Lecture : Kinetic Monte Carlo Simulations

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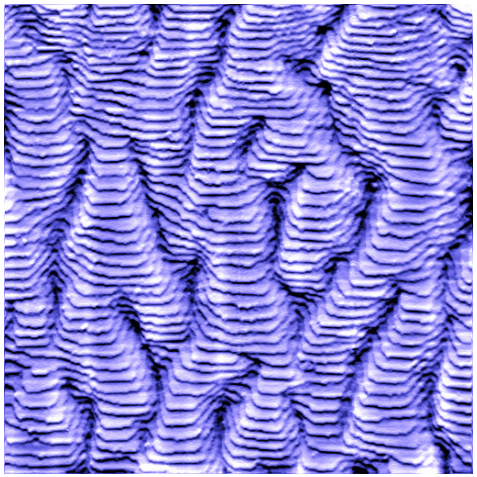
ILM-Lyon, France.

6th October 2017

1. Introduction
   - Models and levels of description
   - Atomic steps and surface dynamics
2. Kinetic Monte Carlo
   - Rates
   - Master Equation
   - Algorithms: Metropolis & KMC
3. KMC Simulations
   - Attachment-detachment model
   - Growth from a surface
   - Solid-state dewetting
   - Step meandering instabilities
   - 3D KMC / Wetting effects
   - Elastic effects
4. Conclusion
   - Conclusion

Growth shapes

Snowflake Yoshi Furukawa, Hokkaido, Japan



Growth Cu(1,1,17) Maroutian, Ernst, Saclay, France

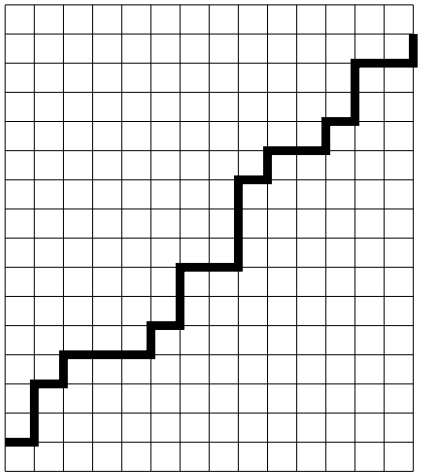
Contents

Modeling Crystal surfaces at different scales

- Atomistic
  - Electrons
    Ab Initio, quantum effects
    Density Functional Theory
    (10^3 at., 10^2 CPU, 10^{-12}s/day)
  - Atoms
    Newton equations
    Molecular Dynamics
    (10^5 at., 10 CPU, 10^{-9}s/day)
  - Lattice
    Effective moves: translation, rotation, ...
    Kinetic Monte Carlo
    (10^6 surface sites, 1 CPU, 10^2s/day)
- ...Intermediate
  - Lattice Boltzmann
    hydrodynamics
  - Phase field Crystal
    continuum but atomic positions
- Continuum
  Diffusion, hydrodynamics, elasticity, etc.
  - Diffuse interface
    Phase field
  - sharp interface
    Continuum macroscopic
  - Stochastic Differential Equations
    Langevin equations

Contents

The roughening transition



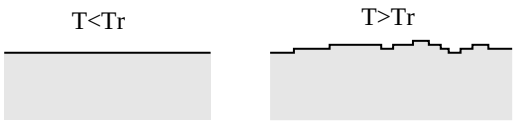
Broken bond energy J
Length N

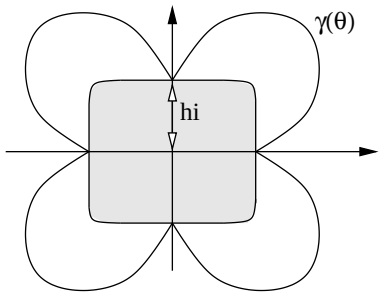
Free energy

$$F = E - TS = NJ - k_B T \ln 2^N = N(J - k_B T \ln 2)$$

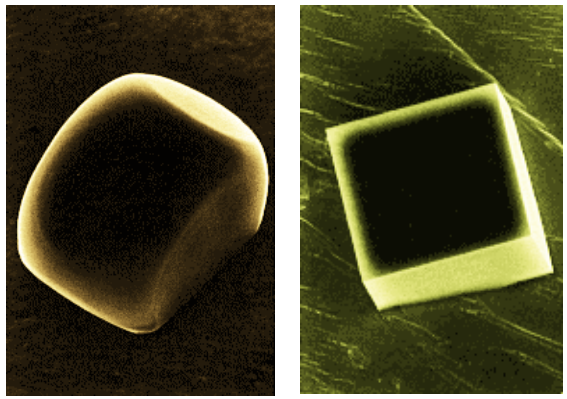
$F \to 0$ as $T \to T_R$
Roughening transition temperature

$$T_R = \frac{J}{k_B \ln 2}$$





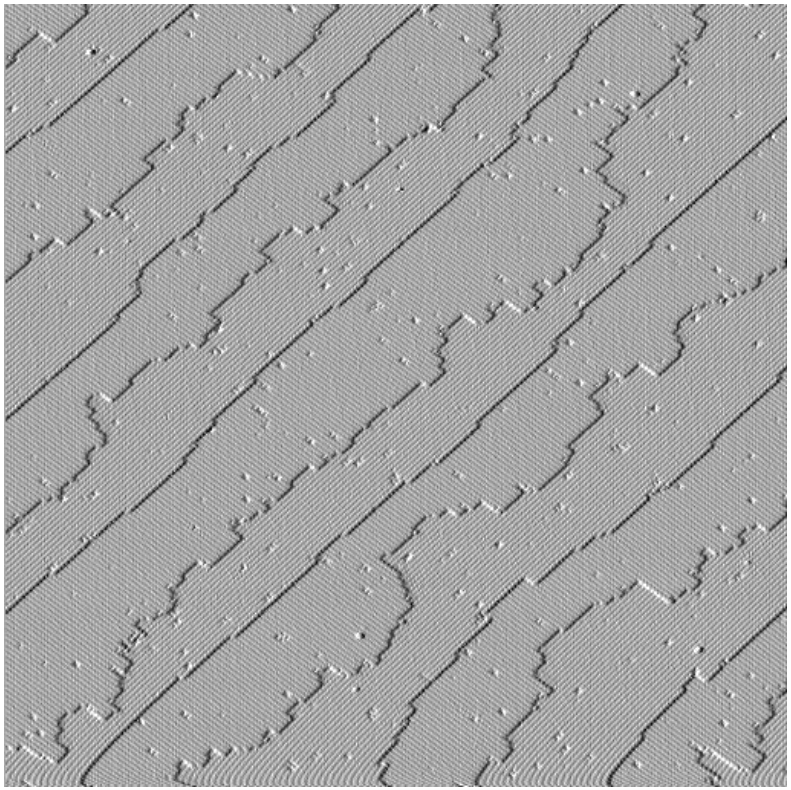
For usual crystals $T_r \sim T_M$



NaCl, Métois et al (620-710°C)

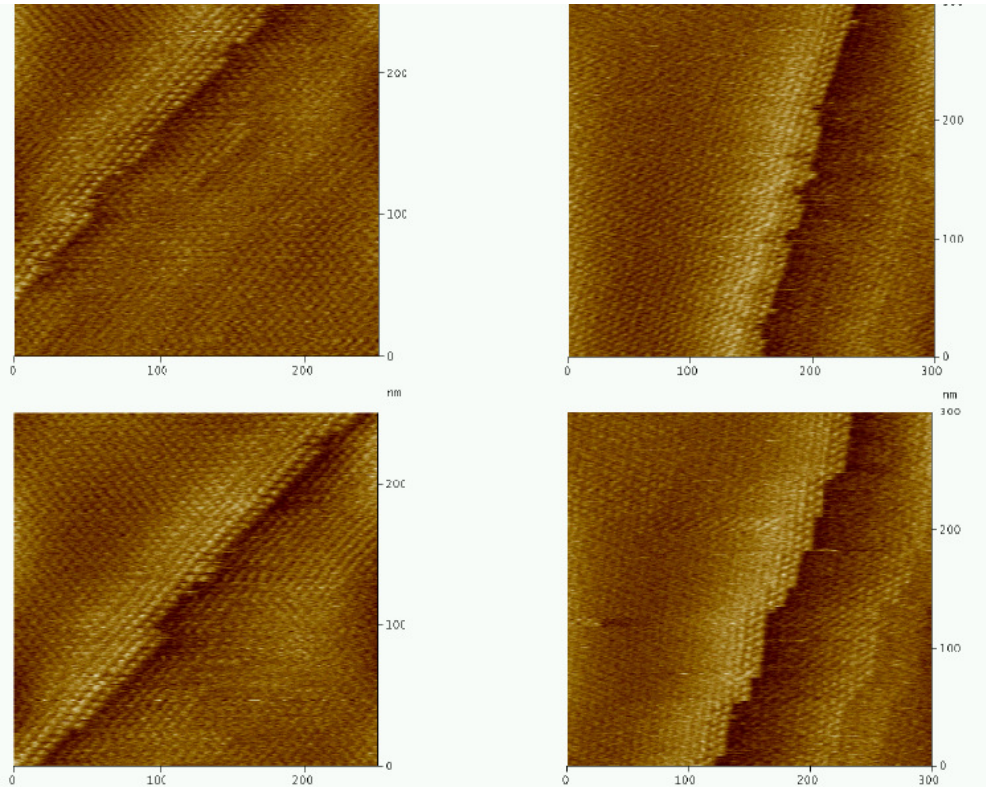
Atomic steps

Si(100)



