Some new tools for simulating nano-scale crystal growth

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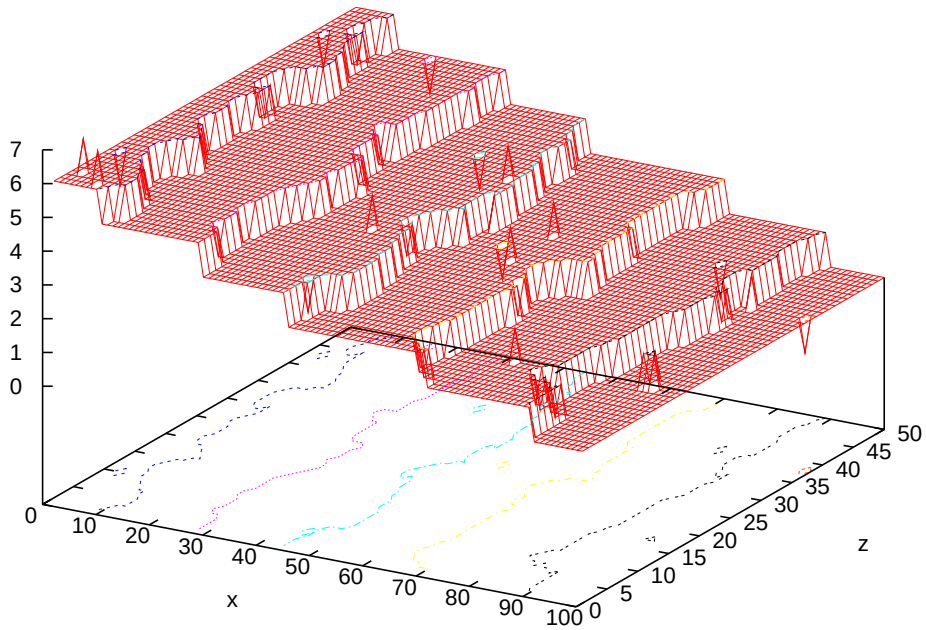
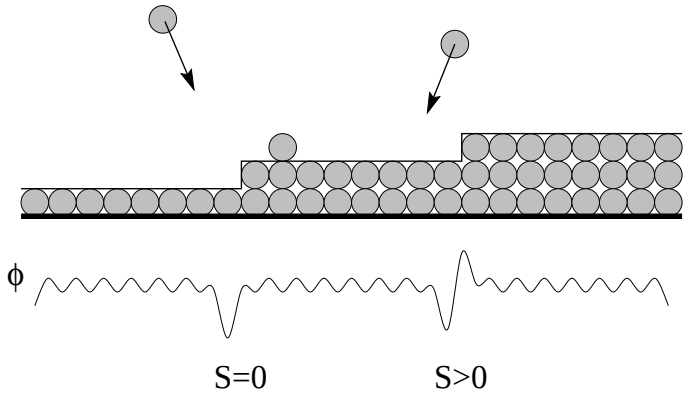
Outline

1. Kinetic Monte Carlo (KMC) & KMC algorithms
2. Burton-Cabrera-Frank (BCF) model & hybrid scheme
3. Off lattice KMC



Kinetic Monte-Carlo

- Early work:
  - F.F. Abraham and G.W. White (1970)
  - G.H. Gilmer and P. Bennema (1972)
- Stochastic adatom deposition.
- Hopping rate $k(\Delta\phi, T) = k_0 \exp(-\Delta\phi/k_B T)$
- Barriers can be measured, calculated or modeled...



- Example:

$$\Delta\phi = E_S + mE_N + \max[(m_i - m_f), 0]E_B$$

(Smilauer & Vvdensky 1995)

Poisson Processes

The Poisson process assumes discrete events with exponentially distributed waiting times:

$$p(t) = r \exp(rt), \quad t > 0,$$

where r is the **rate** at which the process occurs, *i.e.* the average frequency per unit time.

