $\sum_{i < j < k < \dots < n} \Phi_n(r_i, r_j, r_k, \dots, r_n)$  is the sum of the ***n*-body** terms.

Fundamental assumption is that the series converges rapidly & higher order terms are neglected. Based on this expansion, interaction potentials can be classed as:

- **Pair potentials**, exclusively two-body terms -  $\Phi_2(r_i, r_j)$ .
- **Many-body potentials**, three-body and higher terms.

In practice, the *n*-body expanded is usually **truncated** after  $\Phi_3(r_i, r_j, r_k)$ .

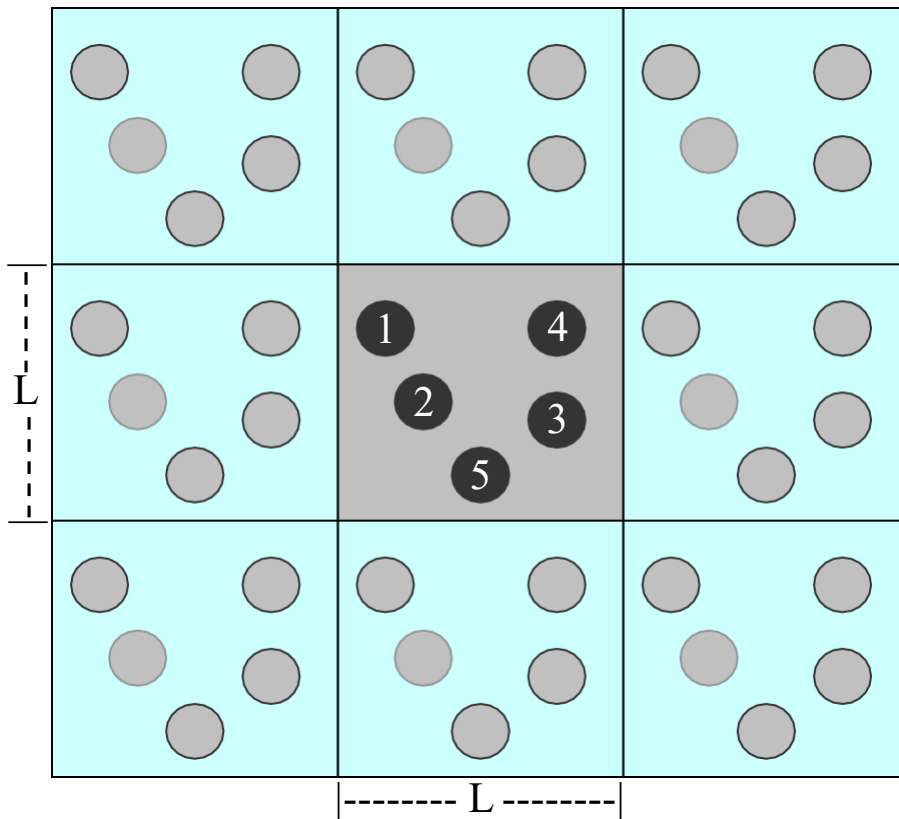
# Methods used for supercell calculations (particularly useful for solid crystals)

## Employed in both MD or MC simulations

(1D, 2D, 3D periodic systems)

## Periodic Boundary Conditions (PBC)

- PBC mimic the presence of infinite bulk surrounding the initial  $N$  particle (supercell) system. Main purpose is to reduce approximations caused by a limited system size



**Obs!** In molecular dynamics, **long-wavelength** lattice vibrations are cut-out due to limited supercell sizes.



# Molecular dynamics (MD)

More specifically defined as “classical” MD (CMD) when forces on atoms computed via semi-empirical mathematical models. Named “ab initio MD” (AIMD) when forces on atoms are calculated from first-principles methods as “tight binding” or “DFT”.

# Molecular dynamics solves the classical equations of motion for each atom

- Set initial nuclei positions  $\mathbf{r}_i(t=0)$
- Initialize nuclei velocities  $\mathbf{v}_i(t=0)$  at temperature  $T$
- Update nuclei positions every timestep  $\Delta t$  ( $\approx 10^{-15}$  s)

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t) \cdot \Delta t + \frac{1}{2} \mathbf{a}_i(t) \cdot [\Delta t]^2$$

In codes, this is implemented with algorithms like Verlet

$$\mathbf{a}_i(t) = \mathbf{F}_i(t) / m_i$$



## Classical molecular dynamics (CMD)

It is based on semi-empirical model interactions which reduce the intricate problem of electron/electron electron/nuclei and nuclei/nuclei interactions to effective nuclei/nuclei interactions. Examples are:

- Lennard Jones
- Embedded atom method
- Stillinger-Weber...

# Molecular dynamics solves the classical equations of motion for each atom

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**First-principles (or ab initio) molecular dynamics (AIMD)**  
solve the “many-body interaction problem” by starting from  
the principles of quantum mechanics (yet several approximations are necessary).

Examples are:

- Density-Functional Theory
- Hartree-Fock
- Tight-Binding...

## Criteria for choosing a model potential

- \* **Accuracy** - reproduce properties as closely as possible.
- \* **Transferability** - applicable to as many systems as possible.
- \* **Computational speed** - force calculations are the most time consuming.
  - 2-body potential  $V(r_{ij}) = V(\|r_i - r_j\|)$
  - 3-body potential  $V(r_{ijk})$  depends on orientation – more computation.

### (Example) Typical Emphasis for Various Disciplines

1. CHEMISTRY – priority is on accuracy.
  - rate constants, for example, require very accurate reaction barriers.
  - Typically need accuracy even beyond density-functional theory.
2. BIOCHEMISTRY – Combination of all criteria is desired.
  - Protein structures, polymers have significantly different configurations.
3. MATERIALS SCIENCE – All three criteria.
  - Calculation of equilibrium atom positions, comparison with experiment.

## Examples of semi-empirical interatomic potentials (derived from quantum-mechanical bonding arguments)

- Lennard Jones
- Embedded Atom Method (EAM)
- Bond order potentials
- Stillinger-Weber
- Finnis and Sinclair (FS)
- Modified embedded atom method (MEAM)
- Tersoff...

\* 2-body interactions:  $\Phi(1, \dots, N) = \sum_{i < j} V_2(i, j)$

- work fine for rare gases (Ar, Ne, Kr, Xe).

- **Lennard-Jones**:  $V_2(r) = 4\varepsilon [x^{-12} - x^{-6}]$

$\varepsilon$  - maximal well-depth of potential.

$x = r/\sigma$  - distance in units of  $\sigma$ , where  $\sigma$  is effective radius.

# Monte Carlo (MC) simulations

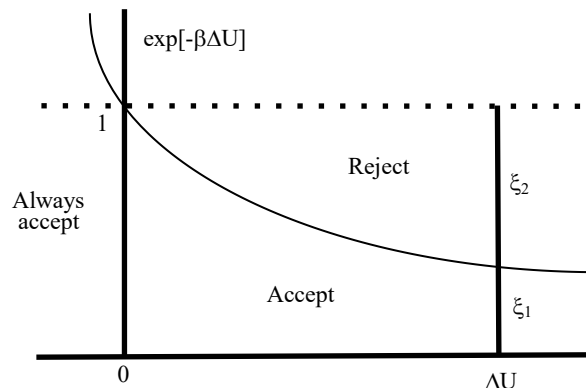
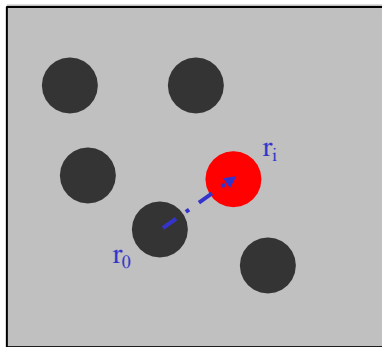
The terminology “Monte Carlo” method addresses a wide range of problem solving techniques by using random numbers and the statistics of probability.

Name is indeed taken after the casino in the small Monegasque municipality, where every game relies upon random events (roulette, dice etc).

One can then name, in principle, any method which uses random numbers to solve a problem a Monte Carlo method.

# Monte Carlo simulations steps

1. **Assign initial position** to particles & calculate  $U$ .
2. **Move one particle randomly** & calculate new  $U'$  and  $\Delta U = U' - U$ .
3. If  $\Delta U < 0$  - **accept** move.
4. If  $\Delta U > 0$  - **accept** move if  $\xi < \exp[-\Delta U/(k_B T)]$ ;  $\xi \in (0,1)$  – random number.
5. If **move rejected** - take the old configuration as the new one  
- repeat 2 - 4 procedure for another arbitrarily chosen particle.
6. For each new configuration **evaluate**  $\langle A \rangle$ .
7. **Repeat** the whole procedure a few million times for adequate statistic



There are different variants of MC... equilibrium MC, kinetic MC, Metropolis

# 2D Ising's spin model: Monte Carlo

Consider the Hamiltonian  $U$  with nearest-neighbor  $i,j$  interactions on a square grid and 2D PBC:

$$U = -J \cdot \sum_{i,j} s_i \cdot s_j - B \cdot \sum_i s_i$$



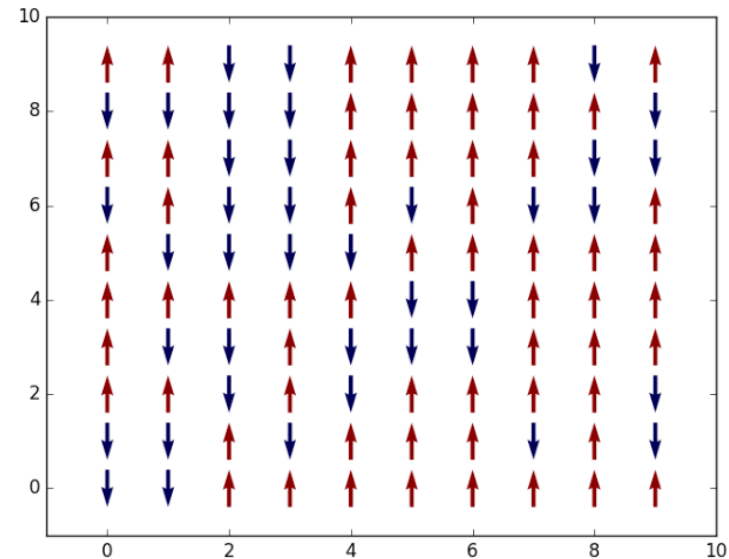
$B$ : energy of magnetization  
(presence of external magnetic field)

$J$ : magnitude of spin/spin interactions

$$P_{\beta}(\sigma_k) = \frac{e^{-\beta \cdot U(\sigma_k)}}{Z_{\beta}}$$

Probability to find the system in  
a given state  $\sigma_k$  at temperature  $T$   
[ $\beta = 1/(k_B T)$ ]

$$Z_{\beta} = \sum_{\sigma_k} e^{-\beta \cdot U(\sigma_k)} \quad \text{Partition function}$$



$\sigma_k$  is a specific spin  
configurational state of  
the entire system. The number  
of possible states is  $2^{n \cdot n}$ , where  $n$   
( $n=10$  in this figure)  
is the lateral size of the lattice.



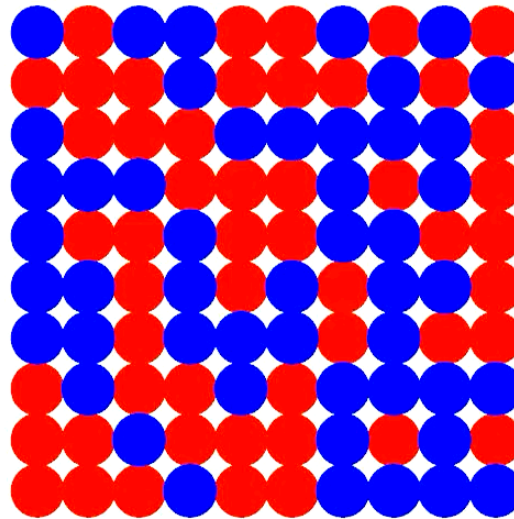
## 2D Ising's spin model: Monte Carlo

$$U = -J \cdot \sum_{i,j} s_i \cdot s_j - B \cdot \sum_i s_i$$

B: energy of magnetization  
(presence of external magnetic field)

J: magnitude of spin/spin interactions

red vs. blue  
balls:  
different  
spin states ( $\pm 1$ )



B=0

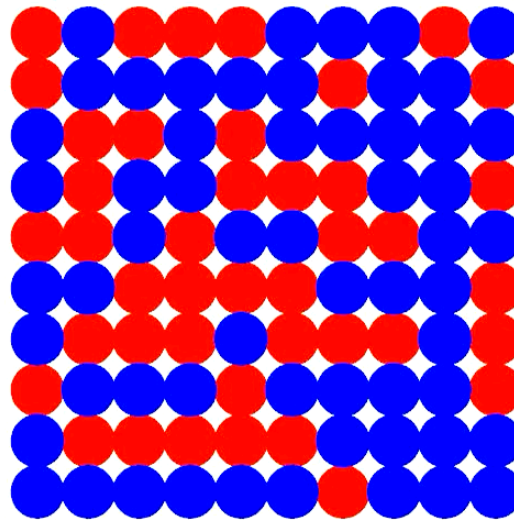
**J very high and positive**  
at very low T

## 2D Ising's spin model: Monte Carlo

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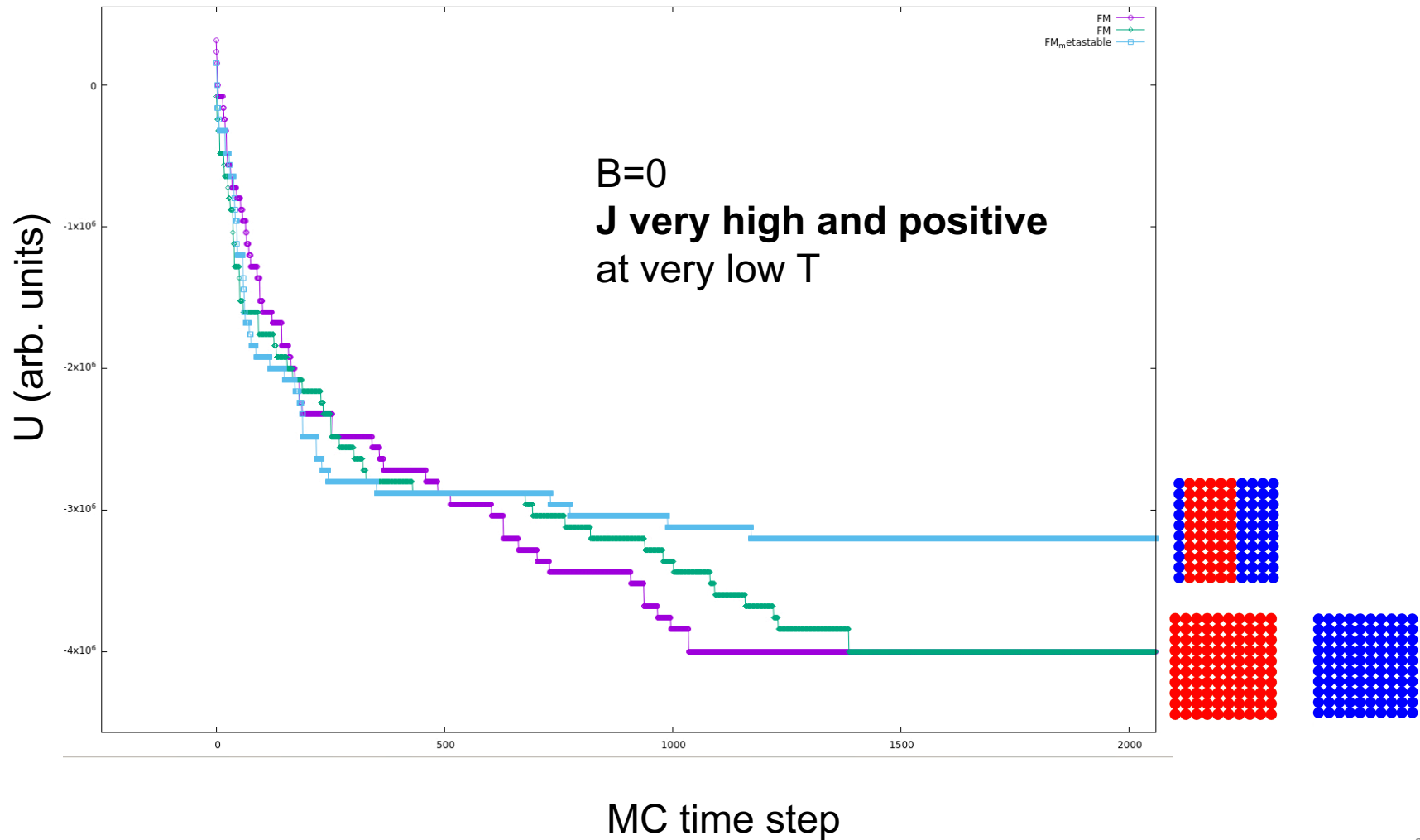
J: magnitude of spin/spin interactions