M. Lagally, Univ. Visconsin

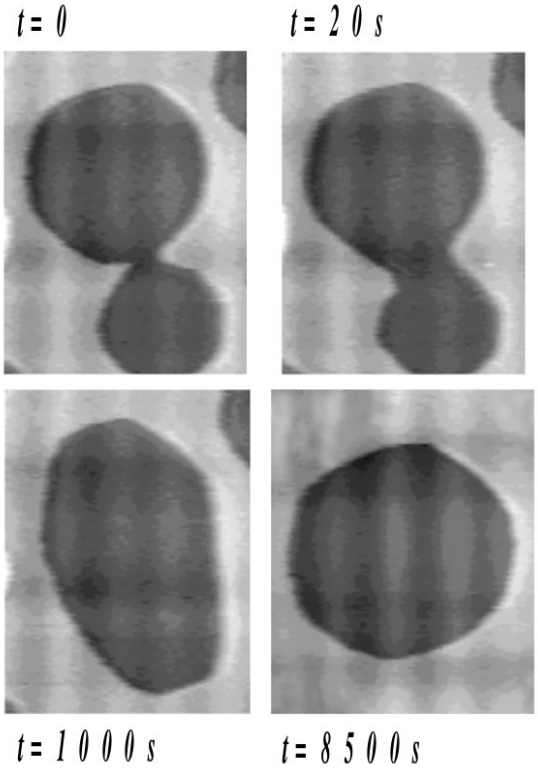
Insulin



P. Vekilov, Houston

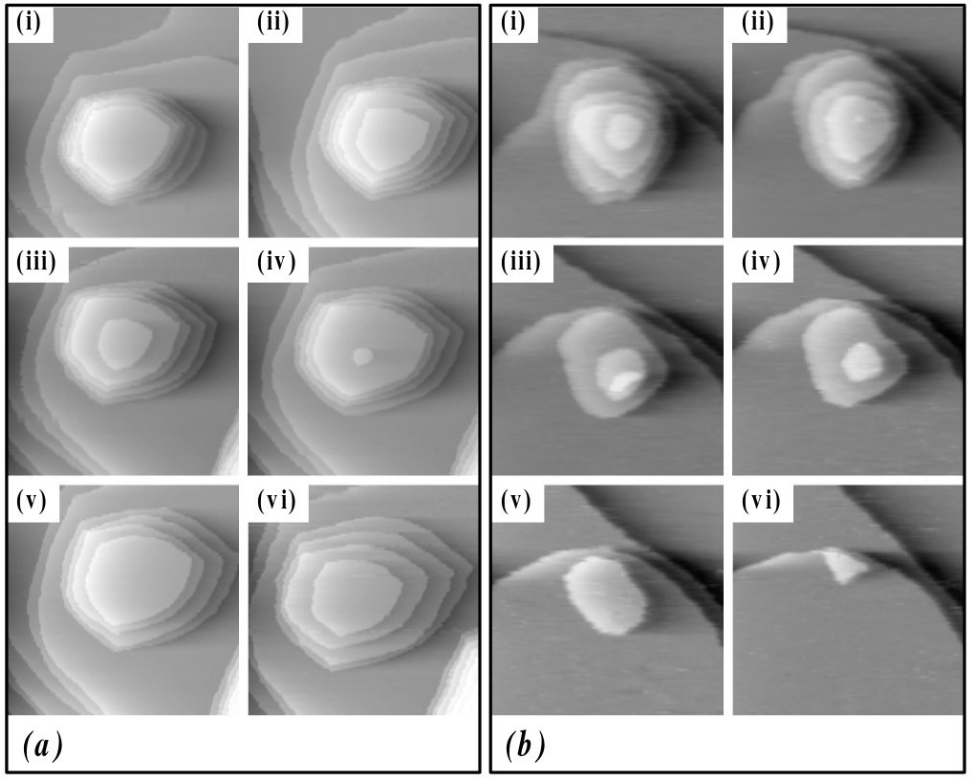
Nano-scale Relaxation

Ag(111), Sintering



M. Giesen, Jülich Germany

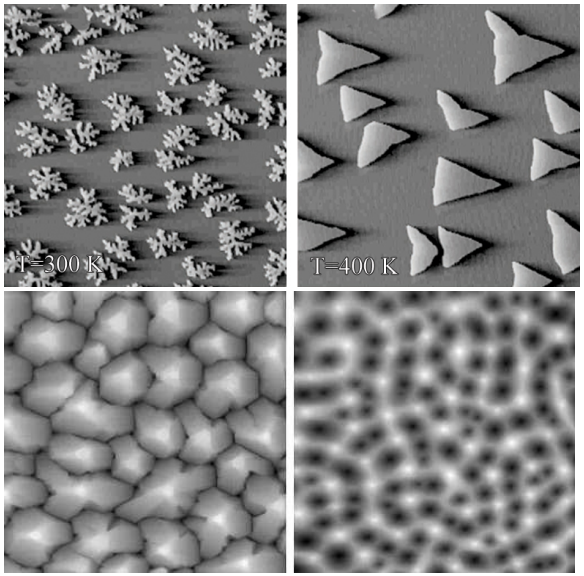
Decay Cu(1,1,1) 10mM HCl at (a) -580mV; and (b) 510 mV



Broekman et al, (1999) J. Electroanal. Chem.

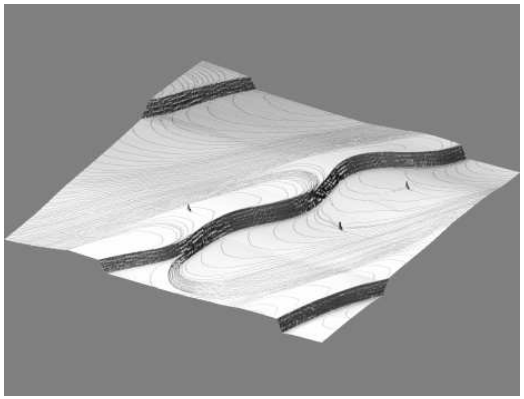
Nano-scale crystal Surface Instabilities out of equilibrium

Growth and Ion Sputtering, Pt(111)



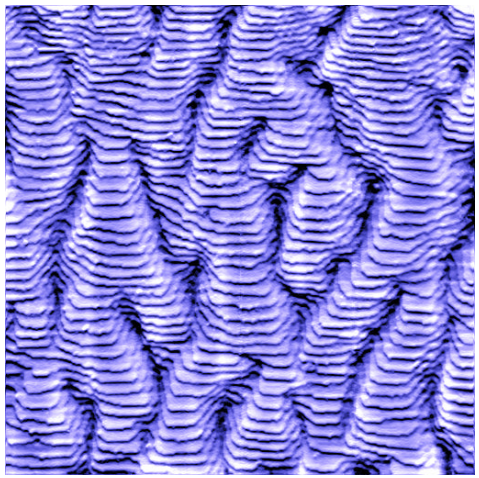
T. Michely, Aachen, Germany

Electromigration Si(111)



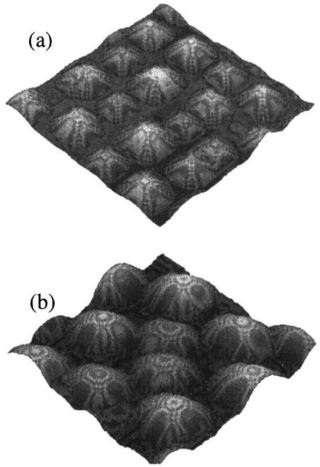
E.D. Williams, Maryland, USA

Growth Cu(1,1,17)



Maroutian, Ernst, Saclay, France

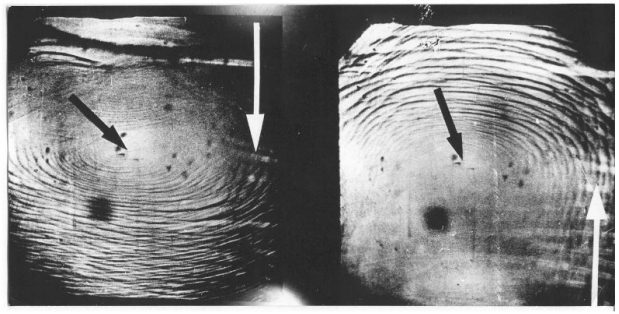
SiGe MBE growth



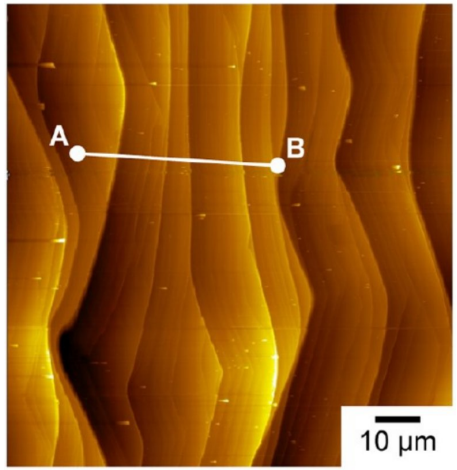
Floro et al 1999

Solution Growth $NH_4H_2PO_4$ (ADP) (5mm)

Chernov 2003



Solution Growth SiC

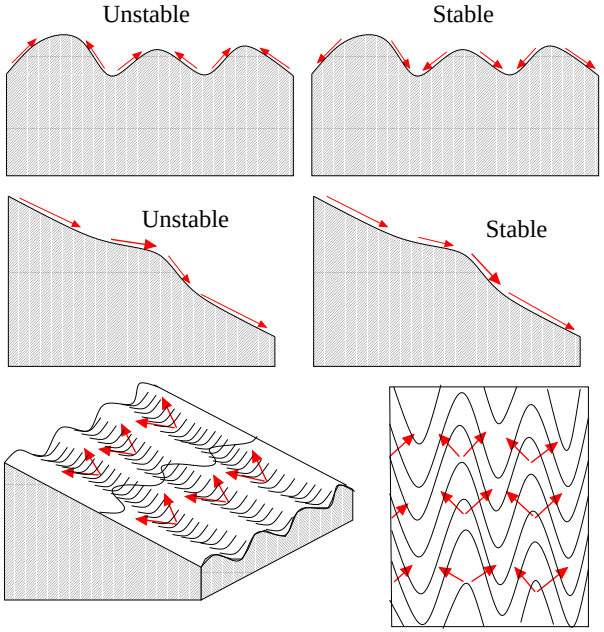


Zu et al Cryst. Growth & Des. 2013

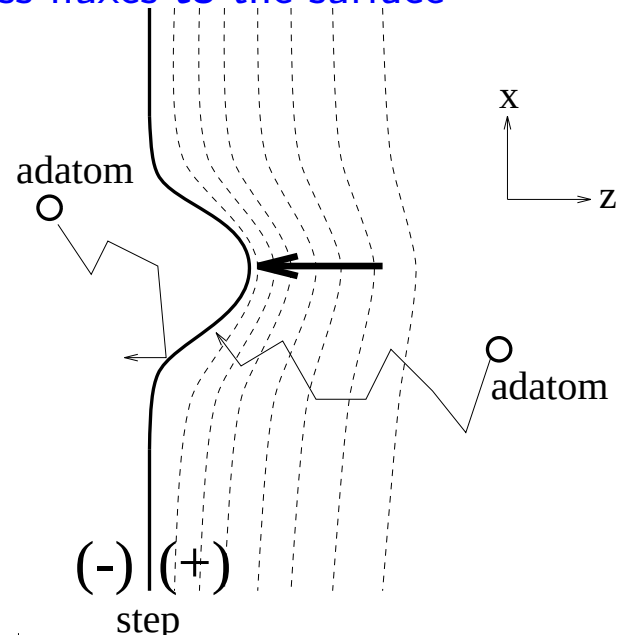
Nano-scale crystal Surface Instabilities out of equilibrium

Kinetic instabilities

Mass fluxes **along** the surface



Mass fluxes **to** the surface

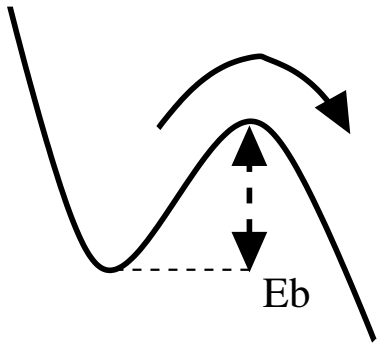


Energy relaxation driven instabilities:

surface energy, elastic energy, electrostatic energy, electronic energy, etc.