The expected waiting time is

$$\langle tp(t) \rangle = \int_0^\infty tp(t)dt = \frac{1}{r}.$$

The CDF, probability of waiting less than time t, is

$$P(\{t < T\}) = \int_0^T p(t)dt = 1 - \exp(-rT).$$

Multiple Processes

For two independent processes occurring with rates r_1 and r_2, the probability of at least one event occurring before time T is

$$P(\{t_1 < T \text{ or } t_2 < T\}) = P_1(T) + P_2(T) - P_1(T)P_2(T)$$

$$= 1 - \exp\left[-(r_1 + r_2)T\right]$$

The corresponding distribution of waiting times remains exponential with a rate that is the sum of the rates of the individual processes:

$$p(t) = (r_1 + r_2) \exp\left[-(r_1 + r_2)t\right].$$

This generalizes to an arbitrary number of processes.

Kinetic Monte-Carlo algorithms

Principal algorithm: Bortz, Kalos &. Lebowitz (1975)

1. Randomly select the time it takes for the next event to occur
2. Decide which event it is using relative rates

This simulates M independent Poisson processes with rates r_m that sum to give an overall rate R.

Performance of KMC algorithms:

- Rejection algorithm: usually not good for KMC
- Vanilla BKL with linear search: $O(M)$
- Binning technique: $O(M^{1/2})$ (Mayksum 1988)
- Binary search: $O(\log(M))$
  (Blue, Beichl & Sullivan 1995)
- Maintaining inverse list can eliminate this cost: (Schulze 2002)

$$E_{nm} : (n, m) \rightarrow (i, j, k)$$

$$E^{-1}_{i,j,k} : (i, j, k) \rightarrow (m, n)$$

Minimal search KMC algorithm:

1. Compute the overall rate $R = S_N = \sum_{n=1}^{N} r_n C_n$; retain the partial sums S_n

2. Select a random number $r \in [0, R)$.

3. Search through the list of partial sums S_n until $S_n > r$

4. Select an event from the set of events that occur at this rate by computing

$$m = \text{Int}\left(\frac{(S_n - r)}{r_n}\right) + 1.$$

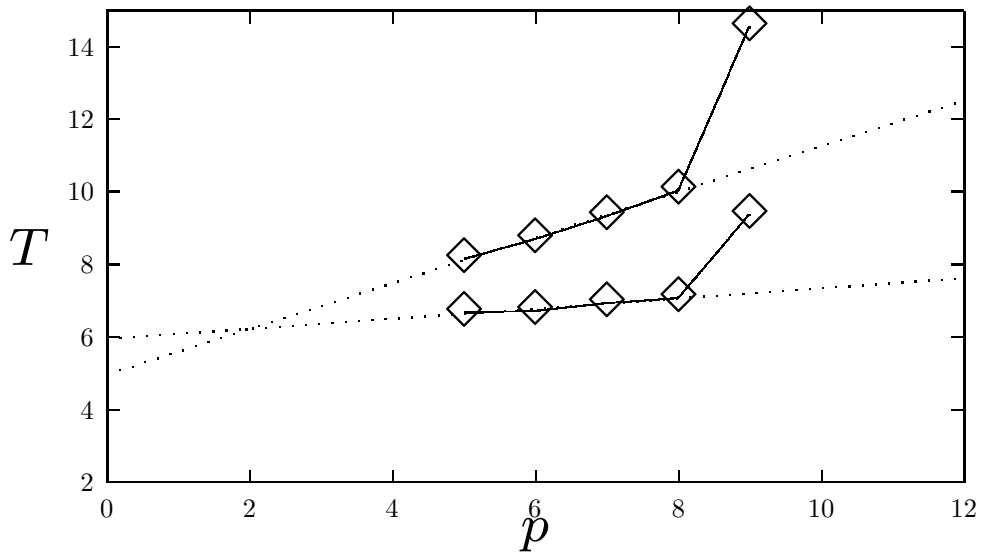
5. Execute that event and update the configuration $\{h_{ij}\}$.

6. For the (local) events that have their rates changed from r_{n_i} to r_{n_f}:

   (a) Move them to the end of column n_f; add one to C_{n_f}; update $E^{-1}_{i,j,k}$.

   (b) Move the event listed as $E_{n_i C_{n_i}}$ into the vacated position in column n_i; reduce C_{n_i} by one; update $E^{-1}_{i,j,k}$.