B=0

**J very high and positive**  
at very low T

# 2D Ising's spin model: energies via MC stochastic sampling

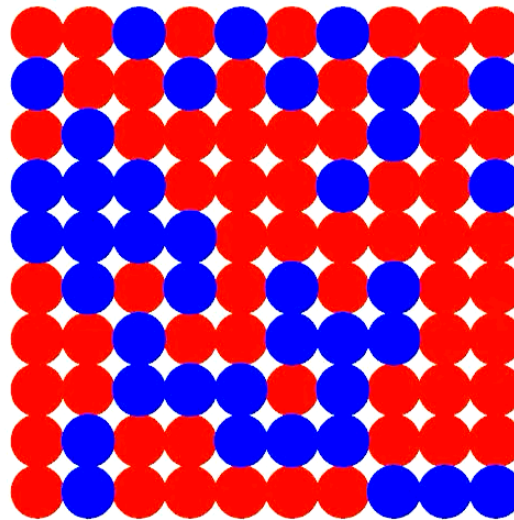


## 2D Ising's spin model: Monte Carlo

$$U = -J \cdot \sum_{i,j} s_i \cdot s_j - B \cdot \sum_i s_i$$

B: energy of magnetization  
(presence of external magnetic field)

J: magnitude of spin/spin interactions



B=0

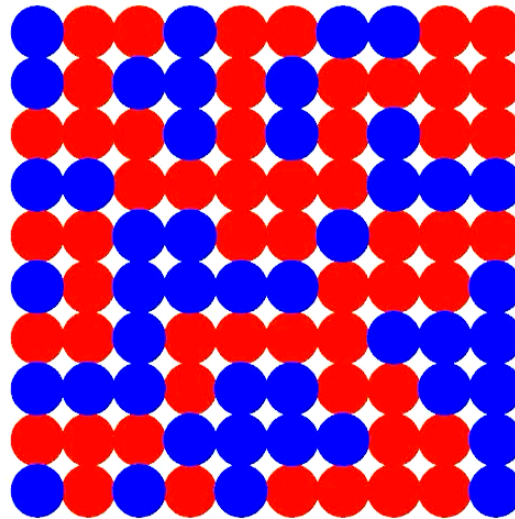
**J very large and negative**  
at very low T

## 2D Ising's spin model: Monte Carlo

$$U = -J \cdot \sum_{i,j} s_i \cdot s_j - B \cdot \sum_i s_i$$

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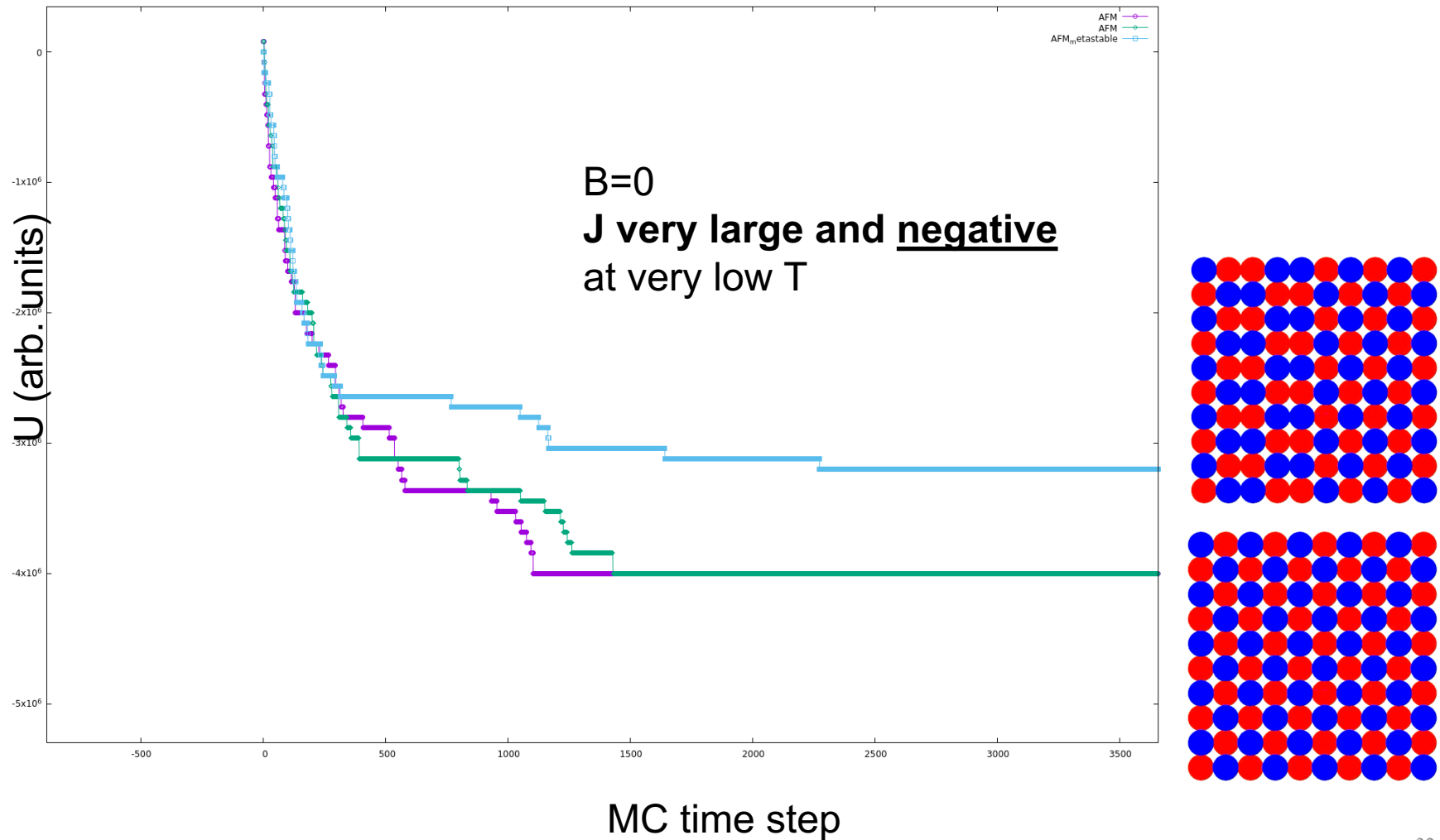
J: magnitude of spin/spin interactions



B=0

**J very large and negative**  
at very low T

# 2D Ising's spin model: energies via MC stochastic sampling

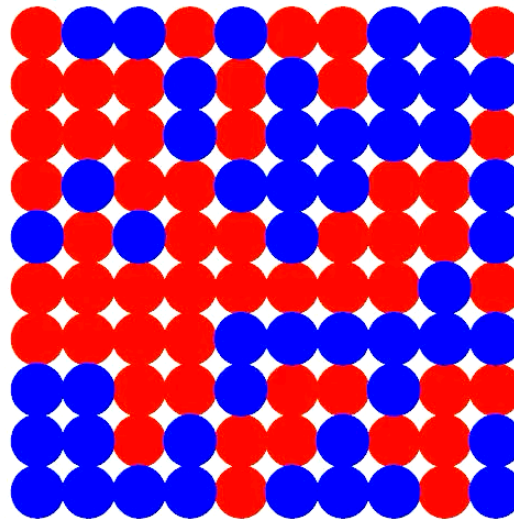


## 2D Ising's spin model: Monte Carlo

$$U = -J \cdot \sum_{i,j} s_i \cdot s_j - B \cdot \sum_i s_i$$

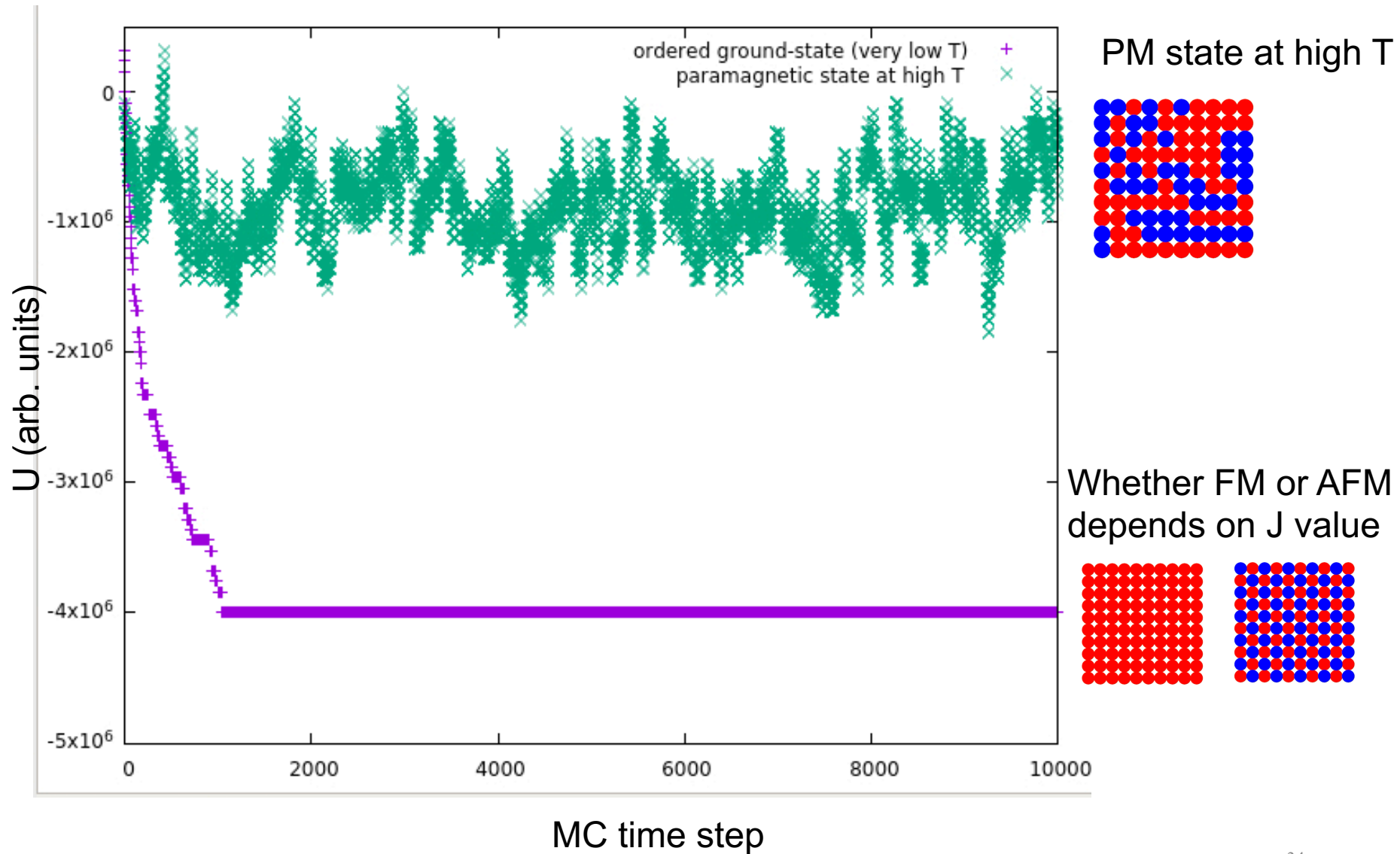
B: energy of magnetization  
(presence of external magnetic field)

J: magnitude of spin/spin interactions



$B=0$   
**J very large, but very  
high T**

# 2D Ising's spin model: energies via MC stochastic sampling



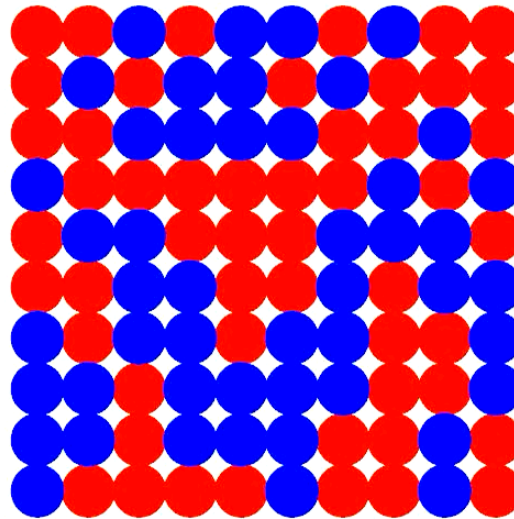


## 2D Ising's spin model: Monte Carlo

$$U = -J \cdot \sum_{i,j} s_i \cdot s_j - B \cdot \sum_i s_i$$

B: energy of magnetization  
(presence of external magnetic field)

J: magnitude of spin/spin interactions



**Very high magnetic field B**  
J=0; very low T

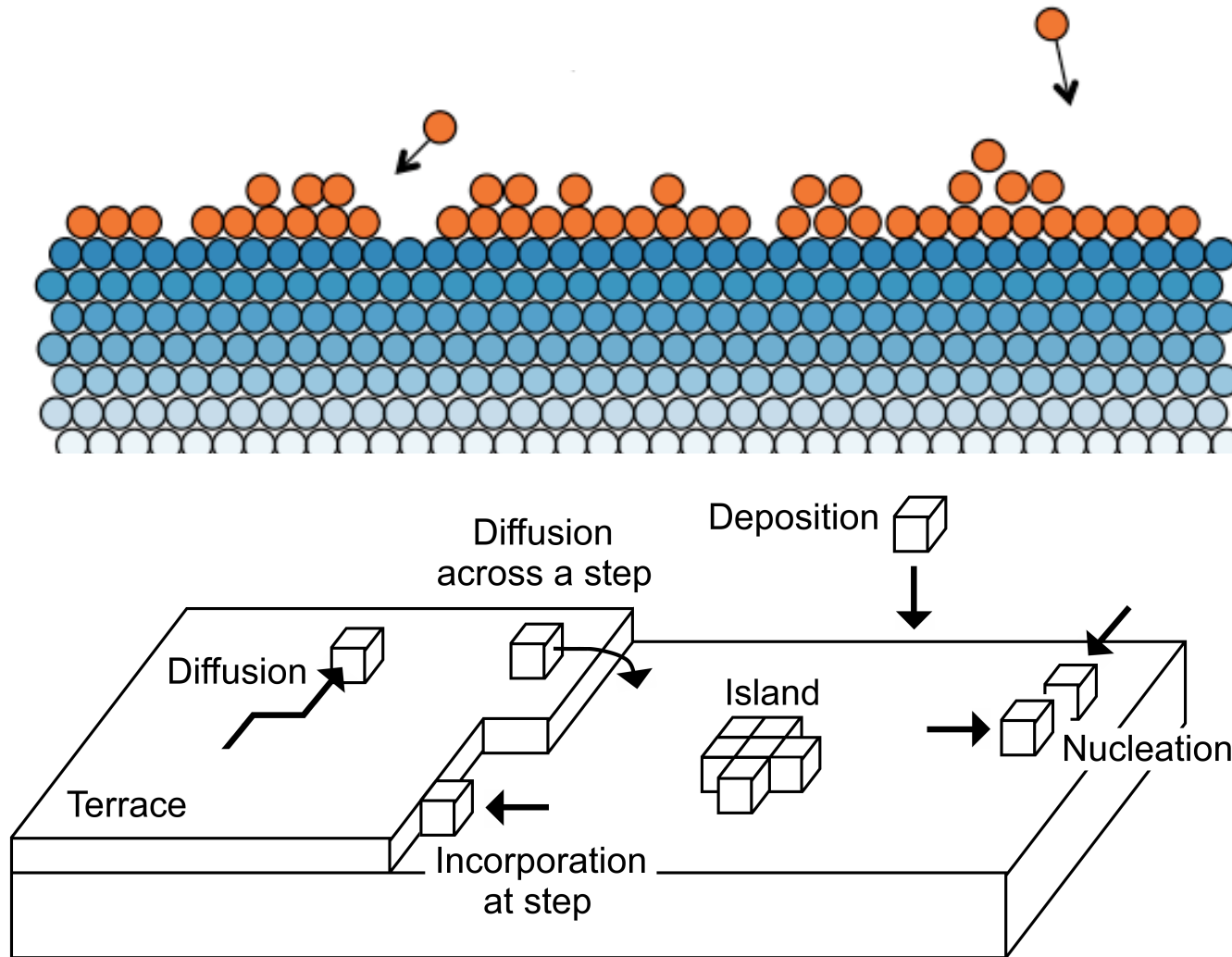
# Molecular dynamics (MD)

Examples of applications in computational materials science

Which information / discoveries / understanding can MD lead to?