Contents

Rates



Transition-state theory $\rightarrow$ Exponential activation

$$R = \nu_0 \mathrm{e}^{-E_b/k_B T}$$

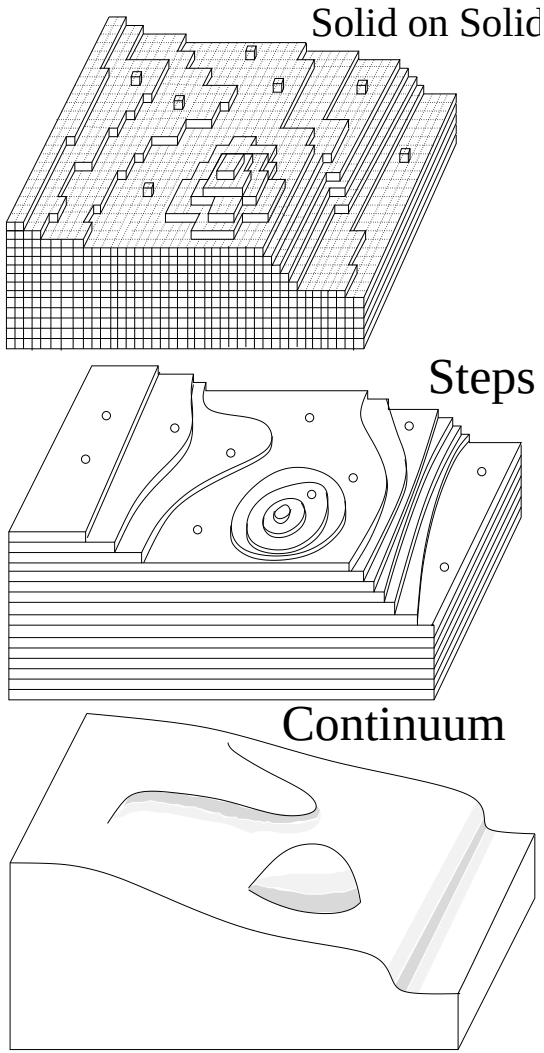
- E_b barrier energy
- ν_0 prefactor

Microscopic Theory or Simulation $\rightarrow$ Transition rates $R(n \rightarrow m)$

Which event should be considered?

Contents

Levels of description



Master equation

Discrete set of configurations, index $n = 1, .., N_{tot}$
Physics: Transition rates $R(n \to m)$
Markovian dynamics (no memory)
Master Equation

$$\partial_t P(n,t) = \sum_{m=1}^{N_{tot}} R(m \to n) P(m,t) - \sum_{m=1}^{N_{tot}} R(n \to m) P(n,t)$$

Ising lattice (0,1), $L \times L = L^2$ sites, $N_{tot} = 2^{L^2}$ configurations
$L = 10 \Rightarrow N_{tot} \sim 10^{30}$ ... too large for direct numerical solution!

Note: number of possible moves from n: $N_{poss}(n) \ll N_{tot}$
$\Rightarrow R(m \to n)$ sparse, i.e. $\Rightarrow R(m \to n) = 0$ for most values of m, n.

Equilibrium and Detailed Balance

Master Equation

$$\partial_t P(n,t) = \sum_{m=1}^{N_{tot}} R(m \to n) P(m,t) - \sum_{m=1}^{N_{tot}} R(n \to m) P(n,t)$$

Equilibrium, steady-state ($\partial_t P_{eq}(n,t) = 0$), Hamiltonian $\mathcal{H}(n)$

$$\begin{aligned} P_{eq}(n) &= \frac{1}{Z} \exp\left[-\frac{\mathcal{H}(n)}{k_B T}\right] \\ Z &= \sum_{n=1}^{N_{tot}} \exp\left[-\frac{\mathcal{H}(n)}{k_B T}\right] \end{aligned}$$

leading to

$$\frac{P_{eq}(n)}{P_{eq}(m)} = \exp\left[-\frac{\mathcal{H}(n) - \mathcal{H}(m)}{k_B T}\right]$$

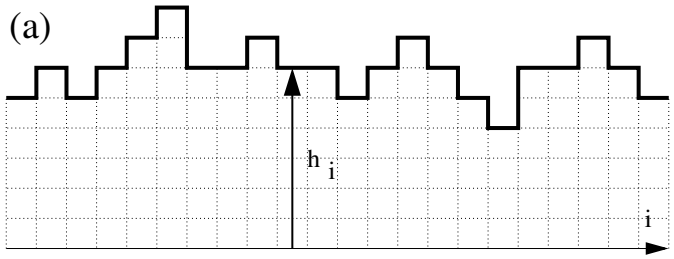
Stonger condition:Detailed Balance

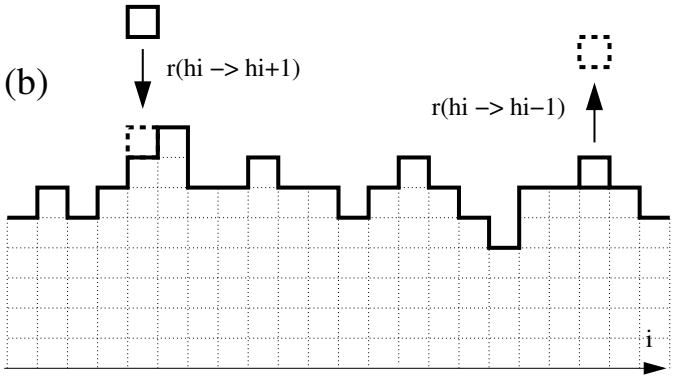
$$R(n \to m) P_{eq}(n) = R(m \to n) P_{eq}(m)$$

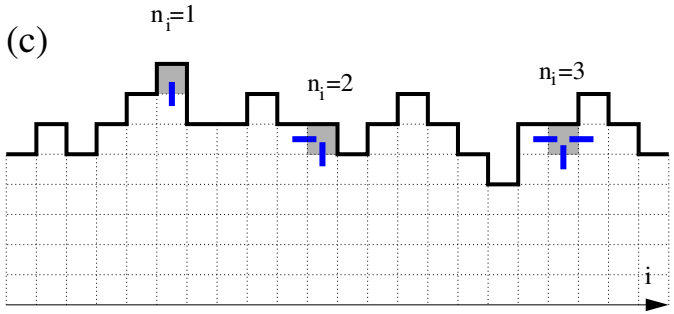
or

$$R(n \to m) = R(m \to n) \exp\left[\frac{\mathcal{H}(n) - \mathcal{H}(m)}{k_B T}\right]$$

Example : Attachment-Detachment model







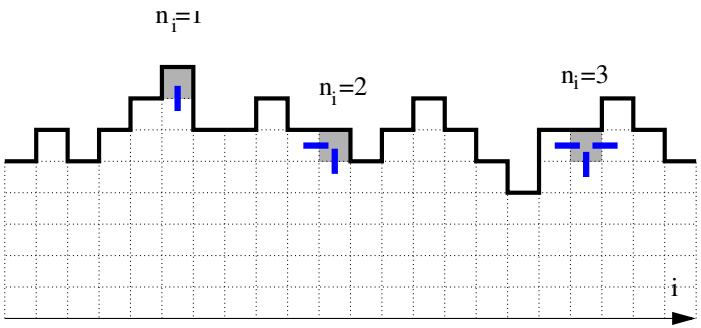
State $n = \{h_i; i = 1.., L\}$
Rates

$$R(h_i \to h_i + 1) = F$$
$$R(h_i \to h_i - 1) = r_0 \exp[-\frac{n_i J}{k_B T}]$$

n_i number nearest neighbors at site i before detachment
(Breaking all bonds to detach / Transition state Theory)

$$F_{eq} = r_0 \exp\left[-\frac{2J}{k_B T}\right]$$

Example: Attachment-Detachment model



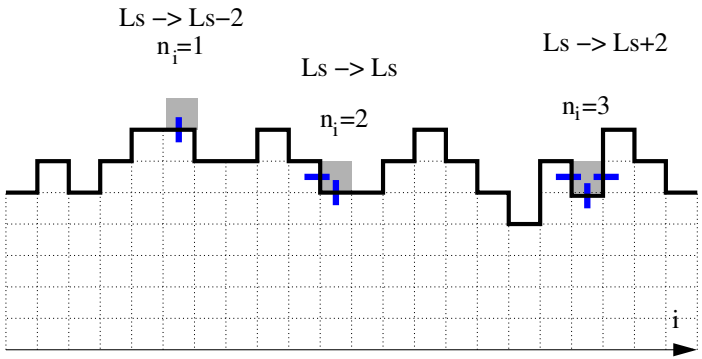
Detailed Balance when $F = F_{eq}$

$$R(h_i - 1 \to h_i) P_{eq}(h_i - 1) = R(h_i \to h_i - 1) P_{eq}(h_i)$$

$$F_{eq} P_{eq}(h_i - 1) = r_0 \exp[-\frac{n_i J}{k_B T}] P_{eq}(h_i)$$

Bond energy $J \Rightarrow$ Broken Bond energy $J/2$
Hamiltonian $\mathcal{H}$, surface length L_s

$$\mathcal{H} = L_s \frac{J}{2}$$



Energy change

$$L_s(h_i) - L_s(h_i - 1) = 2(2 - n_i)$$
$$\mathcal{H}(h_i) - \mathcal{H}(h_i - 1) = (2 - n_i) J$$

Thus

$$\frac{P_{eq}(h_i - 1)}{P_{eq}(h_i)} = \exp\left[\frac{\mathcal{H}(h_i) - \mathcal{H}(h_i - 1)}{k_B T}\right] = \exp\left[\frac{(2 - n_i) J}{k_B T}\right]$$

and

$$F_{eq} = r_0 \exp\left[-\frac{2J}{k_B T}\right]$$

Example: Attachment-Detachment model

Link to the Ising Hamiltonian with field H, $S_i = \pm 1$

$$\mathcal{H}_{Ising} = -\frac{J}{4}\sum_{\langle i,j\rangle} S_i S_j - H\sum_i S_i$$