Performance

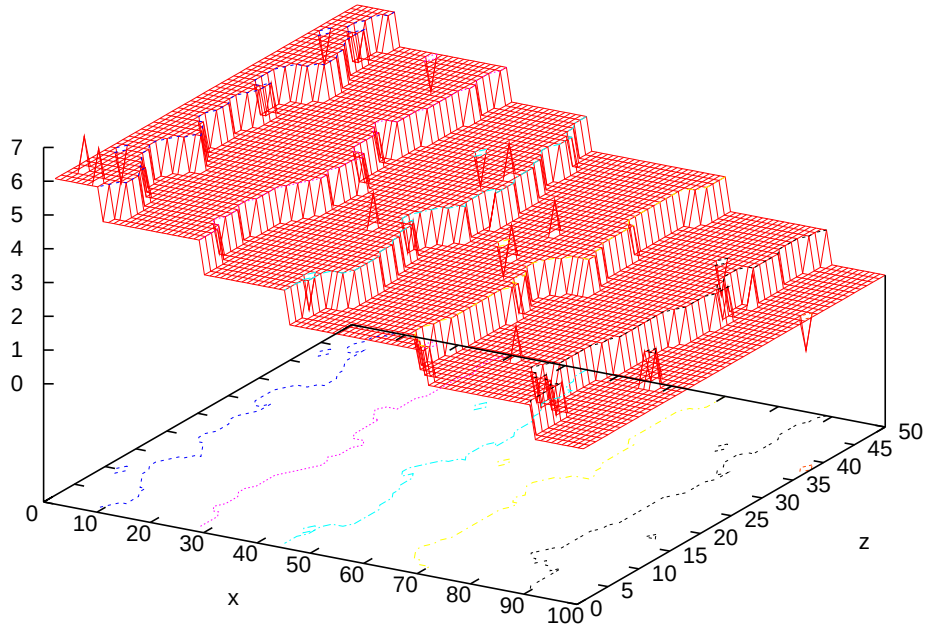


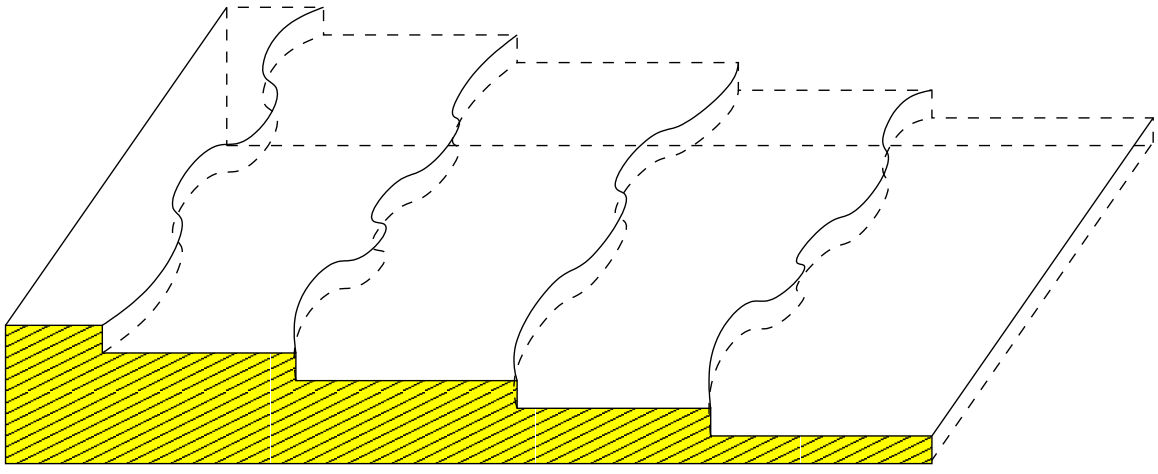
Computation time for 10^5 events of a $2^p \times 2^p$ simulation for binary search (upper curve) and minimal-search KMC (lower curve).

- If necessary, event lists can be packed into a flat array of length M

- For arbitrary rates, this can be combined with the rejection algorithm.