# Vapor deposition and growth of thin films on substrates

Complex phenomenon regulated by interplay between kinetics and thermodynamics



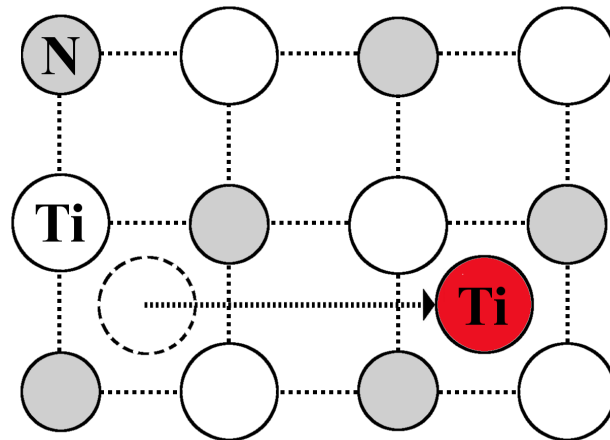
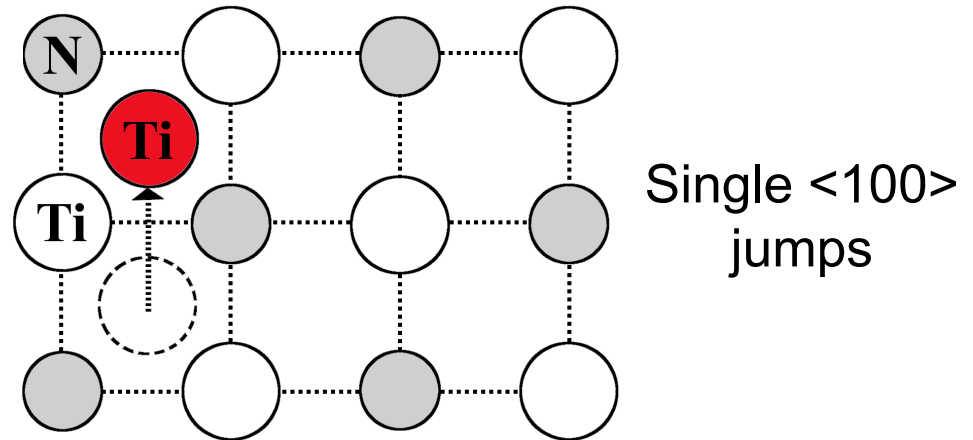
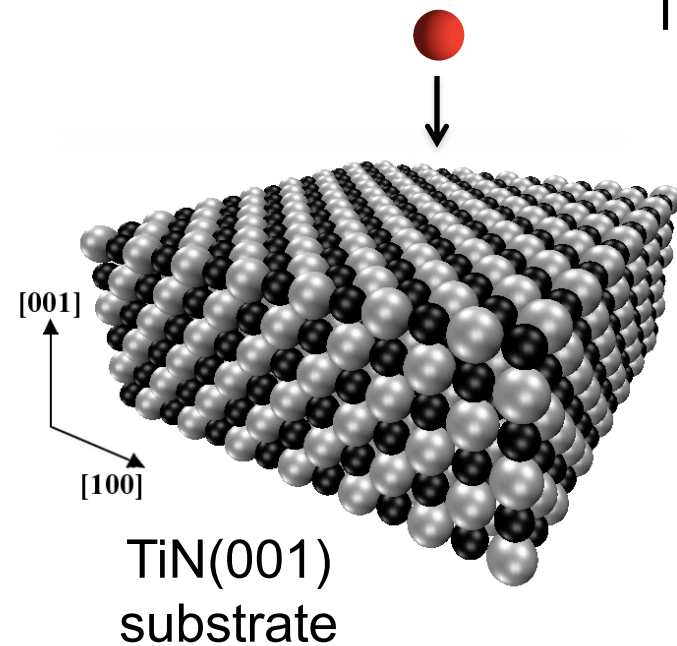
D. Edström, et. al, Journal of Vacuum Science & Technology A 34, 041509 (2016)

D. Edström, et. al, Journal of Applied Physics 121, 025302 (2017)

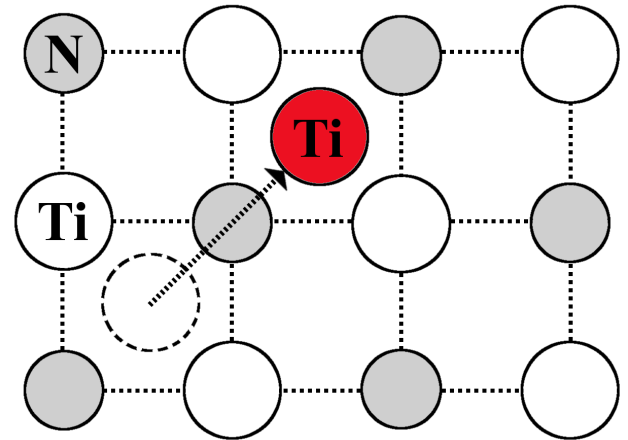
D. Edström, et. al, Thin Solid Films 688, 137380 (2019)

# Surface phenomena during deposition and growth

Ti migration on “atomically-smooth” TiN(001) surface



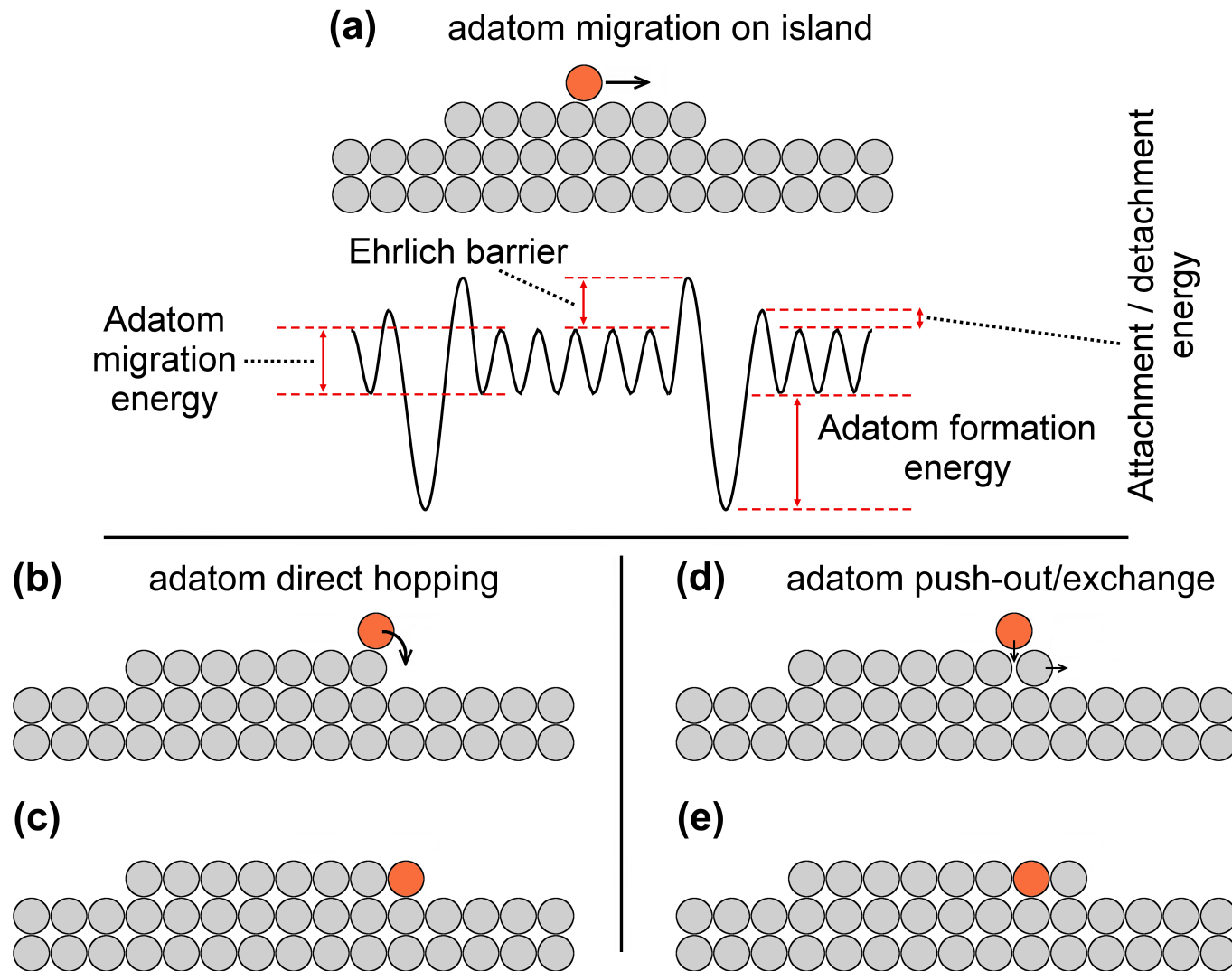
Long  $\langle 100 \rangle$  jumps



Single  $\langle 110 \rangle$  jumps

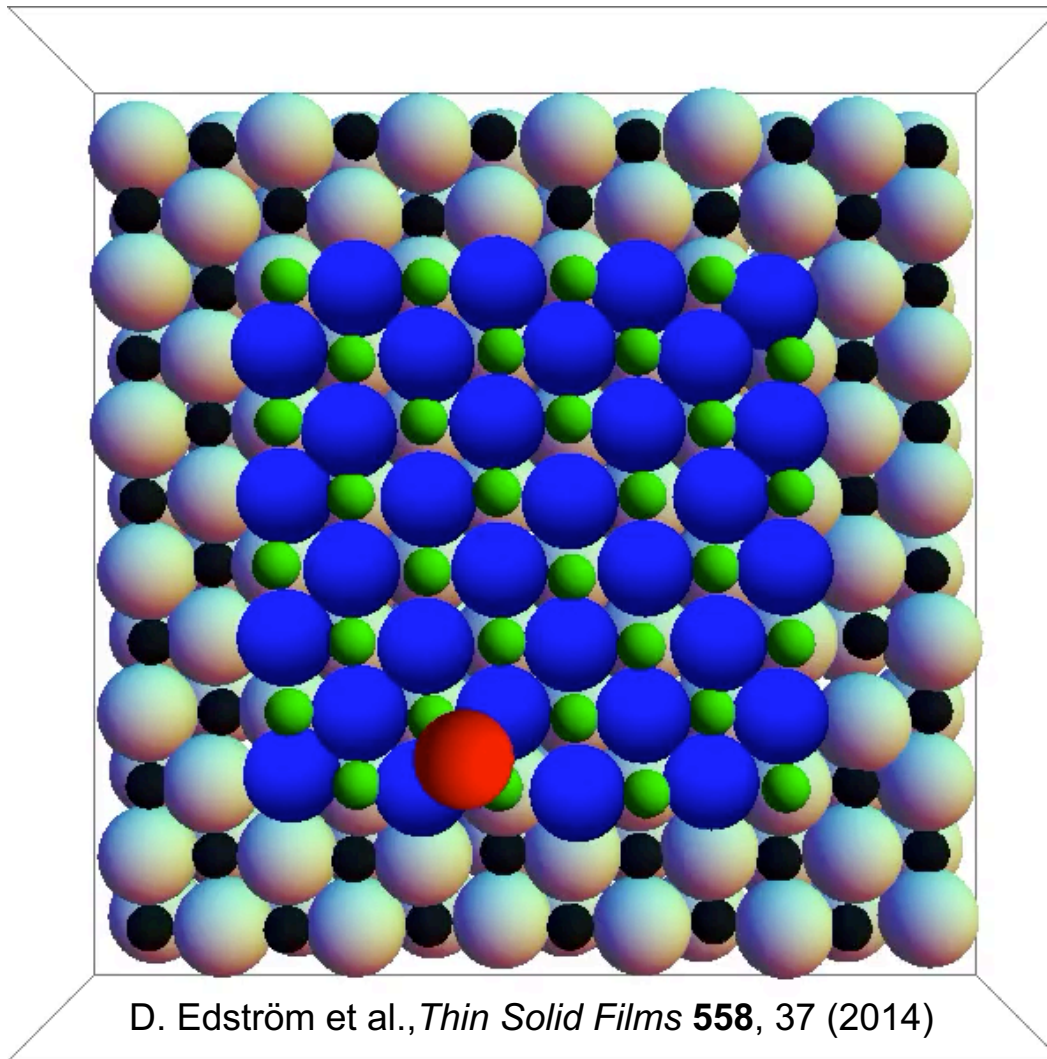
# Surface phenomena during deposition and growth

## Adatom migration across surface step



# Surface phenomena during deposition and growth

## Adatom migration across surface step (push-out/exchange)



The mechanisms observed in CMD simulations can be verified in AIMD simulations done for relatively small supercells. In general, one can expect qualitatively good & quantitatively reasonable agreements between CMD and AIMD results. [See, e.g, D.G. Sangiovanni et al, Phys. Rev. B 97, 035406 (2018)]

surface atoms: Ti=silver ; N=black. Island: Ti=blue ; N=green; adatom: Ti=red

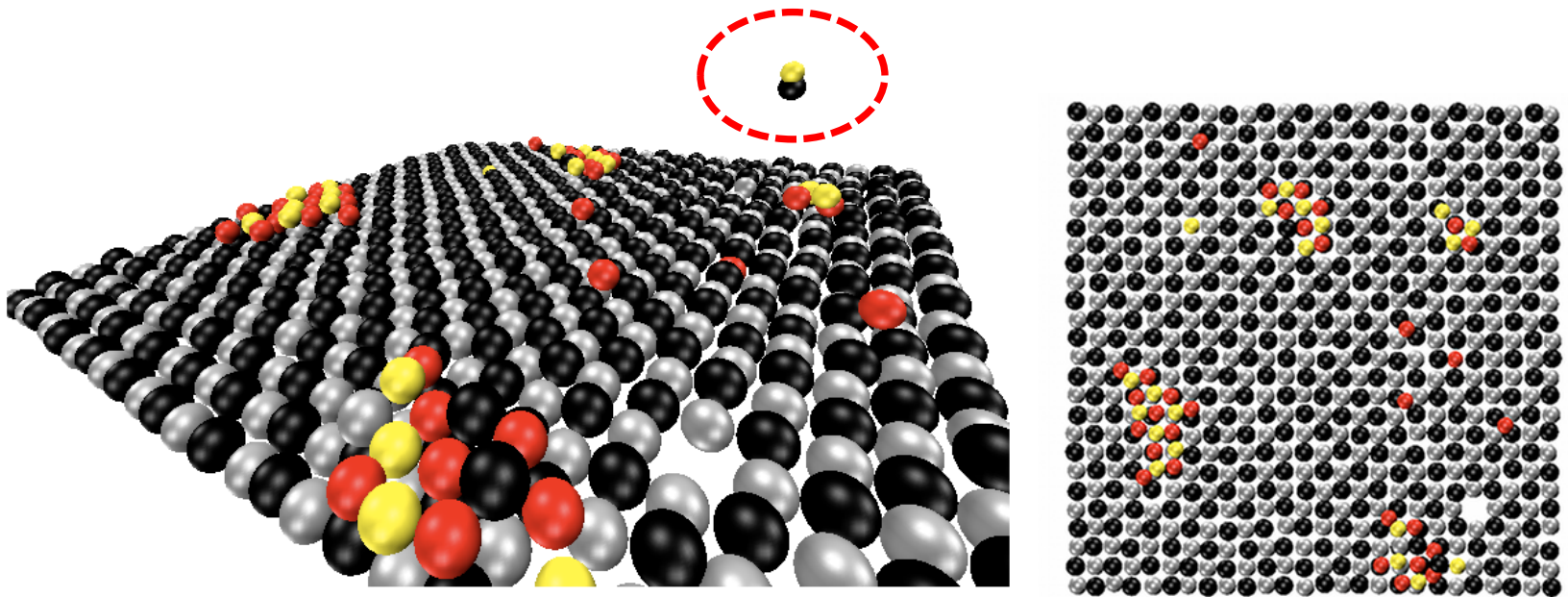


# Surface phenomena during deposition and growth

Discovery of (non-intuitive) reactions

CMD prediction → AIMD validation

N\_adatom/N\_surface ( $N_2$ ) desorption from TiN(001)