Define $n_i = (S_i + 1)/2 \Rightarrow J$ is the bond energy

$$\mathcal{H}_{Ising} = -J\sum_{\langle i,j\rangle} n_i n_j - (J - 2H)\sum_i n_i + \text{const}$$

re-writing $\mathcal{H}$

$$\mathcal{H}_{Ising} = \frac{J}{2}\sum_{\langle i,j\rangle}[n_i(1-n_j) + n_j(1-n_i)] - 2H\sum_i n_i + \text{const} = \frac{J}{2}L_s - \Delta\mu\sum_i n_i + \text{const}$$

Chemical potential $\Delta\mu = 2H$
Number of broken bonds $L_s = \sum_{\langle i,j\rangle}[n_i(1-n_j) + n_j(1-n_i)]$

Example: Attachment-Detachment model

Chemical potential $\Delta\mu = 2H$
Detailed Balance imposed to the Ising system with field H

$$\begin{aligned} F &= R(h_i - 1 \to h_i) = R(h_i \to h_i - 1)\frac{P_{eq}^{Ising}(h_i)}{P_{eq}^{Ising}(h_i - 1)} \\ &= \exp\left[\frac{-n_i J + \mathcal{H}_{Ising}(h_i) - \mathcal{H}_{Ising}(h_i - 1)}{k_B T}\right] \\ &= \exp\left[-\frac{n_i J}{k_B T} + \frac{[L_s(h_i) - L_s(h_i - 1)]J}{2k_B T} + \frac{\Delta\mu}{k_B T}\right] \\ &= \exp\left[-\frac{n_i J}{k_B T} + \frac{2(n_i - 2)J}{2k_B T} + \frac{\Delta\mu}{k_B T}\right] \\ &= F_{eq}\exp\left[\frac{\Delta\mu}{k_B T}\right] \end{aligned}$$

$$F_{eq} = r_0 \exp\left[-\frac{2J}{k_B T}\right]$$

Attachement-Detachment model equivalent to Ising in Magnetic field

Contents

Equilibrium Monte Carlo: Metropolis algorithm

Algorithm

1. Choose an event $n \to m$ at random
2. implement the event with probability

$$\mathcal{H}(n) \geq \mathcal{H}(m) \quad \Rightarrow \quad P(n \to m) = 1$$

$$\mathcal{H}(n) \leq \mathcal{H}(m) \quad \Rightarrow \quad P(n \to m) = \exp[-\frac{\mathcal{H}(m) - \mathcal{H}(n)}{k_B T}]$$

Obeys Detailed Balance

$$\frac{R(n \to m)}{R(m \to n)} = \exp\left[-\frac{\mathcal{H}(n) - \mathcal{H}(m)}{k_B T}\right]$$

Chain of events conv. to equil. $\Rightarrow$ sample configuration space $n \Rightarrow$ Thermodynamic averages
No time!

A way to evaluate observables in equilibrium statistical mechanics

A simple Monte Carlo method with time: random attempts

Using physical rates $R(n \to m)$ from a given model

Algorithm

1. Choose an event $n \to m$ at random
2. Implement the event with probability

$$P(n \to m) = \frac{R(n \to m)}{R_{max}}$$

   where $R_{max} = \max_{n'}(R(n \to n'))$.
3. implement the time by $\Delta t \sim 1/(N_{poss}(n) R_{max})$
   $N_{poss}(n)$ number of possible moves from state n

Problem: when most $R(n \to m) \ll R_{max}$, then most $P(n \to m) \ll 1 \Rightarrow$ most attempts rejected!

Questions

- a rejection-free algorithm?
- time implementation?

Kinetic Monte Carlo algorithm 1: Rejection-free algorithm

implement the FIRST event that occurs

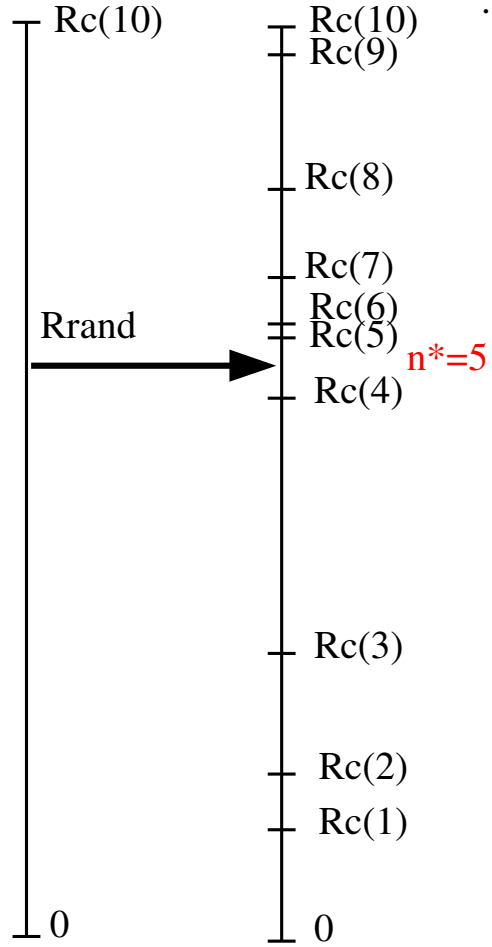
Probability first chosen event $n \to m$ is $\sim R(n \to m)$

Choose event with probability

$$P(n \to m) = \frac{R(n \to m)}{R_{tot}(n)}$$

Rate that one event occurs

$$R_{tot}(n) = \sum_{m=1}^{N_{tot}} R(n \to m)$$



Algorithm

1. Build cumulative rates $R_c(m) = \sum_{p=1}^{m} R(n \to p)$, with $R_c(N_{tot}) = R_{tot}(n)$.
2. Choose random number R_{rand}, uniformly distributed with $0 < R_{rand} \leq R_{tot}(n)$.
3. Choose event n_* such that $R_c(n_* - 1) < R_{rand} \leq R_c(n_*)$.

Kinetic Monte Carlo algorithm 2: comments

Algorithm

1. Build cumulative rates $R_c(m) = \sum_{p=1}^{m} R(n \to p)$, with $R_c(N_{tot}) = R_{tot}(n)$.
2. Choose random number R_{rand}, uniformly distributed with $0 < R_{rand} \leq R_{tot}(n)$.
3. Choose event n_* such that $R_c(n_* - 1) < R_{rand} \leq R_c(n_*)$.

Improved algorithm:

- Groups of events with same rates
- Number of possible events from one state $N_{poss}(n) \ll$ number of states $N_{tot}(n)$
- Update list of possible events at each time step

Kinetic Monte Carlo algorithm 3: implementing time

Define τ time with $\tau = 0$ when arriving in state n
Proba $Q(\tau)$ that no event occurs up to time τ, with $Q(0) = 1$

$$Q(\tau + d\tau) = Q(\tau)(1 - R_{tot}(n)d\tau) \Rightarrow \frac{dQ(\tau)}{d\tau} = -R_{tot}(n)Q(\tau) \Rightarrow Q(\tau) = \exp[-R_{tot}(n)\tau]$$

probability density ρ, i.e. $\rho(\tau)d\tau$ first event occuring between τ and $\tau + d\tau$

$$\rho(\tau)d\tau = -dQ(\tau) = R_{tot}(n)\exp[-R_{tot}(n)\tau]d\tau$$

Easy to generate: uniform distribution $\rho(u) = 1$, and $0 < u \leq 1$
Variable change, with same probability density

$$\rho(\tau)d\tau = -\rho(u)du$$

leading to

$$u = \exp[-R_{tot}(n)\tau] \Rightarrow \tau = \frac{-\log(u)}{R_{tot}(n)}$$

Algorithm

1. Choose random number u, uniformly distributed with $0 < u \leq 1$.
2. Time increment $t \to t + \tau$ with

$$\tau = \frac{-\log(u)}{R_{tot}(n)}$$

Kinetic Monte Carlo algorithm 4: implementing time

Complete rejection-free KMC Algorithm

1. Build cumulative rates $R_c(m) = \sum_{p=1}^{m} R(n \to p)$, with $R_c(N_{tot}) = R_{tot}(n)$.
2. Choose random number R_{rand}, uniformly distributed with $0 < R_{rand} \leq R_{tot}(n)$.
3. Choose event n_* such that $R_c(n_* - 1) < R_{rand} \leq R_c(n_*)$.
4. Choose random number u, uniformly distributed with $0 < u \leq 1$.
5. Time increment $t \to t + \tau$ with

$$\tau = \frac{-\log(u)}{R_{tot}(n)}$$

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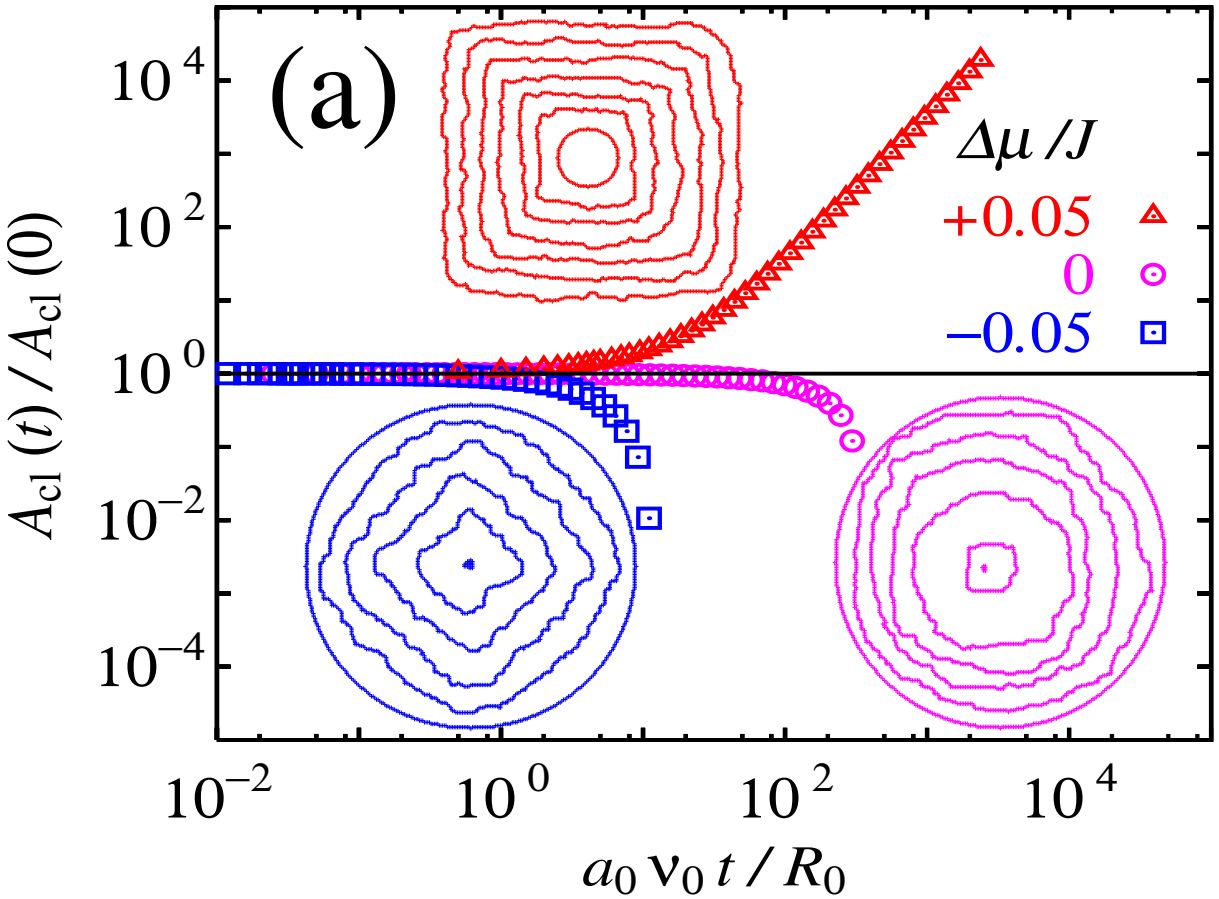
Attachment-detachment model