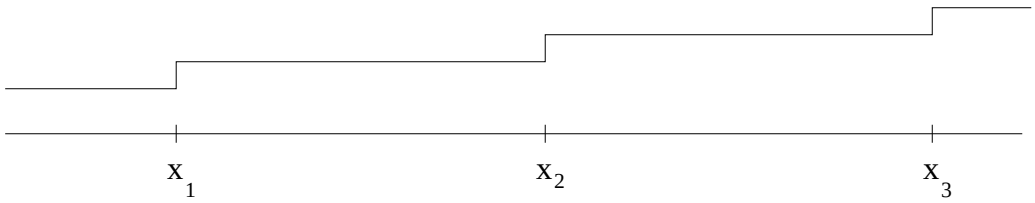
Other facets of film-growth modelling





Terrace/Step models

Reference: Burton, Cabrera and Frank (1954)



$$\rho_t = D\rho_{xx} - \tau^{-1}\rho + F; \quad x \in (x_i, x_{i+1})$$

$$\pm D\rho_x|^{\pm} = \alpha^{\pm}(\rho|^{\pm} - \rho_e), x = x_i$$

$$\nu\frac{dx_i}{dt} = \left[D\rho_x + \frac{dx_i}{dt}\rho\right]_-^+, x = x_i$$

Hybrid Scheme

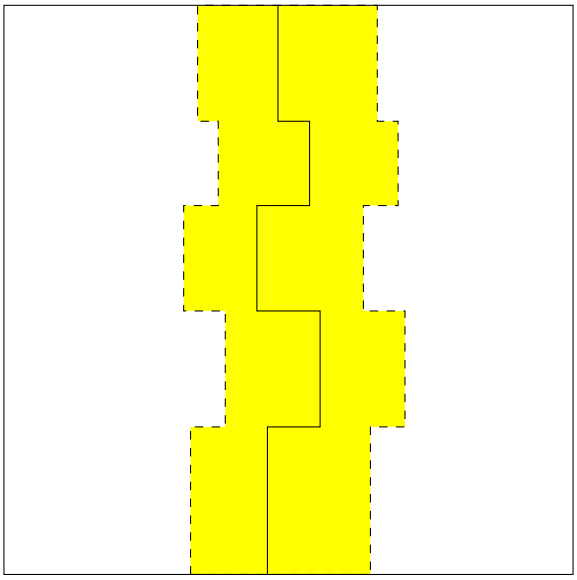
Collaborators: P. Smereka (Mich.), W. E (Princeton)

- Diffusion equation on terraces:

$$\rho_t = D\rho_{xx} + F \qquad \in \Omega_{BCF}$$

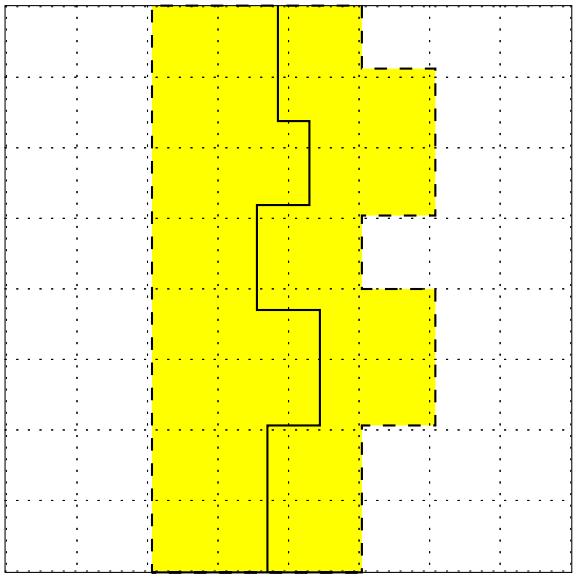
- KMC simulation near step edges:

$$\Omega = \Omega_{BCF} \cup \Omega_{KMC}$$



Two-grid system

- $N \times N$ sites partitioned into $N_c \times N_c$ cells
- Cell-width $M \times M$ $(N = MN_C)$
- Cell is $\in \Omega_{KMC}$ if
  - it contains an edge
  - its neighbors contain an edge