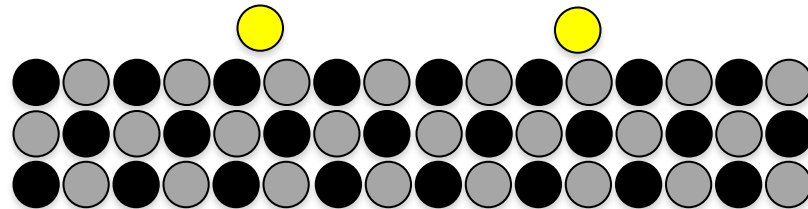


Surface atoms: Ti=silver ; N=black. Adatoms: Ti=red ; N=yellow

# N<sub>2</sub> desorption from TiN(001)

## Assumed mechanism

adatom/adatom  
recombination  
(Langmuir-Hinshelwood  
mechanism)

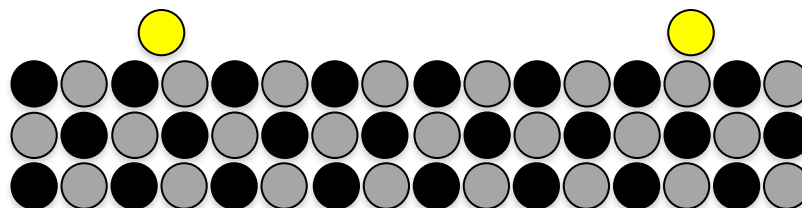




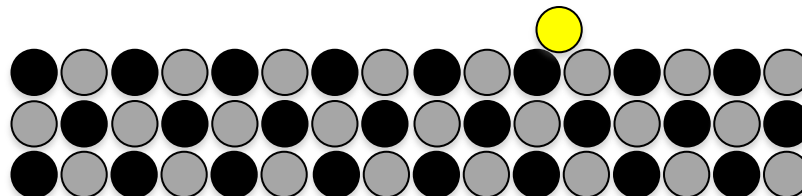
# N<sub>2</sub> desorption from TiN(001)

## AIMD simulations

N<sub>ad</sub>/N<sub>ad</sub> long-range  
repulsive  
interactions

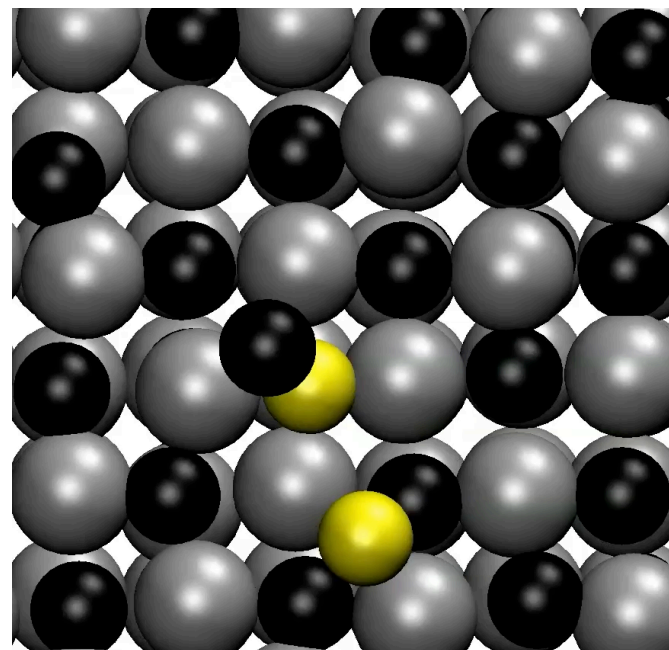
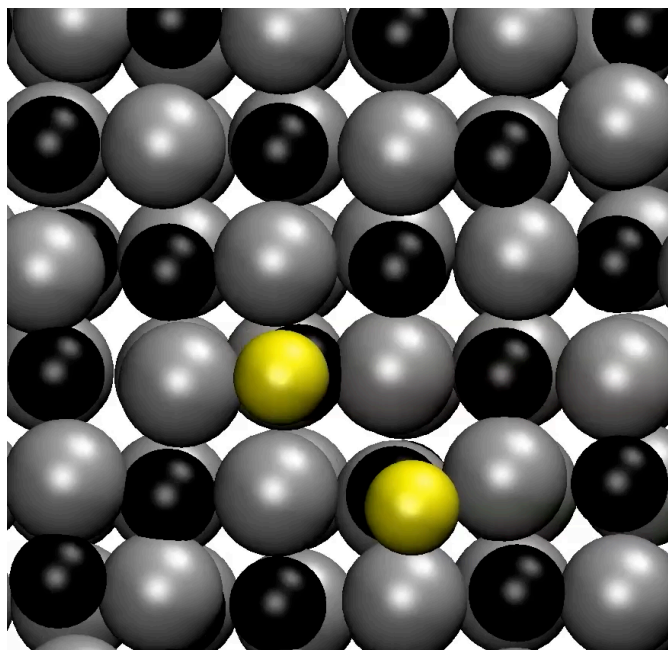


N adatom (N<sub>ad</sub>) removes  
surface N atom (N<sub>surf</sub>)

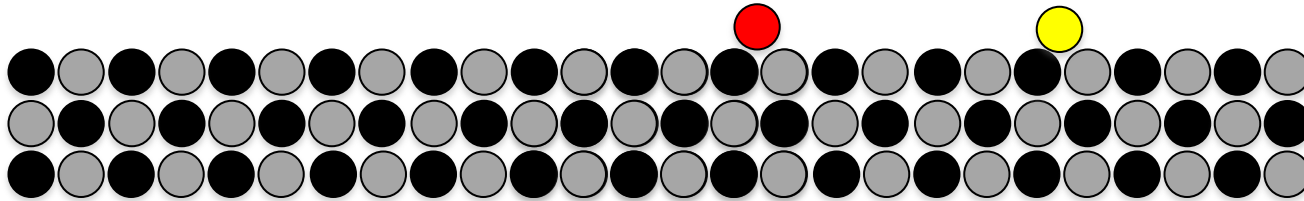


# N<sub>2</sub> desorption from TiN(001)

AIMD 2500 K



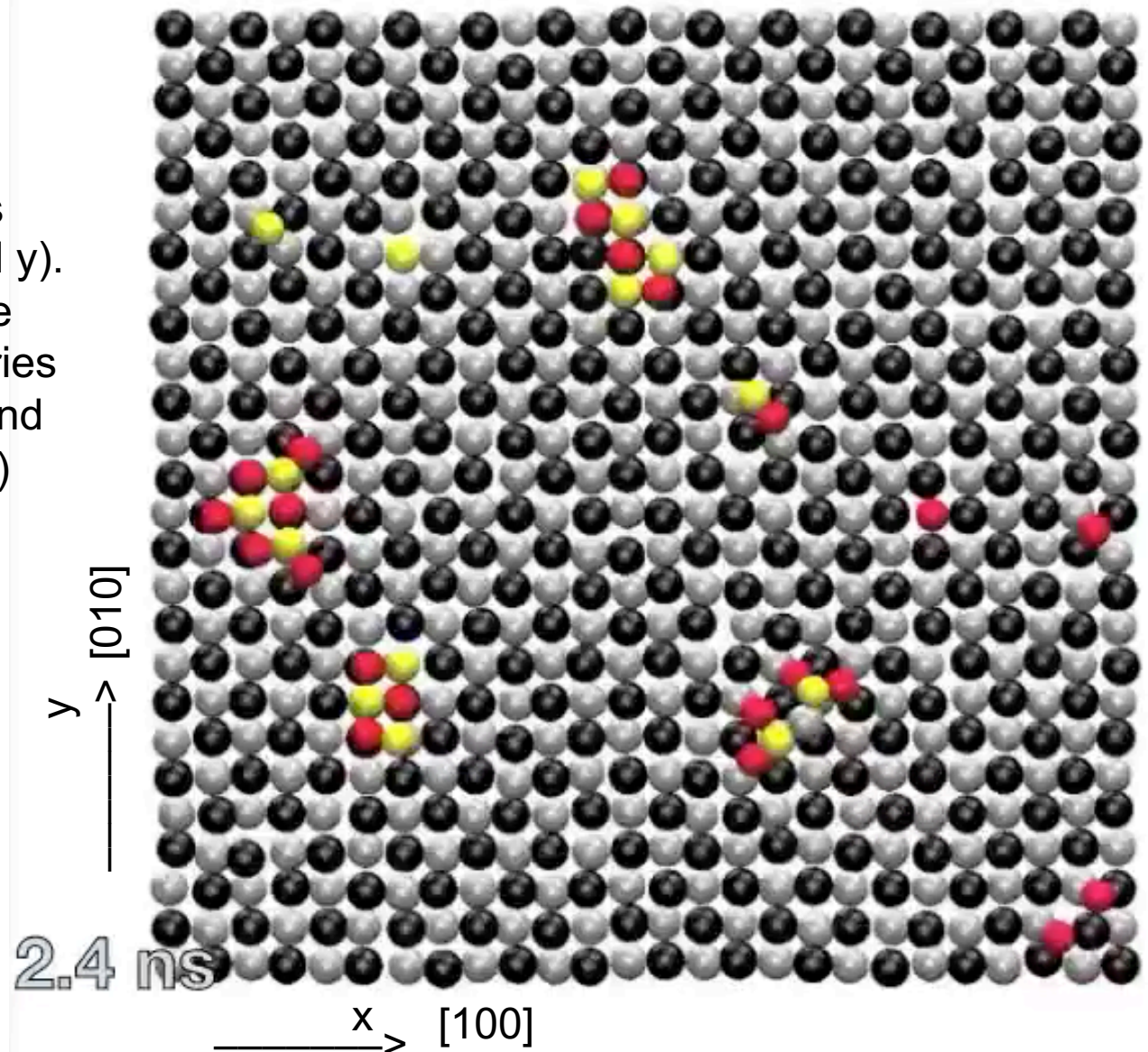
# Formation of Ti-N molecules necessary for growth



- Ti adatoms highly mobile on TiN(001)
- N adatoms essentially stationary
- Desorbing  $N_{ad}/N_{surf}$  pairs leave anion vacancies in the surface

# CMD deposition of Ti and N on TiN(001) surface at 1200 K

The supercell slab has periodicity in-plane (x and y).  
Note atoms that migrate across supercell boundaries (disappear on one side and re-appear on the other)

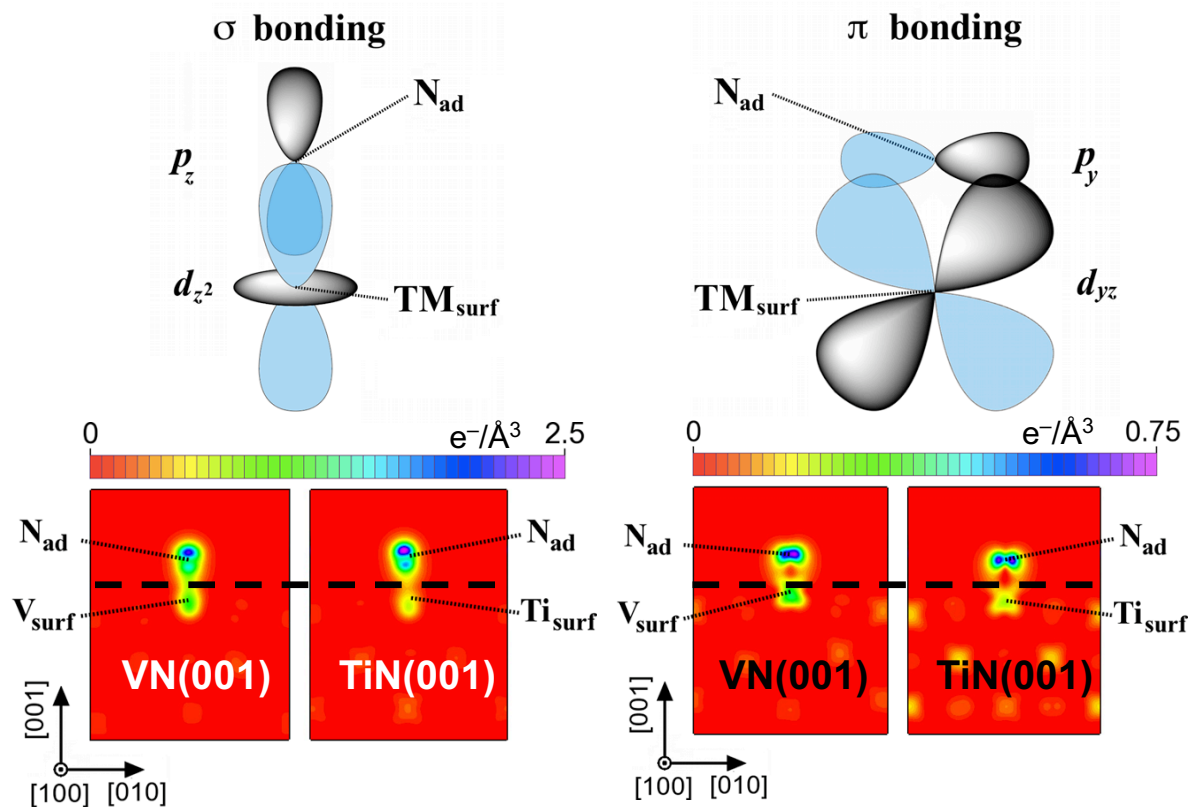
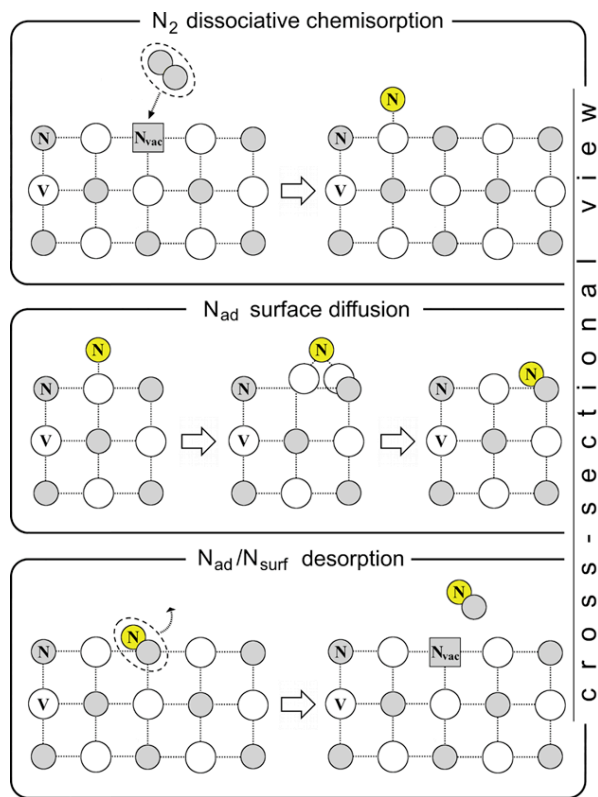


D. Edström, et. al, Journal of Vacuum Science & Technology A 34, 041509 (2016)

D. Edström, et. al, Journal of Applied Physics 121, 025302 (2017)

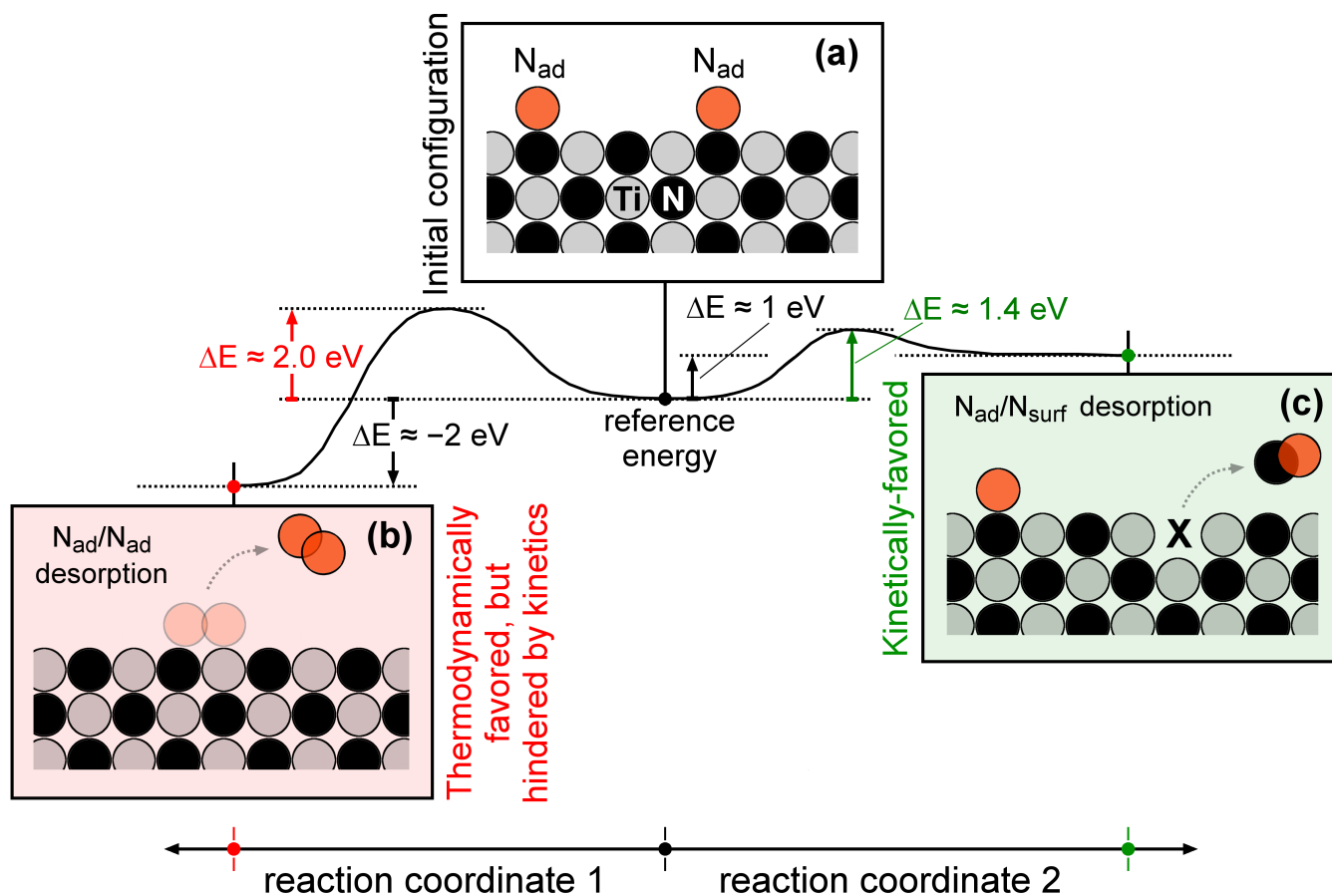
D. Edström, et. al, Thin Solid Films 688, 137380 (2019)