$F = F_{eq} e^{-\Delta\mu/k_B T}$

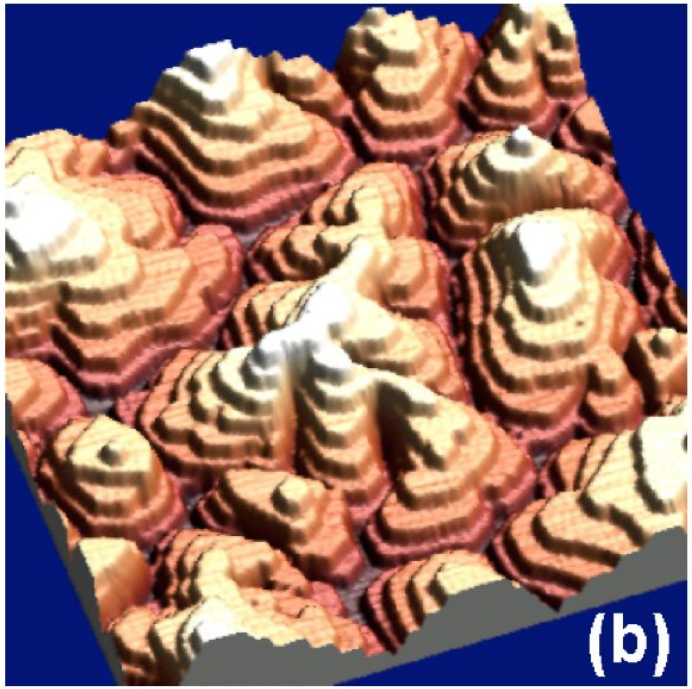
Saito, Pierre-Louis, PRL 2012

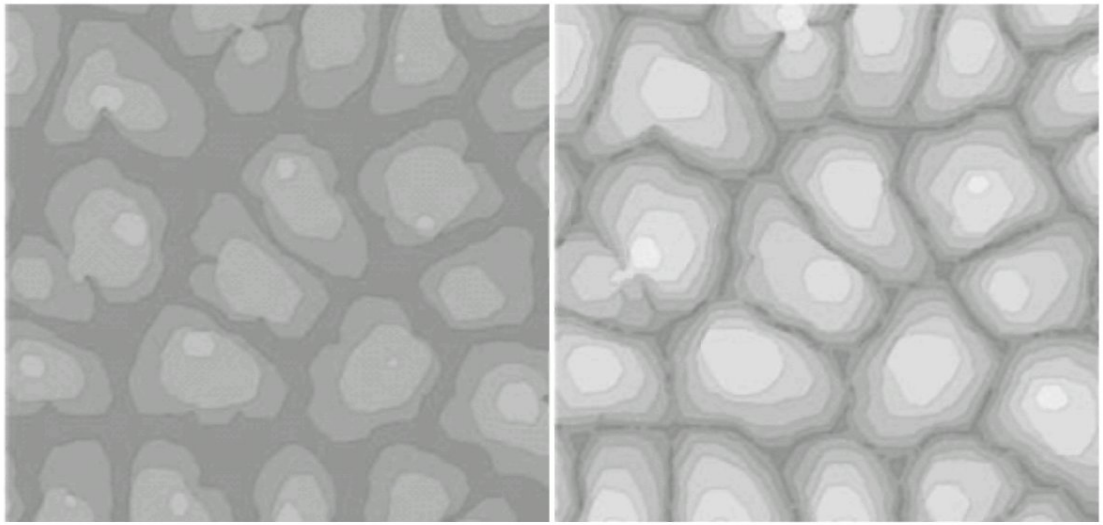
Contents

Nano-scale crystal Surface Instabilities out of equilibrium

Movie...

KMC results





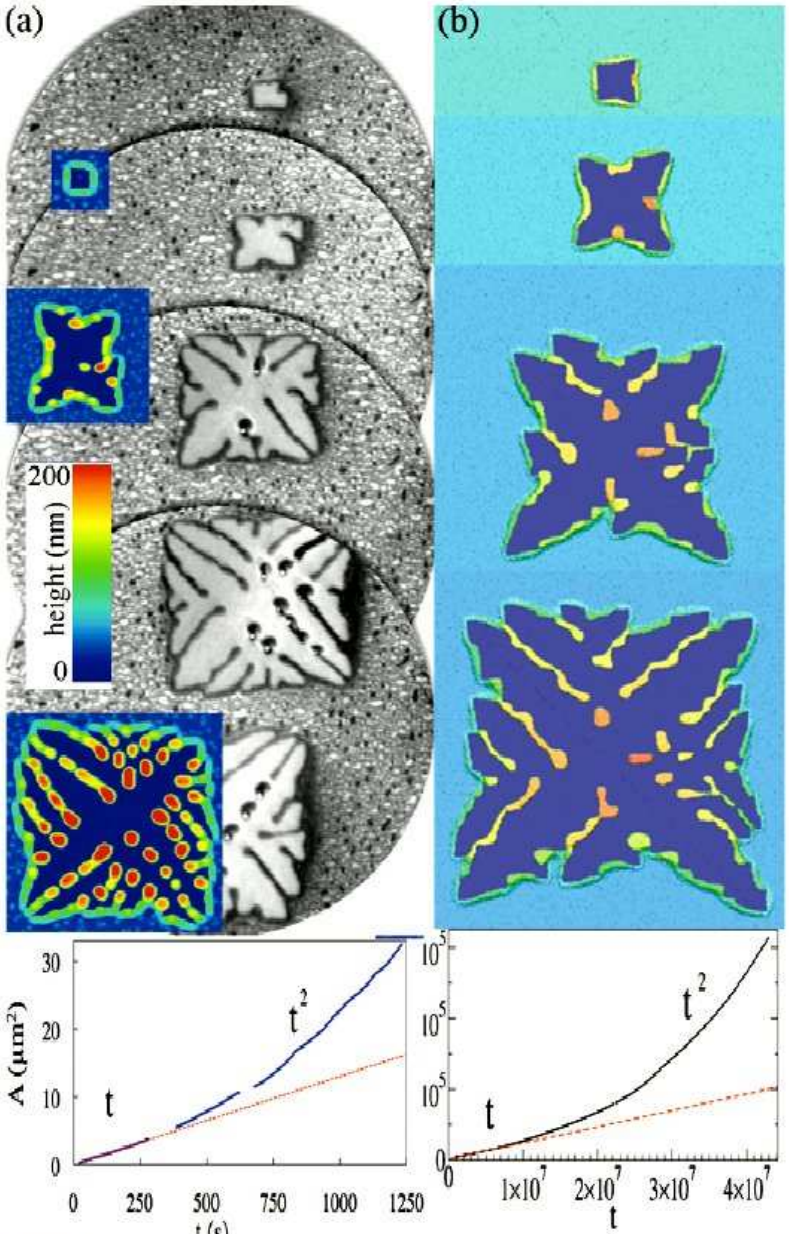
1 ML Ag/Ag(111) @ 150K 3 ML Ag/Ag(111) @ 150 K

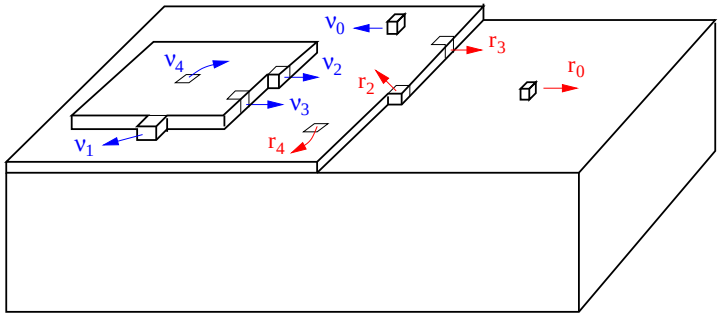
FIGURE 12. Simulation predictions for the morphologies of multilayer Ag/Ag(111) films grown at 150 K with F= 0.004 ML/s. Images sizes are ~160×160 nm^2.