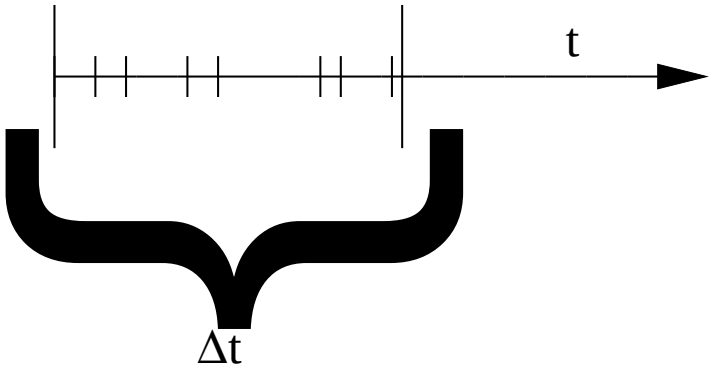
KMC region

- Adatoms are defined as sites where h_{ij}
  - is one greater than at lateral nearest neighbors,
  - all of which have the same height.
- For Hybrid simulation, we add events corresponding to:
  - hops out of the continuum with rate $\sim D\rho$
  - nucleation $\sim \rho^2$?
  - other processes as desired...
- This requires a list of boundary segments

Continuum region

$$\rho_j^{n+1} = \rho_j^n + D\frac{\Delta t}{\Delta x^2}\left(\rho_{j-1}^n - 2\rho_j^n + \rho_{j+1}^n\right) + F\Delta t$$

- ρ_j^n is average "adatom" density in $cell\ j$
- Discrete time step Δt,
- Coarse grid $\Delta x = aM$,
- There are many KMC events per Δt



Interface

- If adatom $\Omega_{KMC} \rightarrow \Omega_{BCF}$
  - remove the adatom from list
  - set $\rho_j^{n+\nu} = \rho_j^n + 1/M$
  - mass is immediately spread over cell
- If adatom $\Omega_{BCF} \rightarrow \Omega_{KMC}$
  - add adatom to list
  - set $\rho_j^{n+\nu} = \rho_j^n - 1/M$
  - rate for this event type is $D\rho_j$
  - event not added to list if $\rho_j < 1/M$
- ν indicates fractional timestep (one event)