# Elucidate catalysis mechanisms with help from DFT calculations

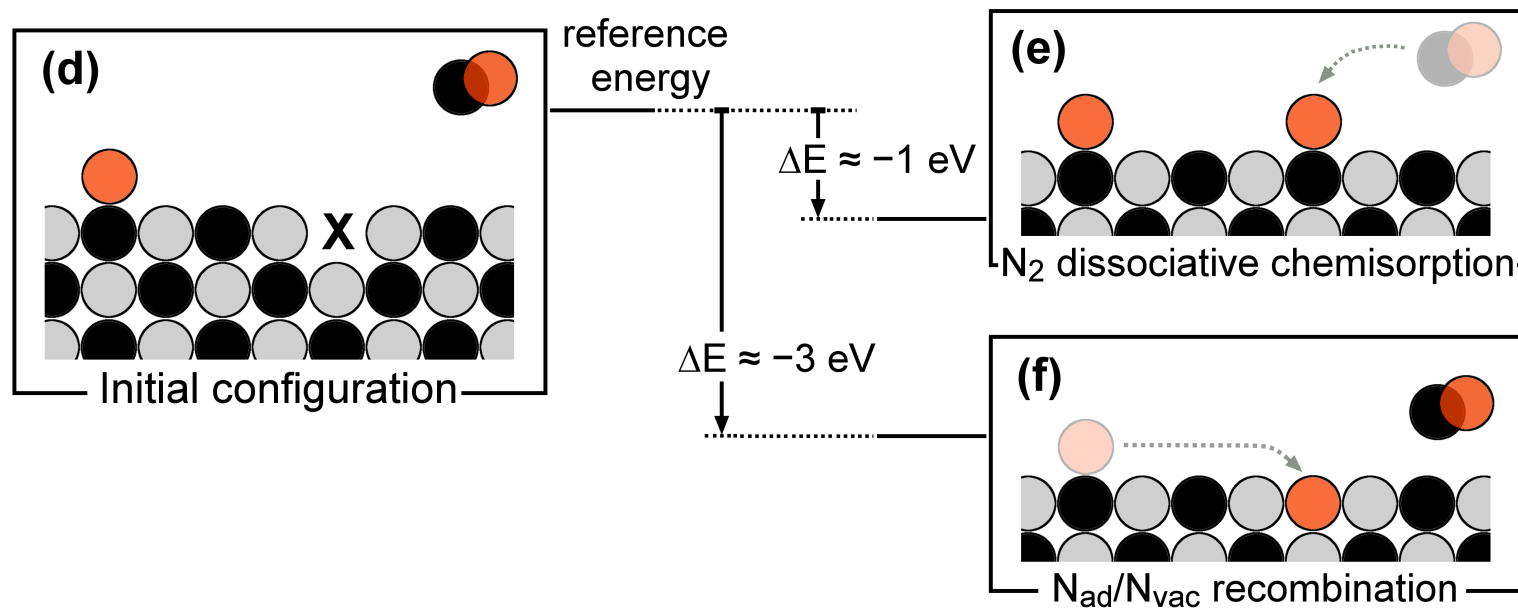


D.G. Sangiovanni, et al. J Phys Chem C **120**, 12503 (2016)

# Kinetics overshadows thermodynamics



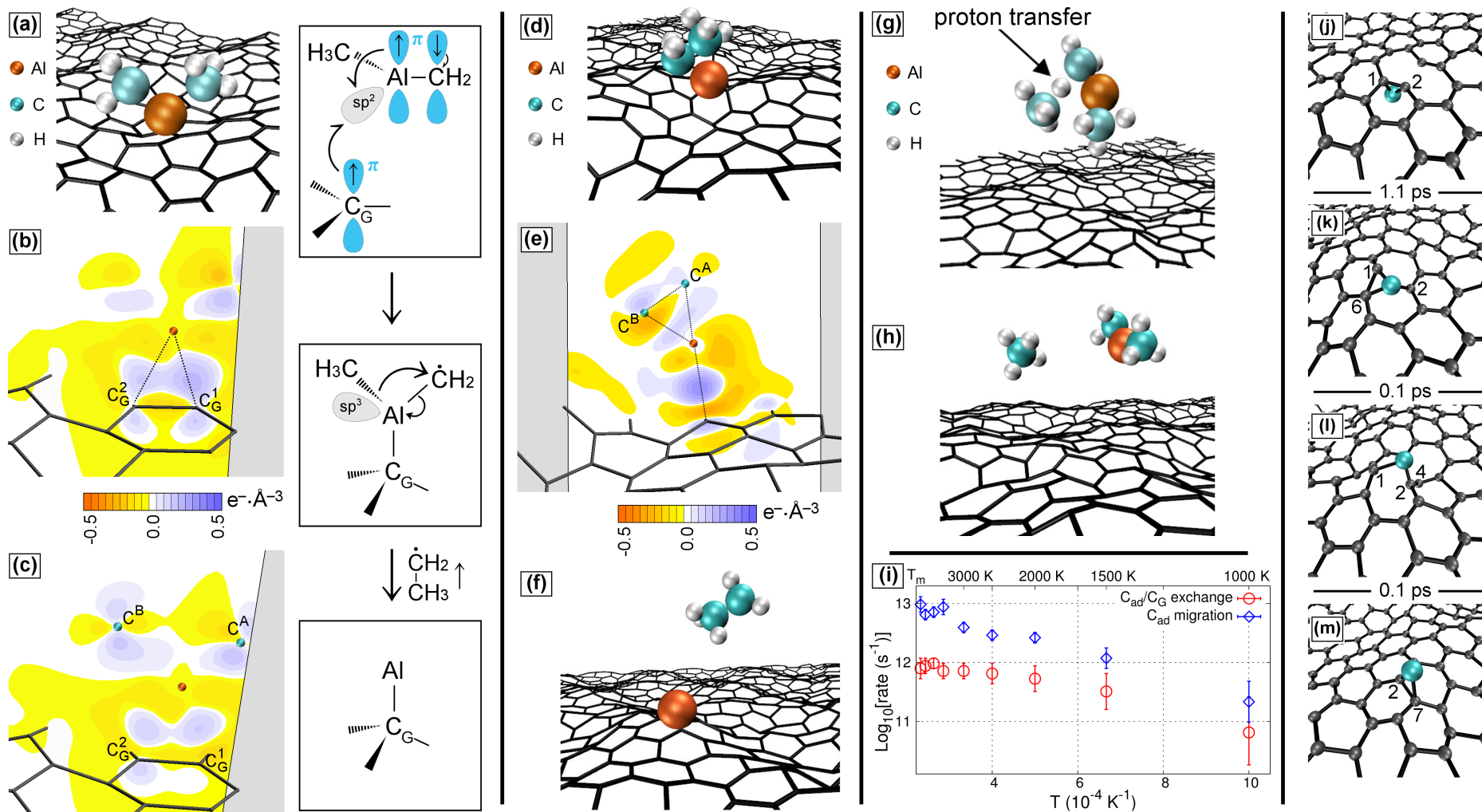
# Kinetics overshadows thermodynamics





# Metal-organic chemical vapor deposition

## Example of AlN precursor reactions on graphene

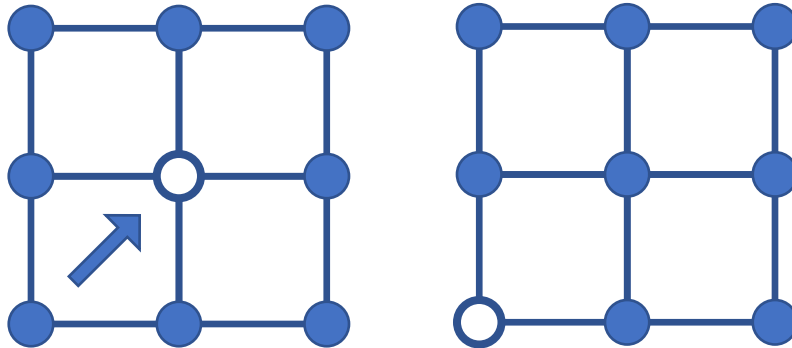




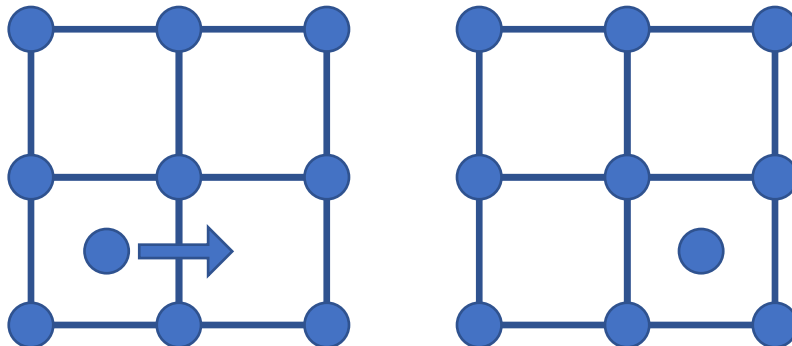
# MD to study diffusion of atoms in crystals at extreme conditions

## “Conventional” mass transport mechanisms in solid crystals

Vacancy migration



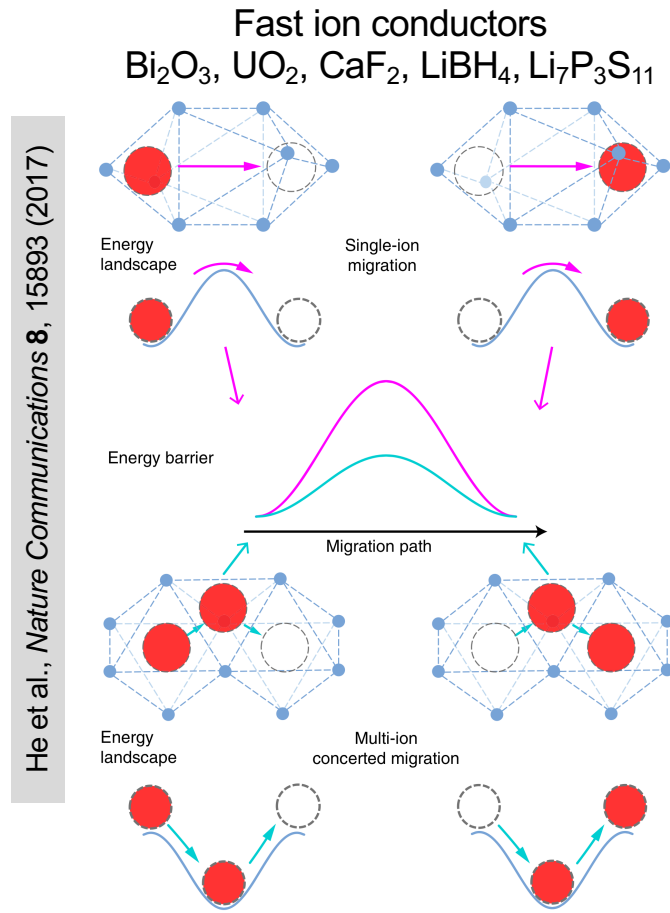
Self-interstitial migration



- Well-described by single uncorrelated atomic jumps
- Diffusivity reproduced by random-walk kinetics
- Migration rates  $\rightarrow$  Arrhenius-like behavior

# MD to study diffusion of atoms in crystals at extreme conditions

## Rapid, concerted atomic/ionic migration



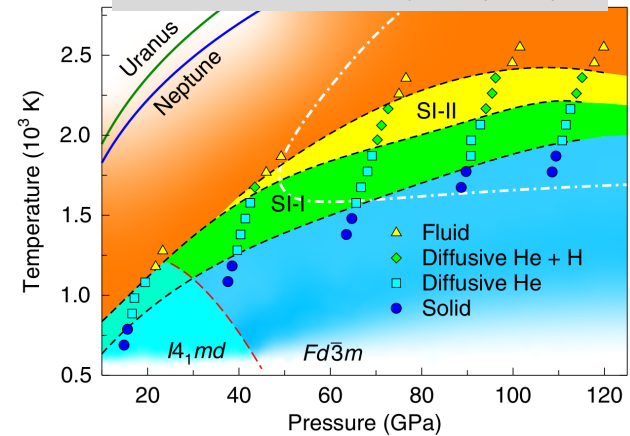
## Superionic-water in giant icy Uranus and Neptune

Millot et al., *Nature* 569, 251–255 (2019)



## Superionic helium-water compounds

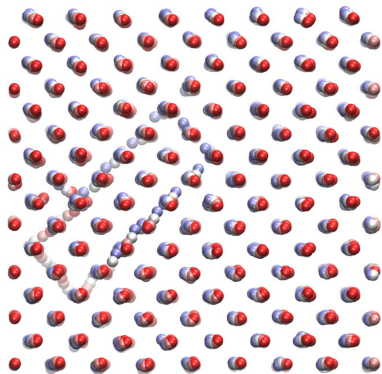
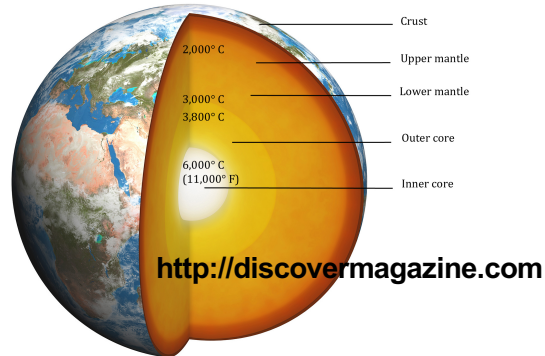
Liu et al., *Nature Physics* (2019)



# MD to study diffusion of atoms in crystals at extreme conditions

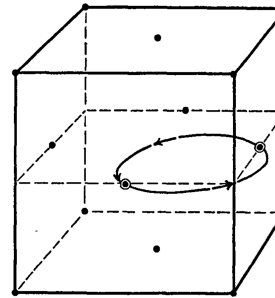
## Concerted atomic transport in elemental crystals

Predicted for bcc Iron  
at inner core conditions



Belonoshko et al., *Nature Geoscience* **10**, 312 (2017)

Speculated for elemental crystals at  
ambient pressures



⊙ ring atoms after Huntington  
& Seitz (1942)

Fig. 1. 2-ring diffusion in f.c.c. lattice.

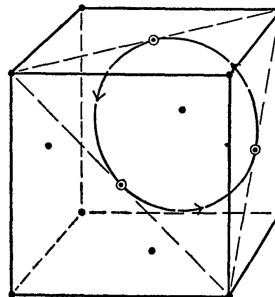


Fig. 2. 3-ring diffusion in f.c.c. lattice.

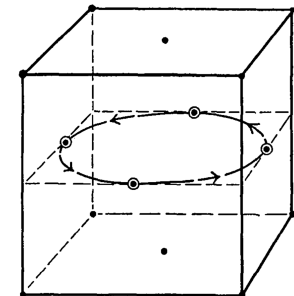


Fig. 3. 4-ring diffusion in f.c.c. lattice.