Thiel and Evans 2007

Contents

KMC vs SOI solid-state dewetting





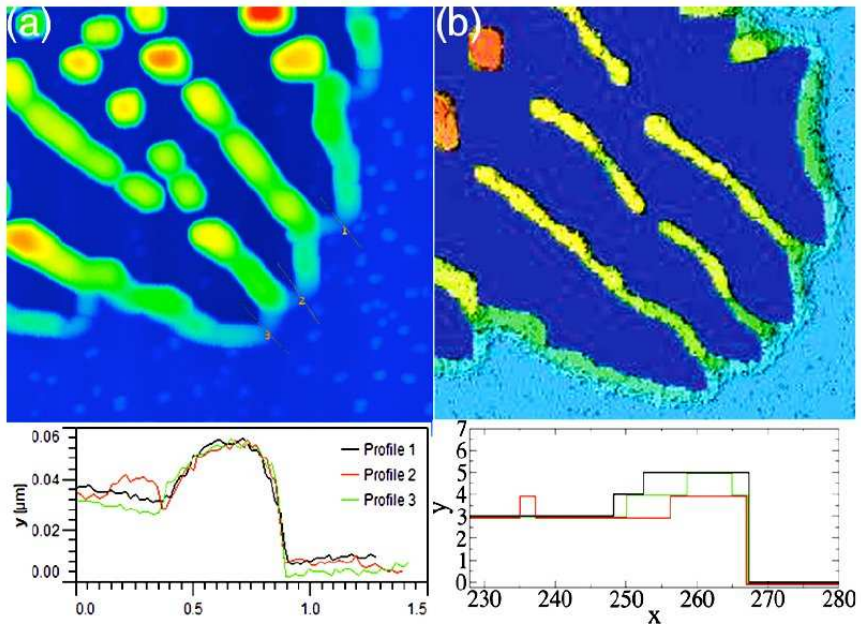
KMC simulations SOS Hopping rates

A/S: $r_n = \nu_0 \, \mathrm{e}^{-nJ/T + E_S/T}$

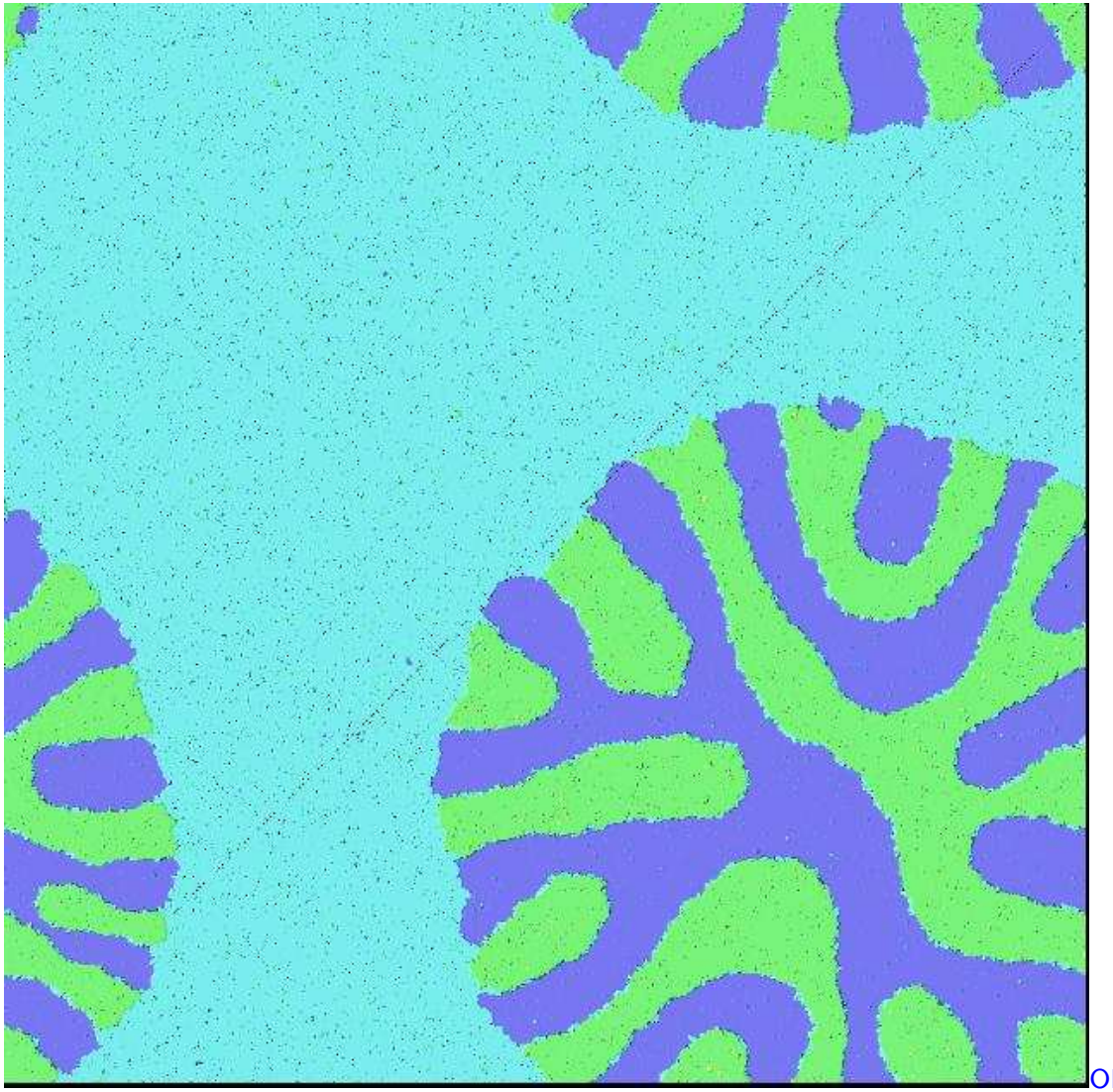
A/A: $\nu_n = \nu_0 \, \mathrm{e}^{-nJ/T}$

J bong energy

$h = 3,\ E_S = 1,\ T = 0.5$



Monolayer → no dewetting rim



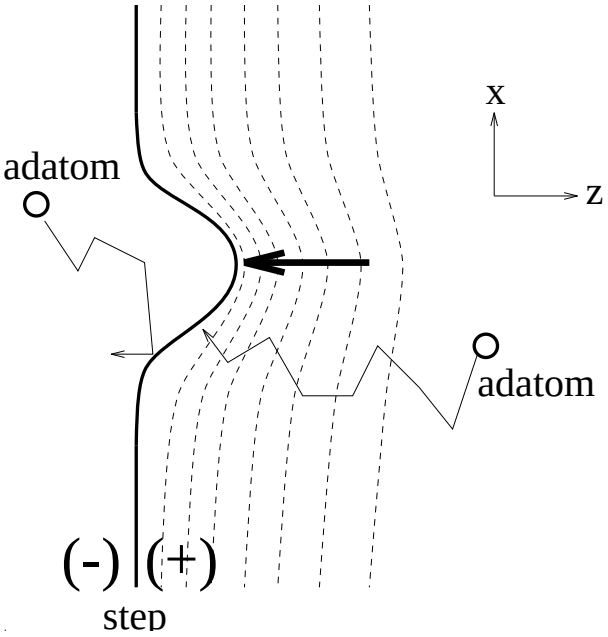
OPL, A. Chame, Y. Saito, PRL 2007

Contents

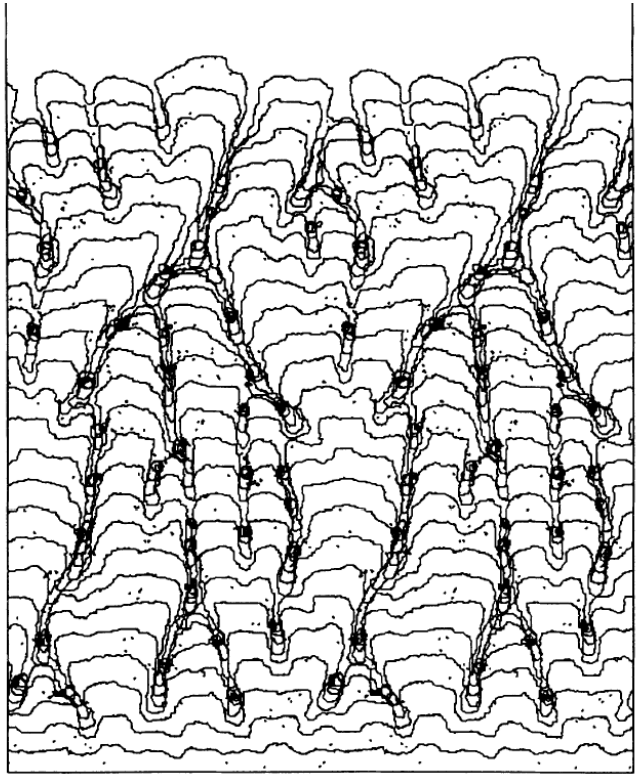
Step meandering Instabilities

Non-equilibrium meandering of a step
Schwoebel effect + terrace diffusion

Bales and Zangwill 1990



Y. Saito, M. Uwaha 1994



Solving step dynamics
$\rightarrow$ morphology and coupling to a diffusion field

Contents

3D KMC Model

3D KMC
Hopping along the surface

$$\nu = \nu_0 \, \mathrm{e}^{-(n_1 J_1 + n_2 J_2 + n_{s1} J_{s1} + n_{s2} J_{s2})/T}$$

J bond energy, n_i nb neighbors
$i = 1, 2$ NN, NNN adsrobate
$i = s1, s2$ NN, NNN substrate
Moves to NN
Allowed when there is NN or NNN

Shape controlled by

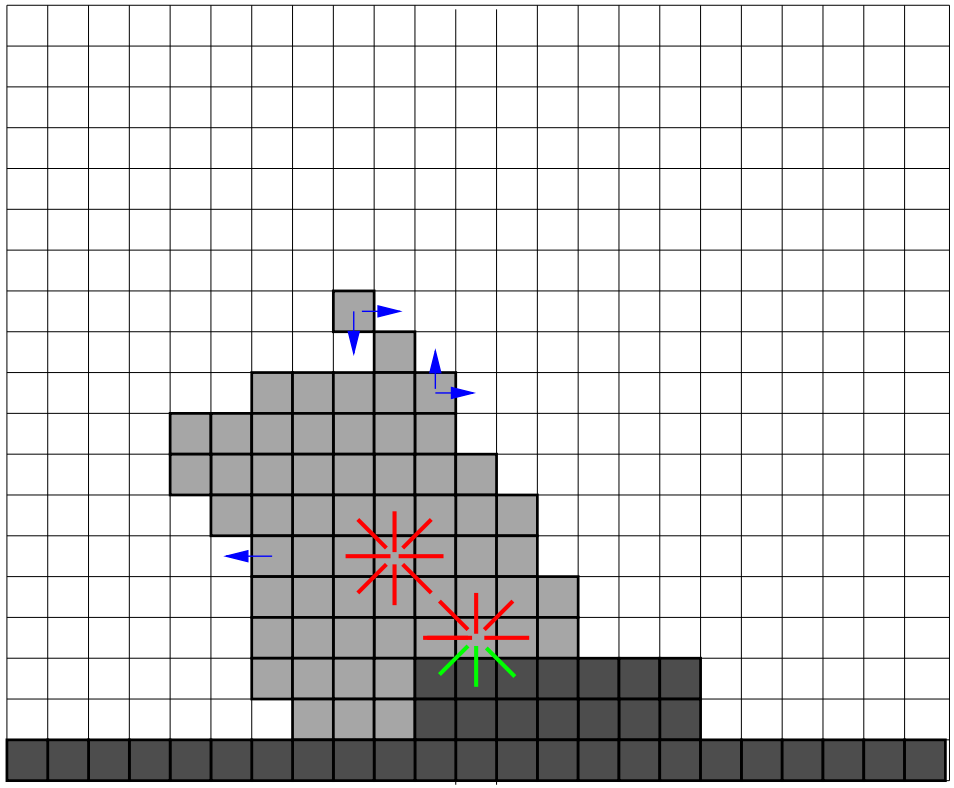
$$\zeta = \frac{J_2}{J_1} = \frac{J_{s2}}{J_{s1}}$$