Moving boundary

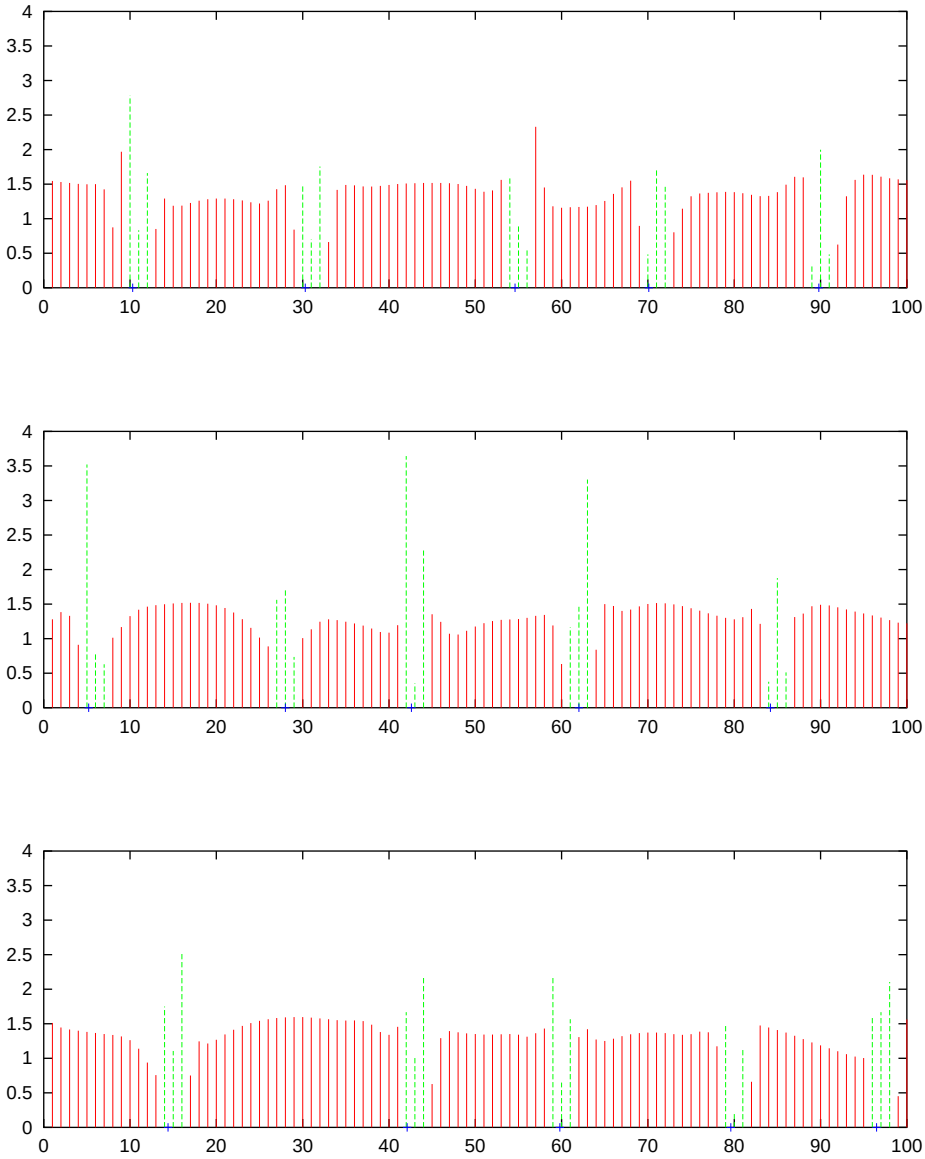
- If a cell changes type, a local conversion process takes place:
  - To change KMC-cell $\rightarrow$ BCF-cell
    - Locate adatoms using inverse list
    - Remove hopping events from list
    - Update cell-list
  - To change BCF-cell $\rightarrow$ KMC-cell
    - Randomly position Int($M\rho_j$) adatoms in cell
    - Add hopping events to list
    - Update cell-list

Nucleation, etc.

- To nucleate islands within the BCF region
  - Add nucleation events with rate $\sim (M\rho_j)^2$?
  - If event is chosen, convert cell and its neighbors
- This approach has proven useful in level-set simulations of BCF model
- A similar procedure applies to vacancy formation, chemical reactions, etc.
- Deposition and evaporation can be handled at the continuum level.