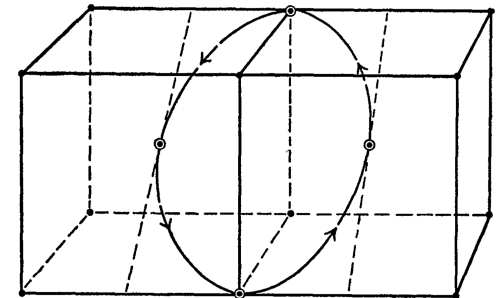
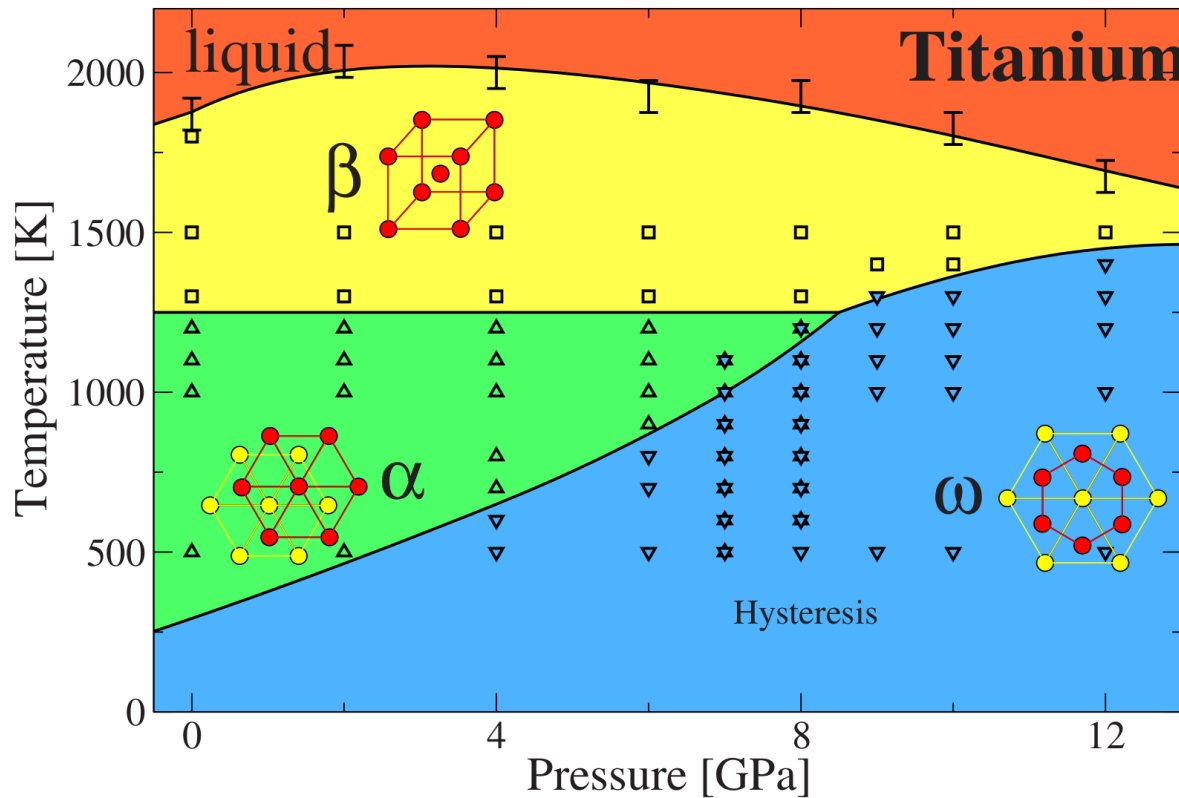


Fig. 4. 4-ring diffusion in b.c.c. lattice.

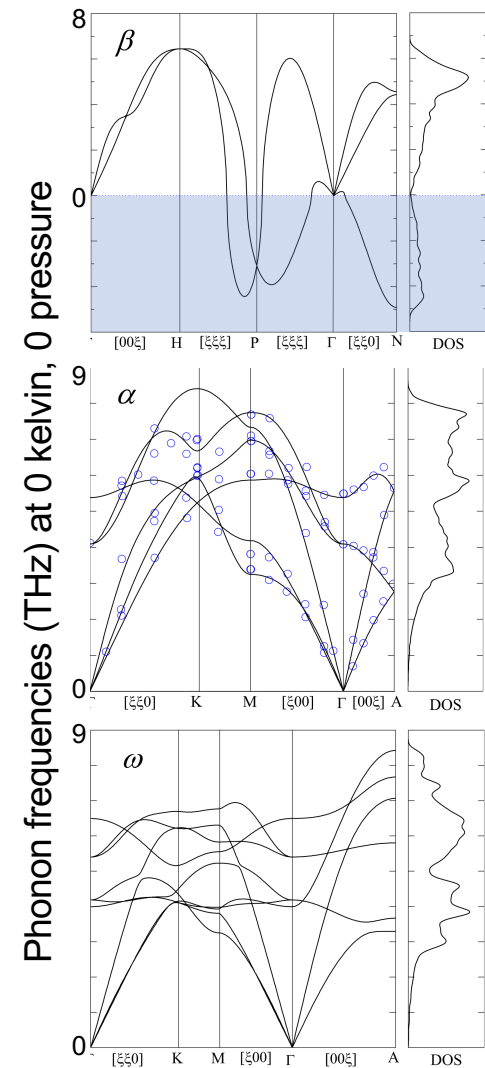
Zener, *Acta Crystallographica* **3**, 346 (1950)

# MD to study diffusion of atoms in crystals at extreme conditions

Phase diagram of Titanium



Hennig et al., *Physical Review B* **78**, 054121 (2008)



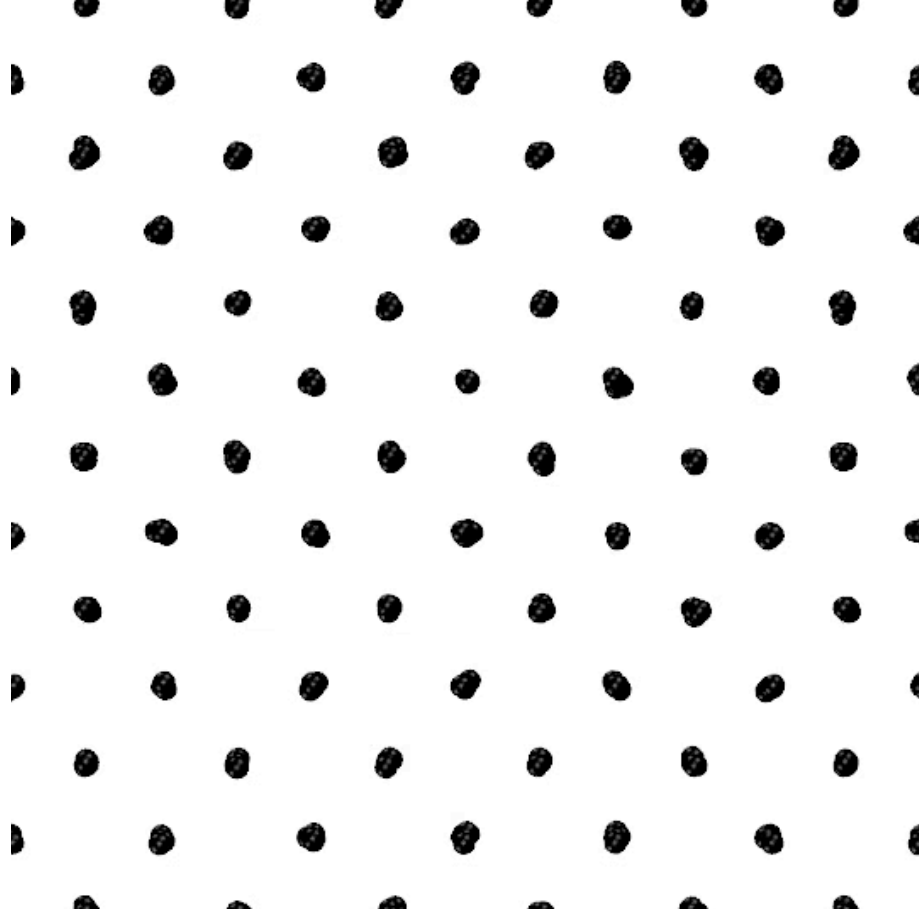
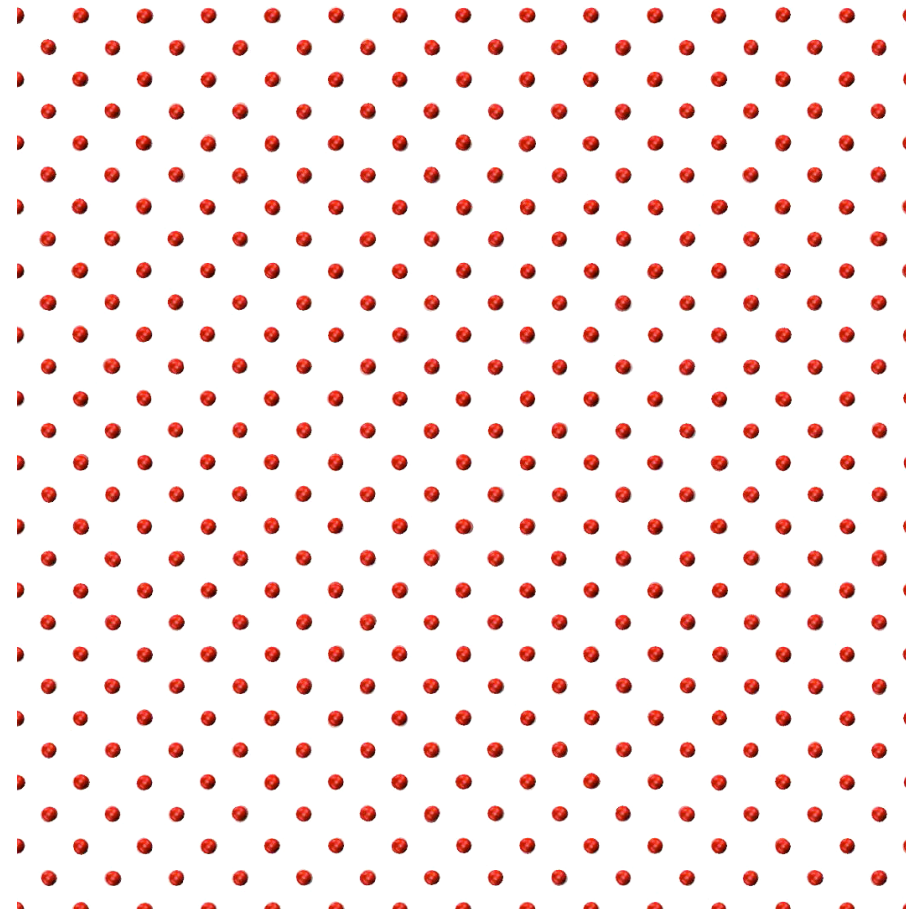
Mei et al., *Physical Review B* **80**, 104116 (2009)

# MD to study diffusion of atoms in crystals at extreme conditions

Temperature  $\approx 0.9 \cdot T_{\text{melt}}$

Classical MD

Ab initio MD



Sangiovanni et al., *Physical Review Letters* **123**, 105501 (2019)

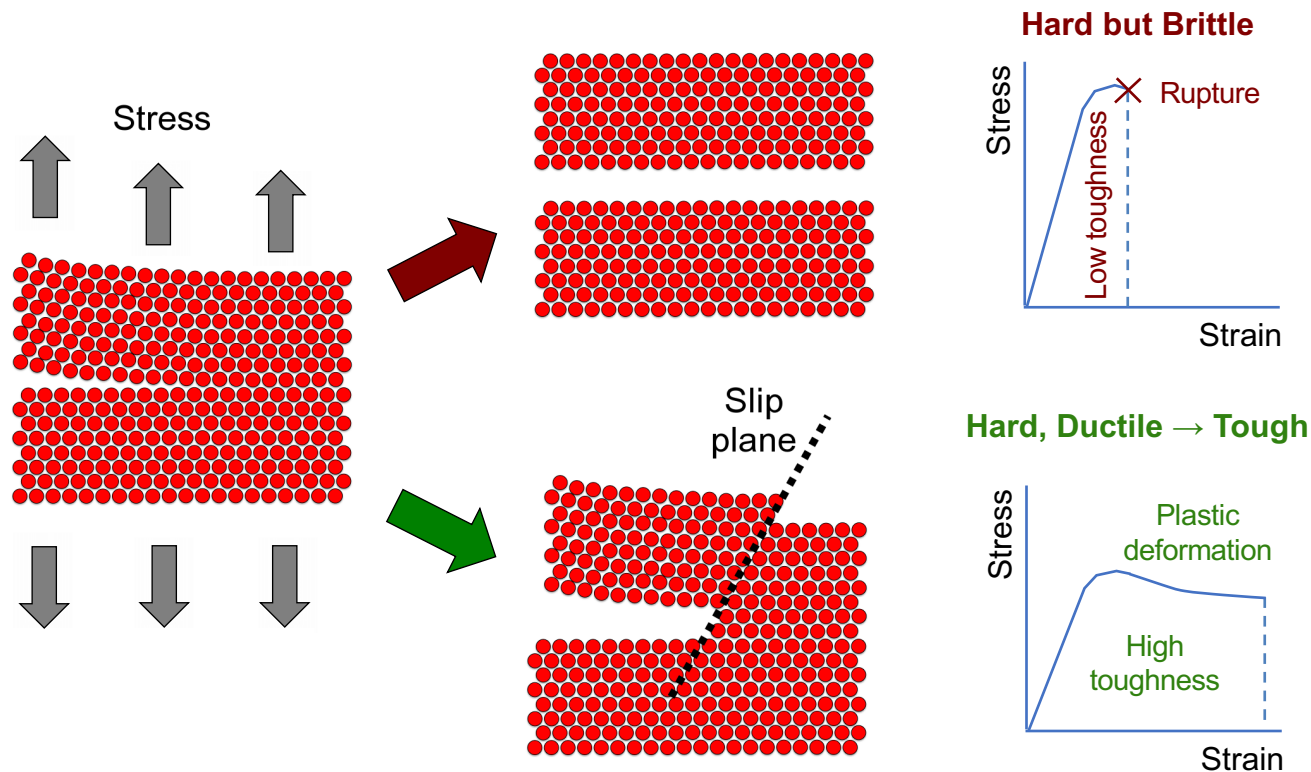
# MD to guide design of materials with improved properties



Rapid metal machining: high temperature and pressures

# MD to guide design of materials with improved properties

## Hardness & ductility *not* mutually exclusive!

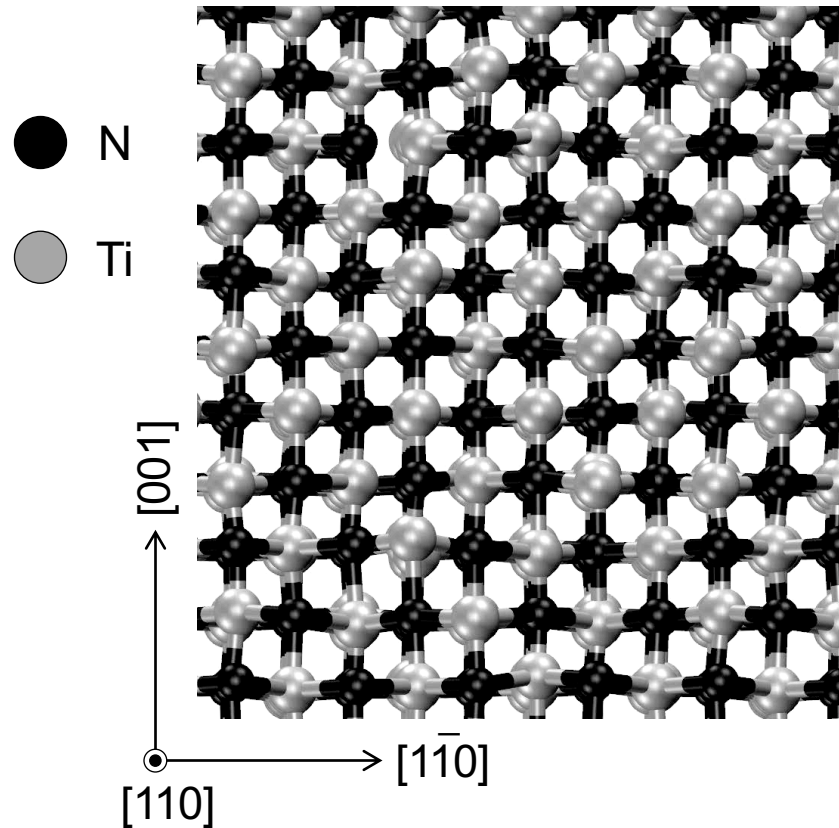


ME Eberhart, DP Clougherty, JM MacLaren, J Am Chem Soc **115**, 5762 (1993)