Wetting controlled by

$$\chi = \frac{J_{s1}}{J_1}$$

Link $T \to O$:

$$1 - \chi = \frac{-\mathcal{S}}{2\gamma(0)}$$



$\chi \to 0$: Complete de-wetting
$\chi \to 1$: Complete Wetting

Wetting on a flat substrate

Wulff-Kaishiew
Contact angle not a good parameter for facetted crystals!

$$\psi = \frac{\mathcal{S}_{AV}}{\mathcal{S}_{AS}}$$

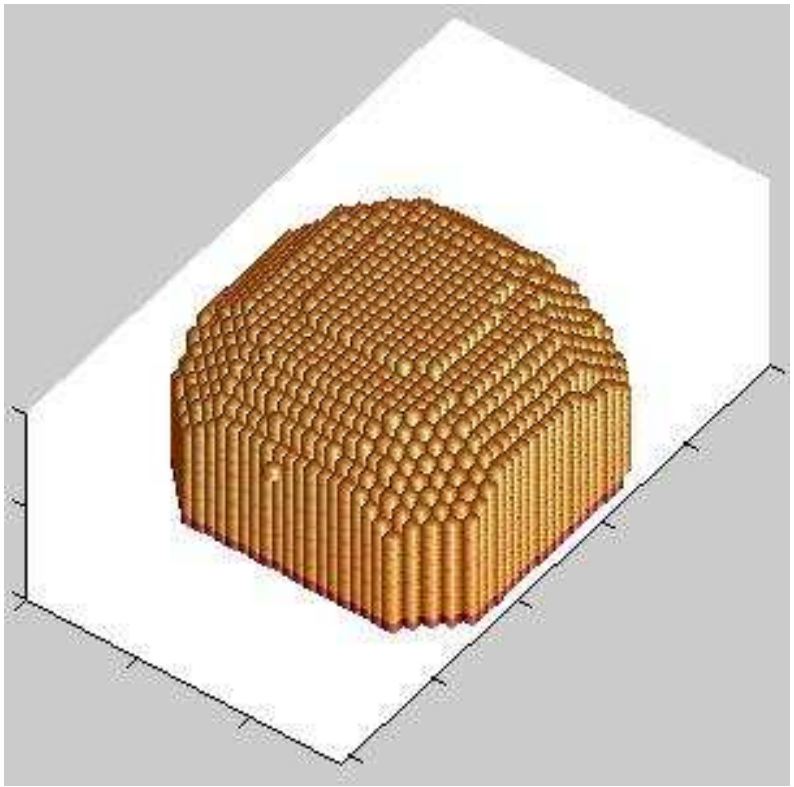
Wetting control parameter

$$\chi = \frac{J_{s1}}{J_1}$$

Cube $\zeta = 0$

$$\psi = 5 - 4\chi$$

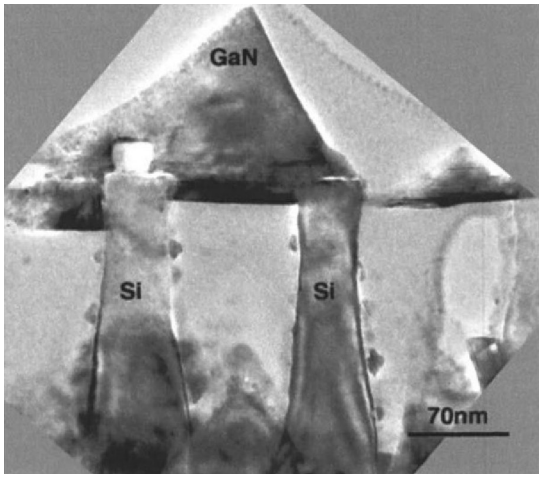
KMC:
$N = 11025$, $\zeta = 0.2$, $\chi = 0.4$, $T/J_1 = 0.5$
Error: Energy 1%; ψ 3%.



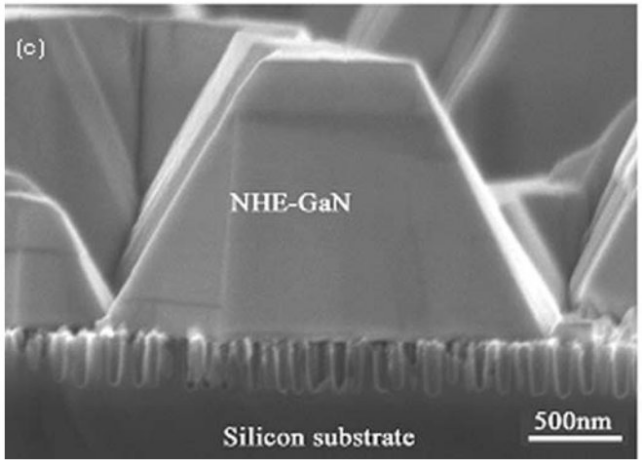
Nanocrystals in Cassie-Baxter state

Growth of GaN on Si nano-pillars

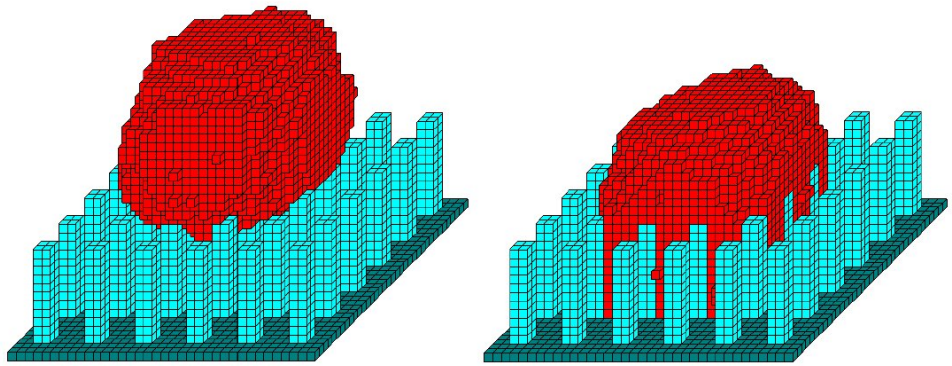
Hersee *et al* J.A.P. 2005



Zang et al, APL 2006



- Avoiding dislocations?
- Growing without collapse?
- Stability?

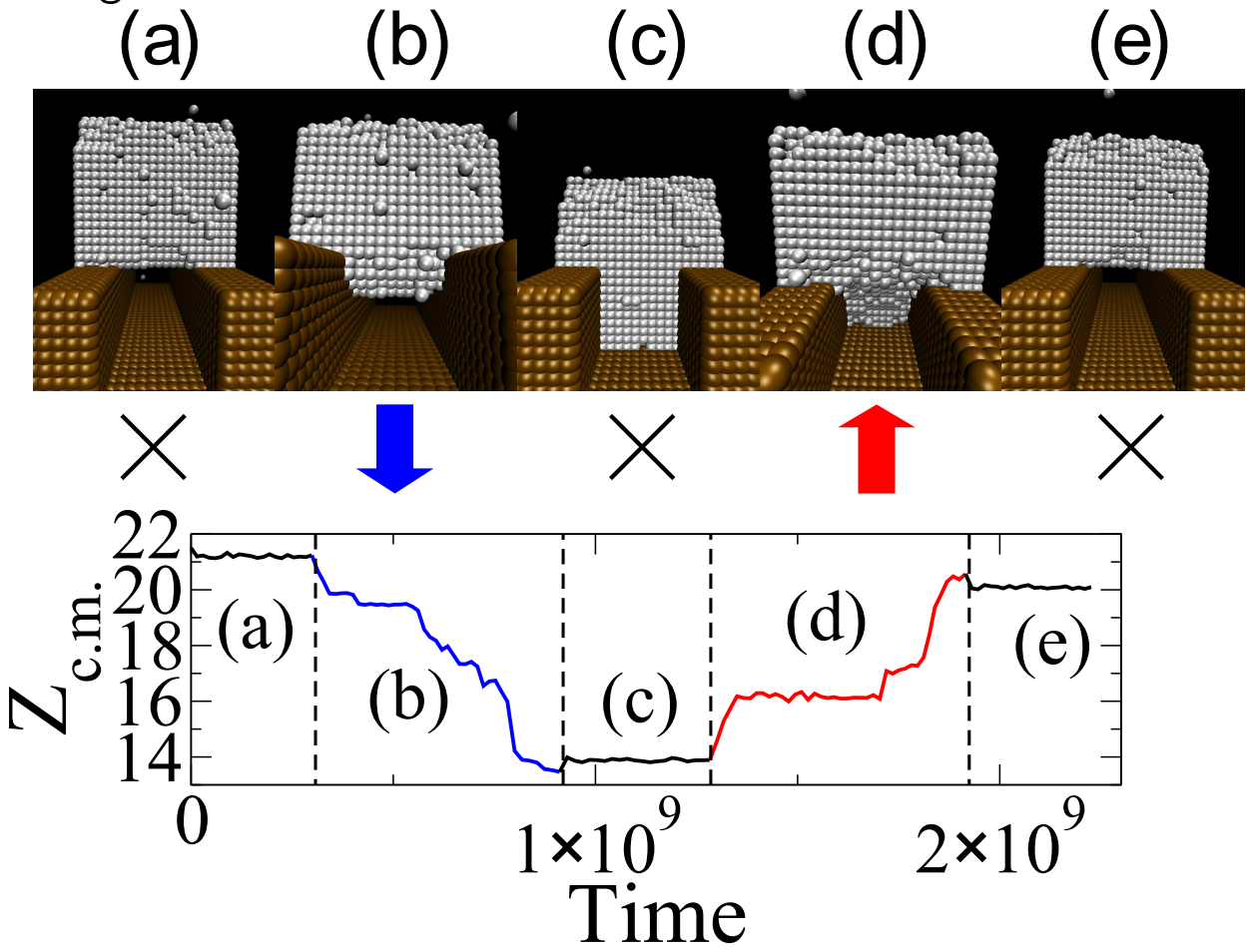


(a) (b)