# MD to guide design of materials with improved properties

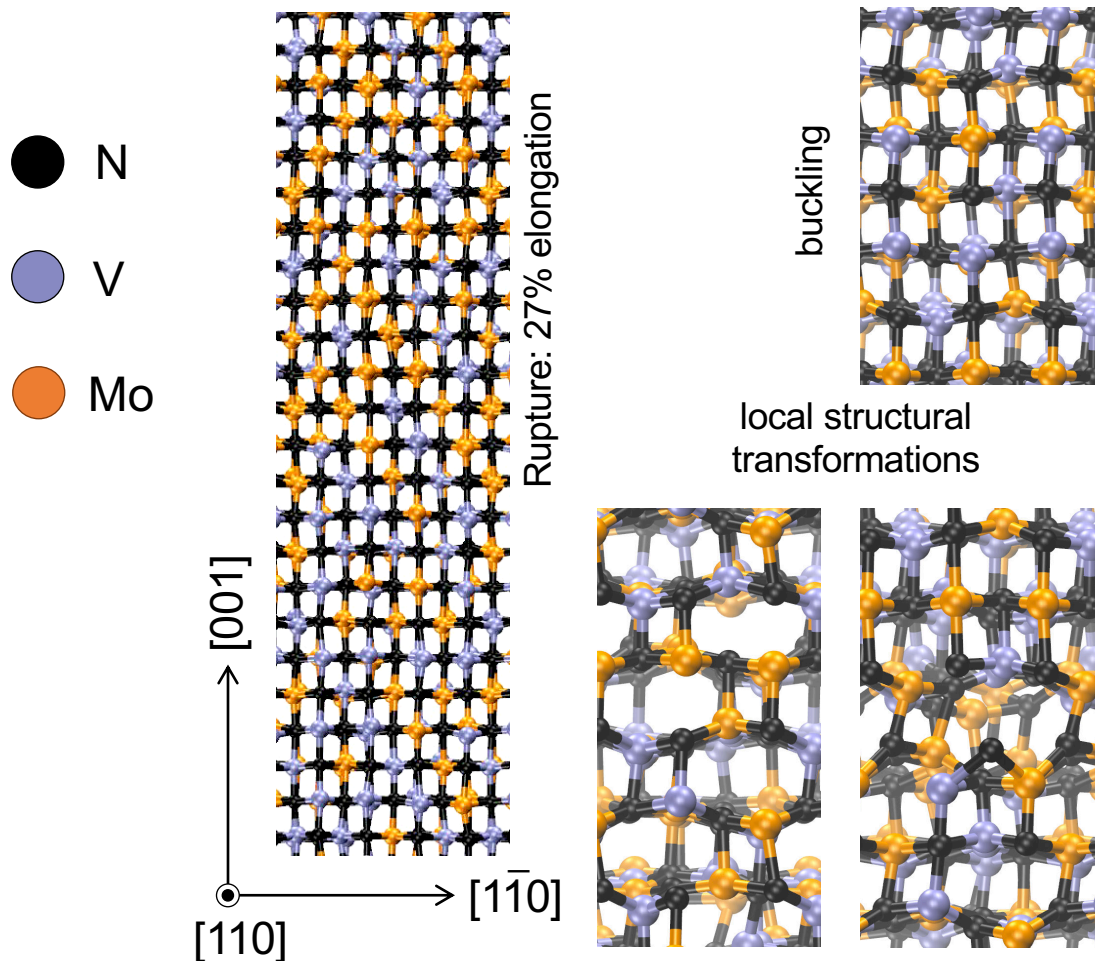
[001]-oriented TiN at 9.0% tensile strain  
along [001] direction (300 K)



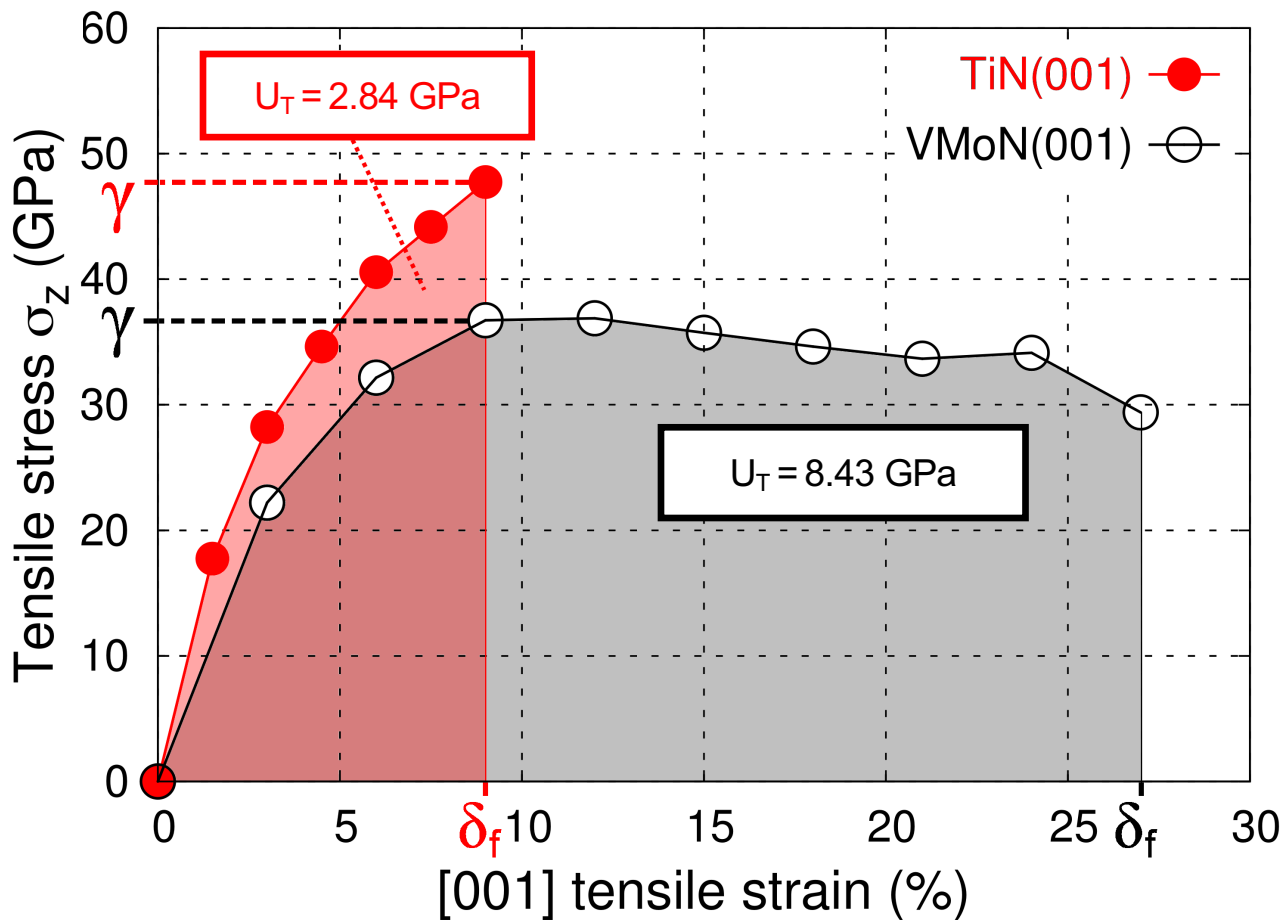


# MD to guide design of materials with improved properties

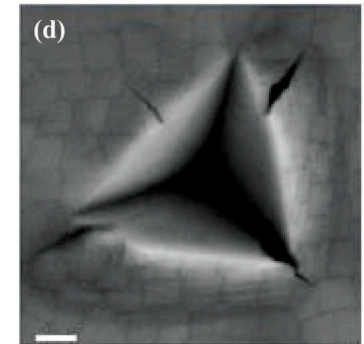
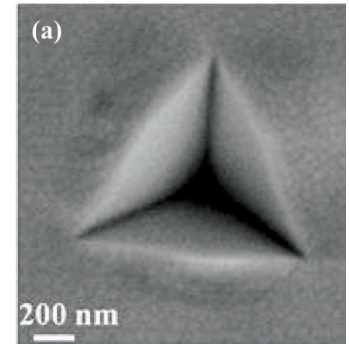
[001]-oriented (V,Mo)N alloy : tensile strain  
along [001] direction (300 K)



# MD to guide design of materials with improved properties



VMoN: tough

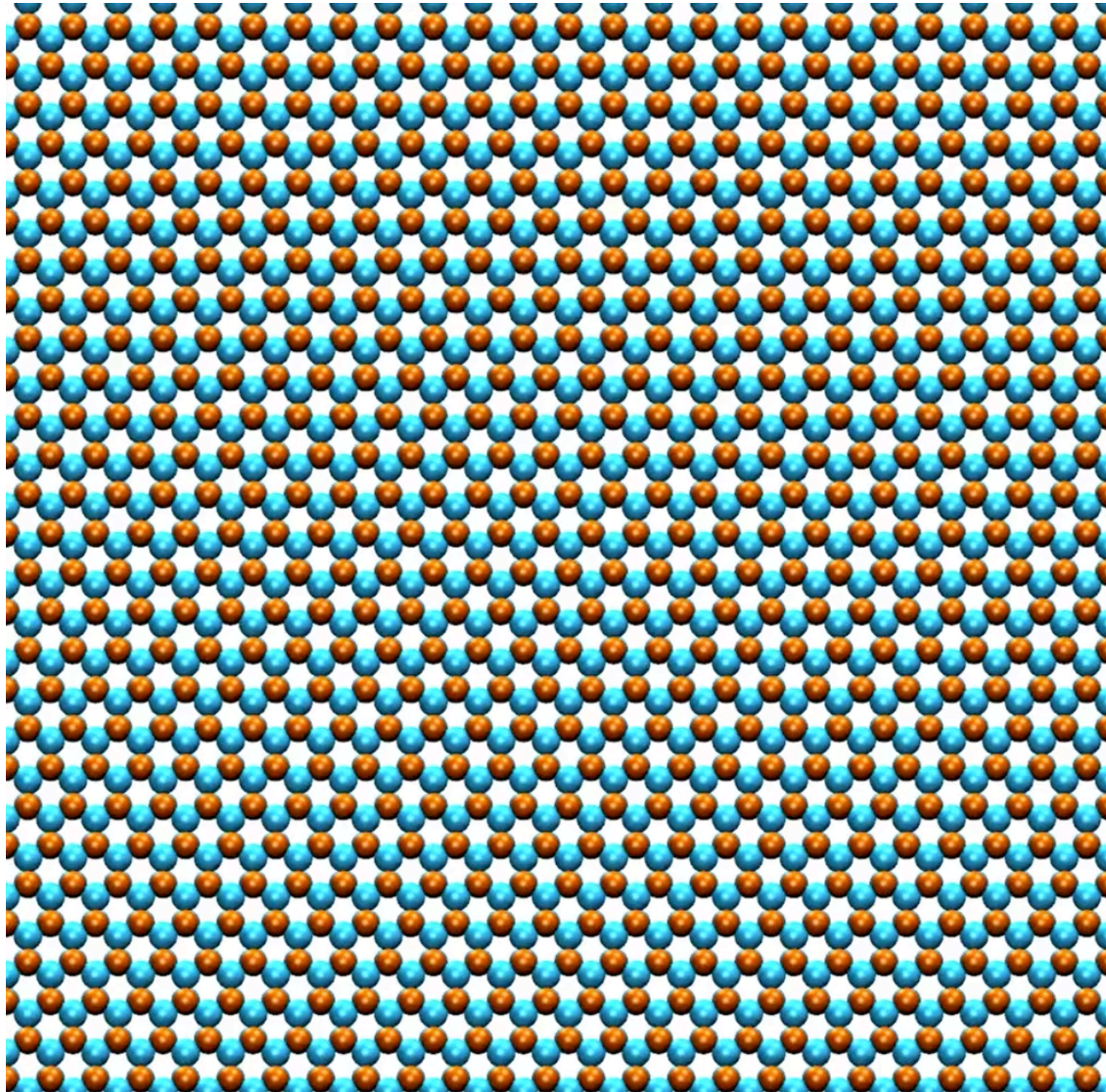


TiN: brittle

Kindlund et al.,  
APL Materials 1, 042104 (2013)

# Predict/understand solid→solid phase transitions

B4→B1 lattice transformation in Aluminum Nitride

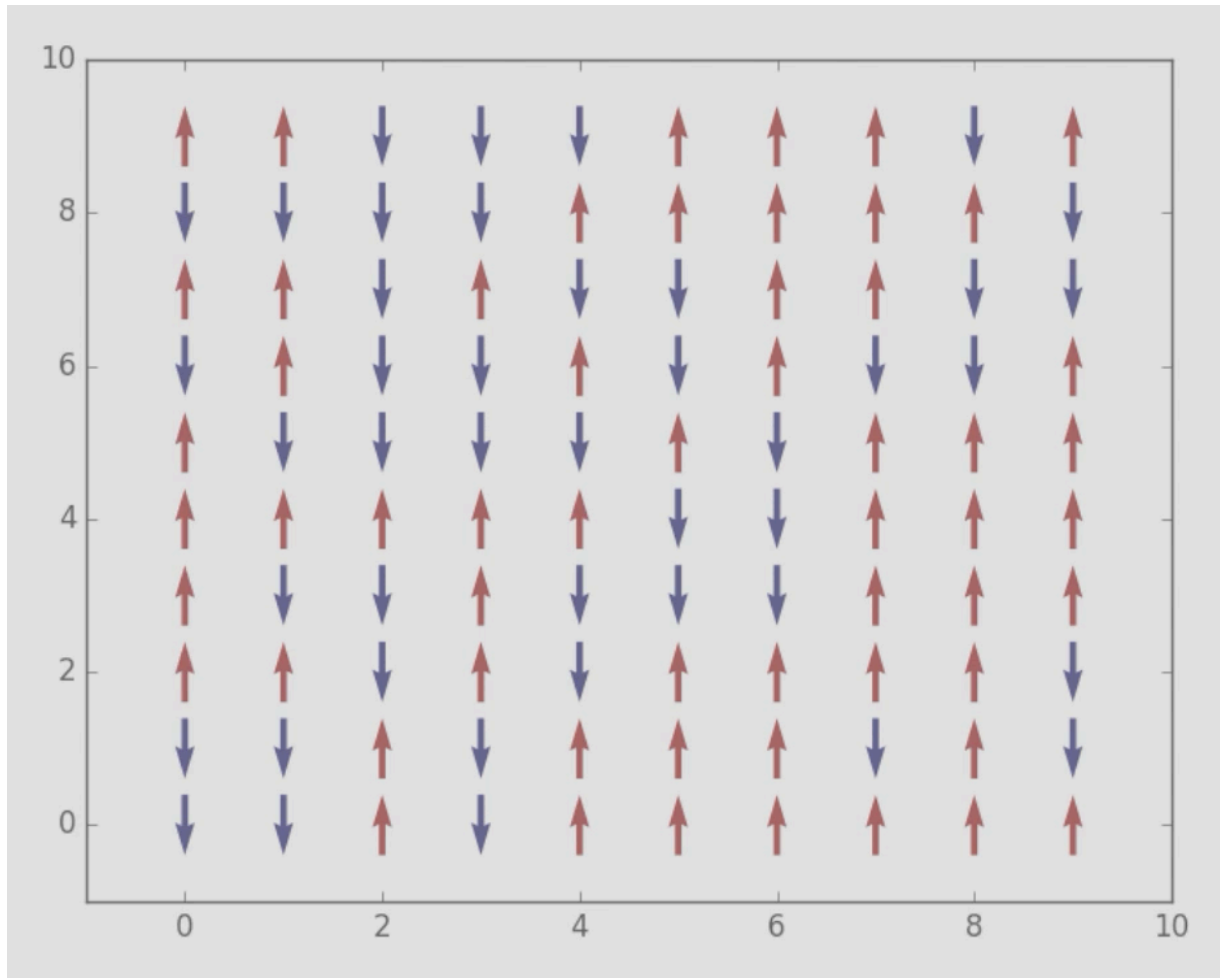


# Monte Carlo (MC)

Examples of applications in computational materials science

Which information / discoveries / understanding can MC lead to?

## 2D Ising spin model: famous example of MC application



<https://www.ibiblio.org/e-notes/Perc/ising.htm>

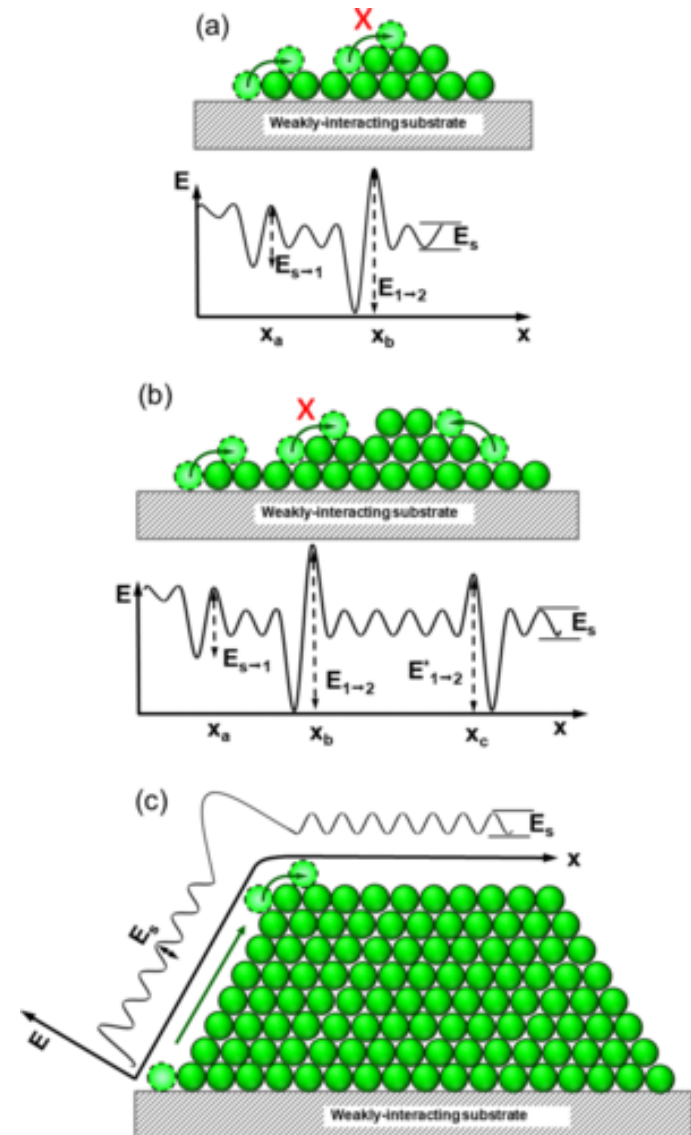
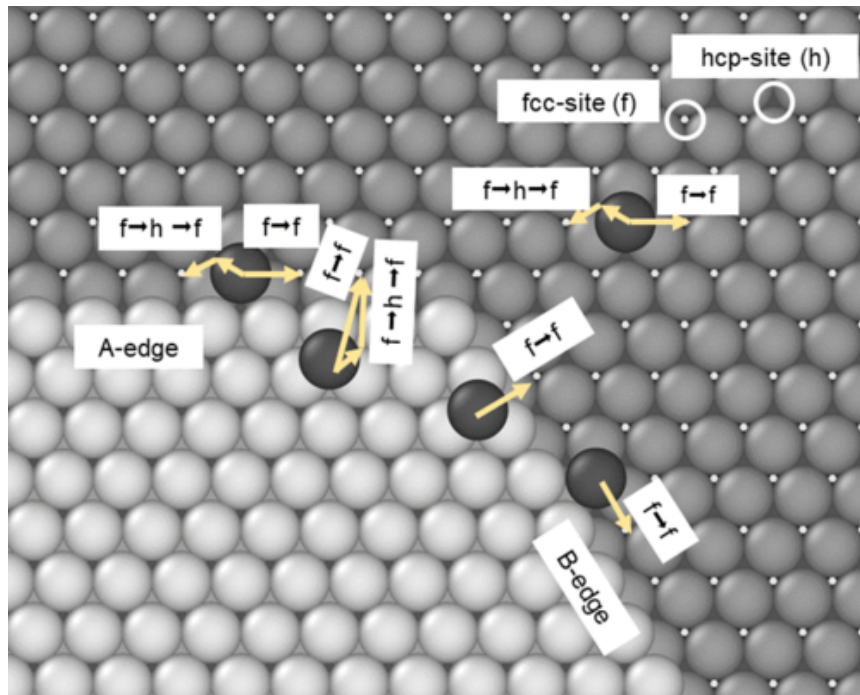
<https://ruihaoqiu.github.io/MC-Magnetic-Phase-Transition/>



# Kinetic Monte Carlo:

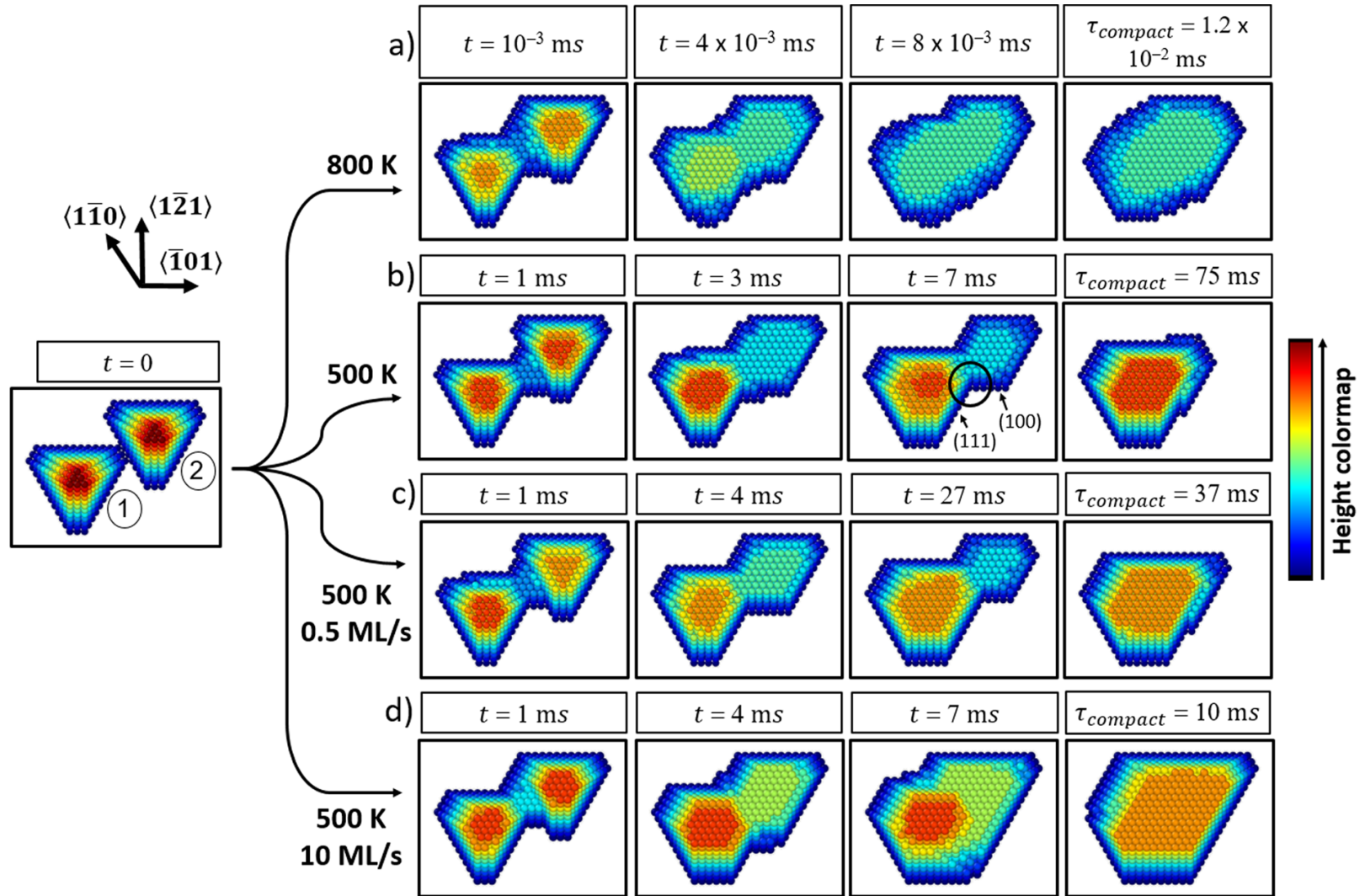
## Surface evolution for weakly-interacting adsorbate/substrates

Schematic illustrations of atomic structure, potential energy landscape, and upward atomic transport mechanisms during 3D island formation on weakly interacting substrates.



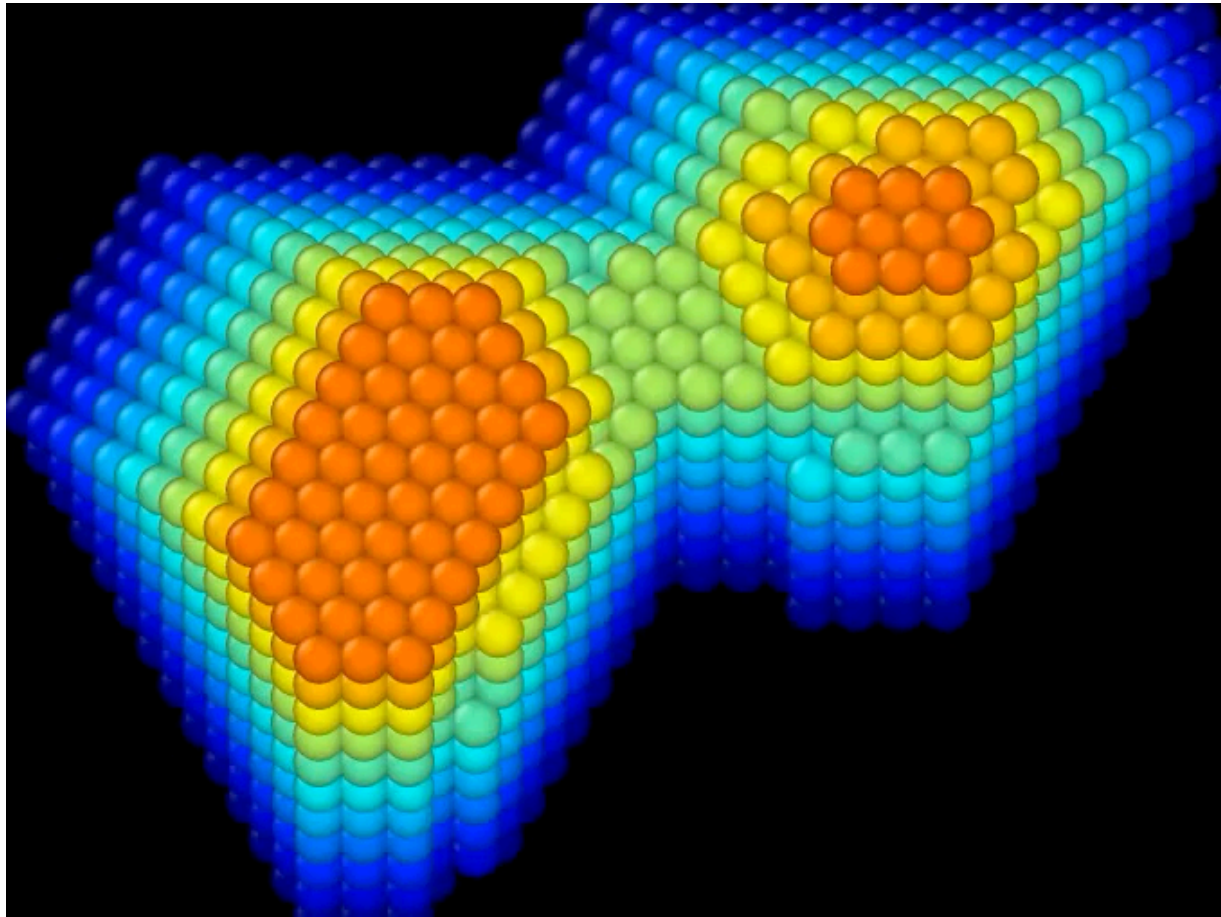
Formation and morphological evolution of self-similar 3D nanostructures on weakly interacting substrates  
B. Lü, G. A. Almyras, V. Gervilla, J. E. Greene, and K. Sarakinos Phys. Rev. Materials 2, 063401 (2018)

# KMC: Coalescence of 3D islands on weakly-interacting substrate



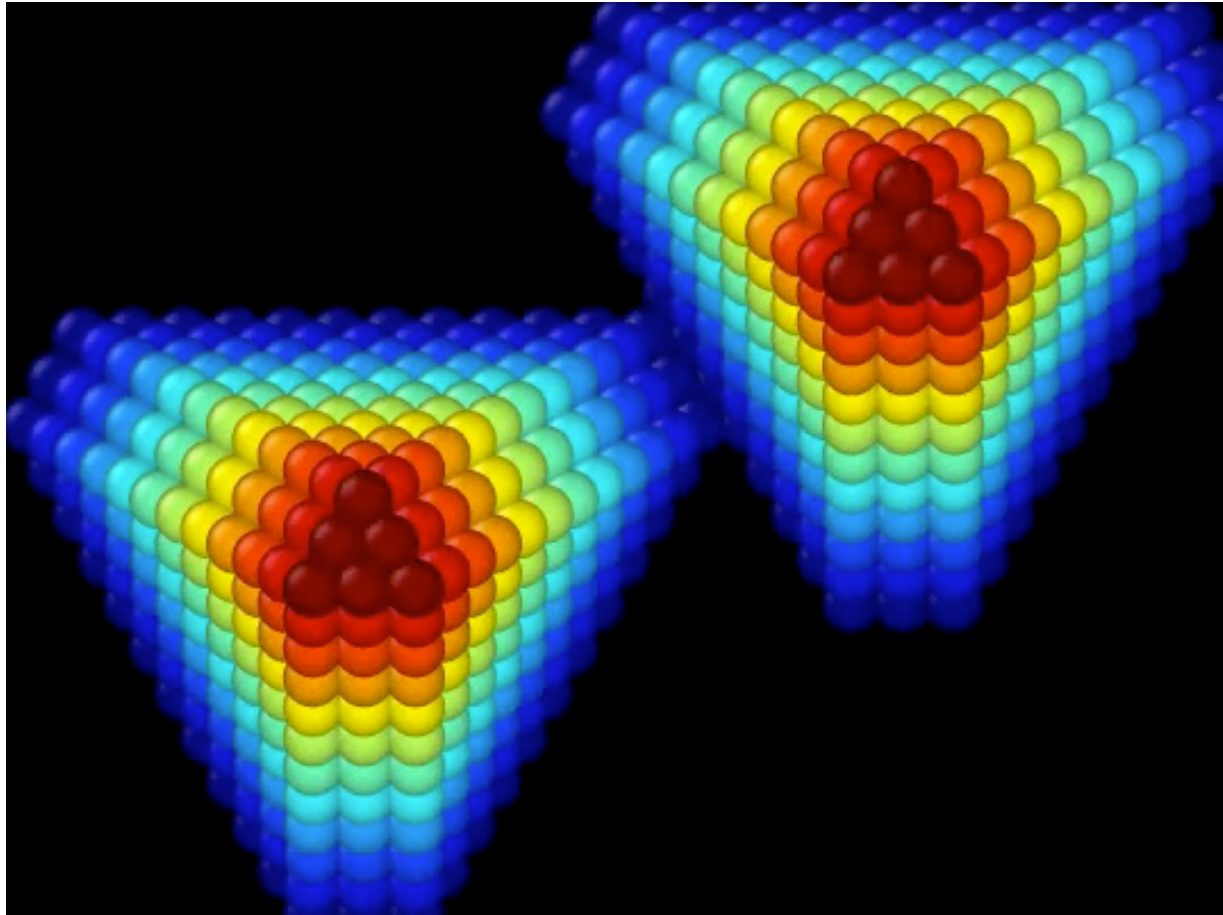
Coalescence dynamics of 3D islands on weakly-interacting substrates

V. Gervilla, G. A. Almyras, B. Lü & K. Sarakinos, Scientific Reports 10, 2031 (2020)



For  $T_s = 800$  K (Fig. 1(a)), the island surface becomes rough, hosting a large density of kink sites, most notably for  $t > 4 \text{ Å} \sim 10^{-3} \text{ ms}$ . The simulations show that atoms detach from kinks at the island tops and diffuse to occupy the highly-coordinated sites adjacent to the intersection of the islands to form a neck





at  $T_s = 500$  K, the cluster undergoes a relaxation through a different pathway than at  $T_s = 800$  K, in which island (2) (right top) is absorbed by island (1) (bottom left) via repeated facet migration

Coalescence dynamics of 3D islands on weakly-interacting substrates  
V. Gervilla, G. A. Almyras, B. Lü & K. Sarakinos, Scientific Reports 10, 2031 (2020)