$\chi = 0.390$, $\chi = 0.405$

Migration-induced switching

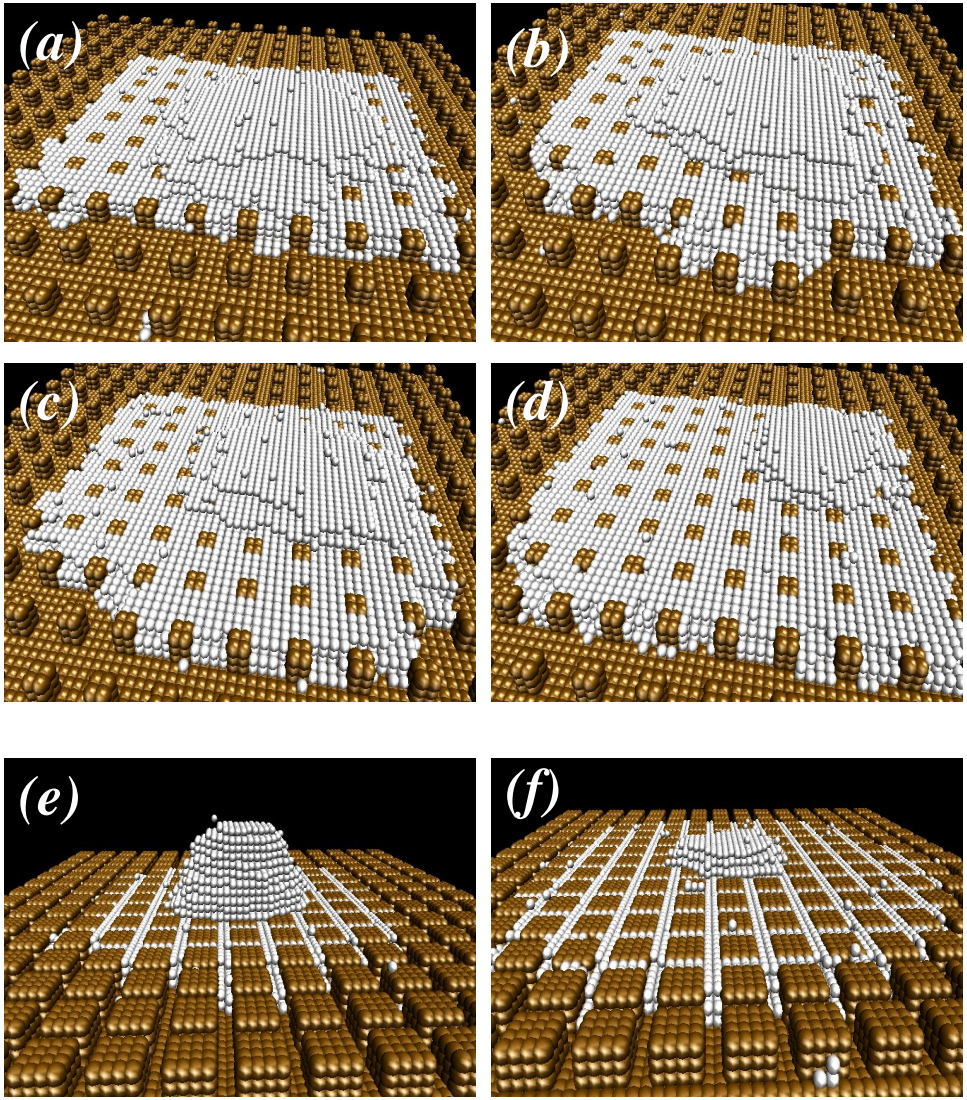
Nanoswitch controlled by an electron beam
KMC wih imposed migration



M. Ignacio, OPL, PRE (2015)

Nucleation-limited vs diffusion-limited imbibition front motion

$\chi = 0.8,\ \ell_x = 6,\ h = 3,\ \ell_p = 2, 4$



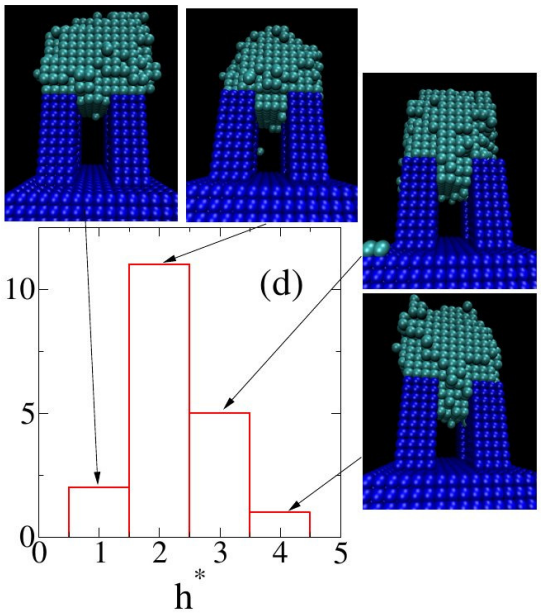
P. Gaillard, Y. Saito, OPL, Phys Rev Lett 2011

Contents

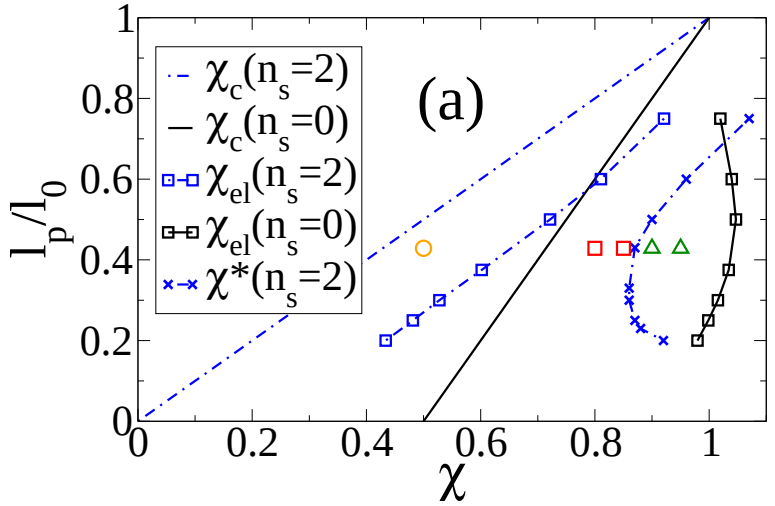
Elastic islands on nano-pillars

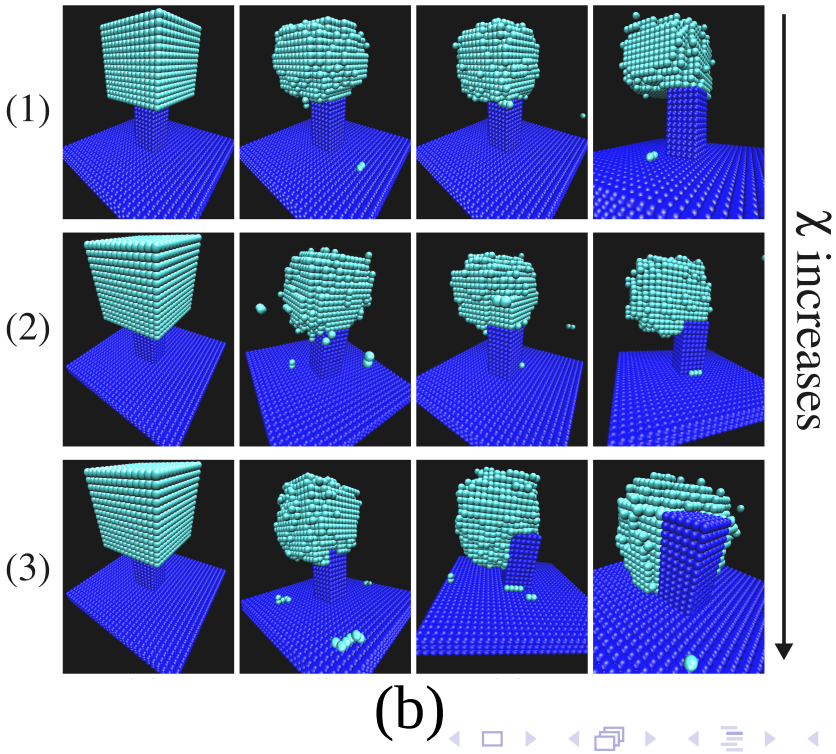
3D KMC with elastic effects

- Extended stability
- Asymmetric CB state
- Partially collapsed state



M. Ignacio, Y. Saito, P. Smereka, OPL, PRL 2014



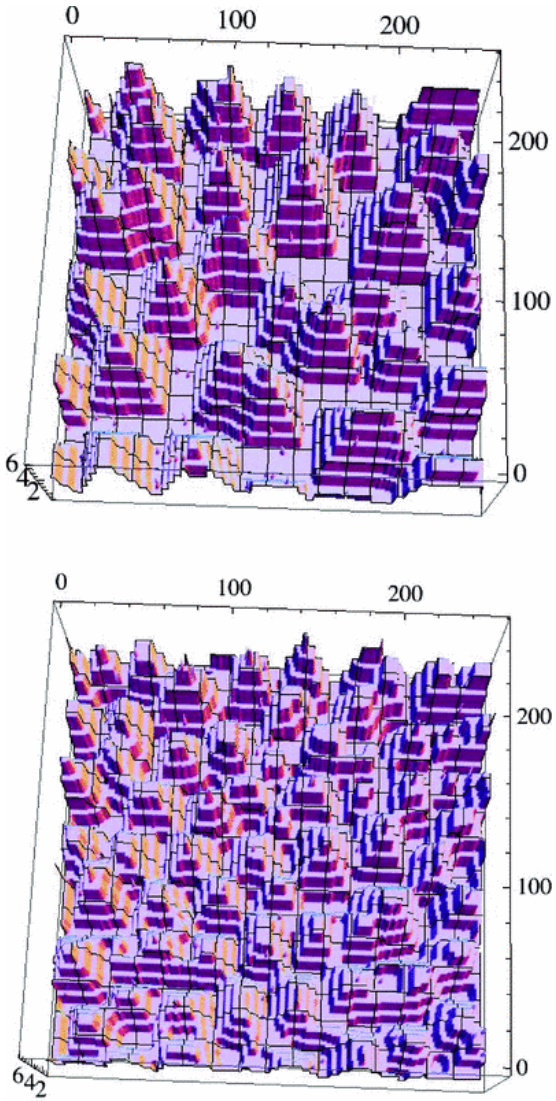


Elastic islands on flat substrate

2D KMC with elastic effects

Green function method

P. Gaillard, T. Frisch, J.N. Aqua, PRB (2013)



Contents

KMC conclusion

- KMC versatile method to look at crystal shape evolution
- Improved methods to obtain physical rates (DFT, MD)
- Built-in thermal fluctuations

Difficulties

- parallelization
- finding the list of events

Conclusion

References

Books

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- A. Pimpinelli and J. Villain, Physics of crystal growth, Cambridge, (1998)
- J. Krug, and T. Michely, Islands, Mounds, and Atoms, Springer (2004)
- A.L. Barabási, H.E. Stanley, Fractal Concepts in Surface growth, Cambridge, (1995)

Reviews

- **M. Kotrla, Computer Physics Communications 97 82-100 (1996)**
- **A. Voter, Introduction to the KMC method, Radiation effects in solids, Springer Nato Series 235**
- C. Misbah, O. Pierre-Louis, Y. Saito, Rev Mod Phys 82 981 (2010).
- Burton Carbrera Frank, The Growth of Crystals and the Equilibrium Structure of their Surfaces, Phil. Trans. A, (1951)