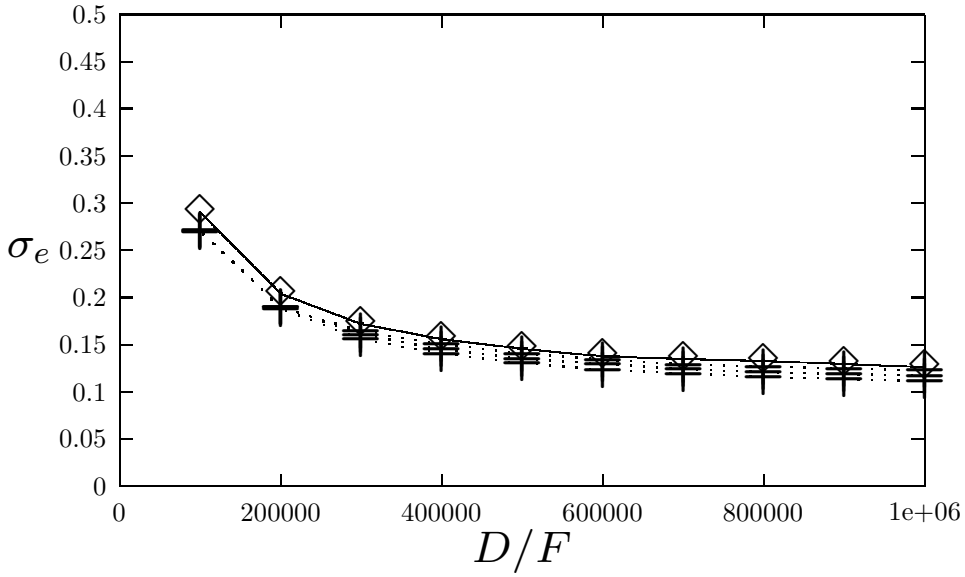
1D Hybrid Simulations

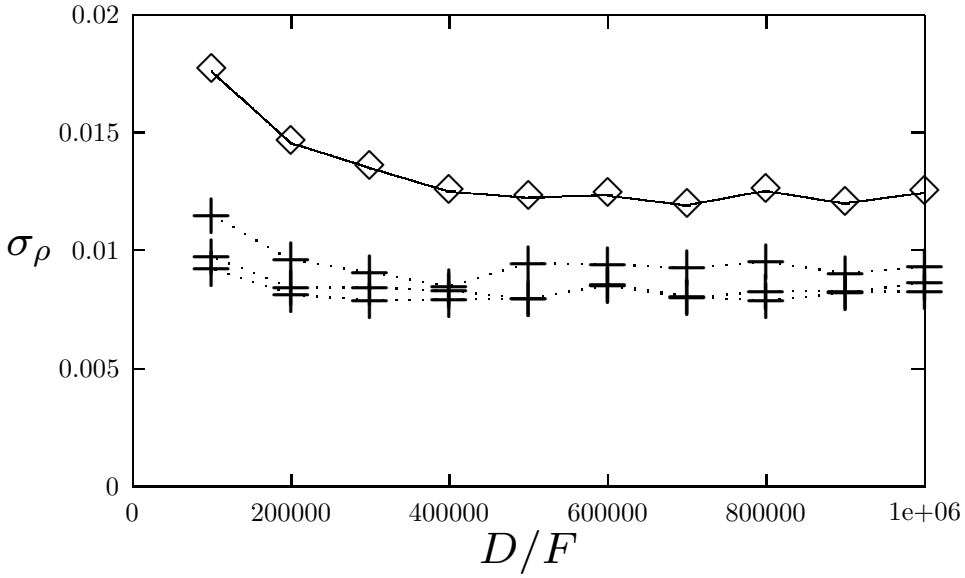
Adatoms per cell



- Continuum regions tend toward parabolic adatom density profile
- Step velocities, step widths and number of adatoms on surface fluctuate

Average density and fluctuations





Computational cost (1D)

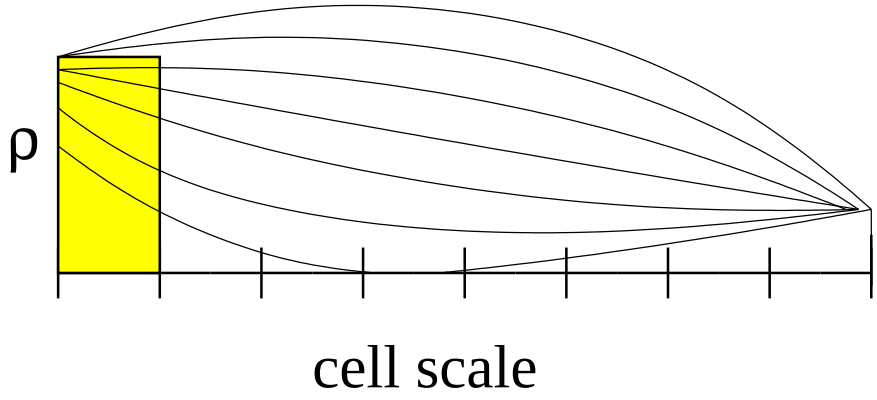
- For 1D KMC:
  - N net attachment events per layer
  - Each adatom performs $O(L^2)$ hops
  - Total cost is $O(NL^2)$ (or $O(N \log N\, L^2)$)
- For 1D hybrid scheme:
  - Total cost = KMC-cost + BCF-cost
  - KMC-cost reduced to $\Rightarrow O(NM^2)$
  - BCF-cost is: $O\left((NM^2)(\frac{L}{NMD})(\frac{1}{\Delta t})(\frac{N}{M})\right)$

    (events/layer)(time/event)(calls/time)(operations/call)

  - CFL condition requires $\Delta t < \frac{M^2}{2D}$
  - Total cost is $O(NM^2) + O(\frac{NL}{M^2})$

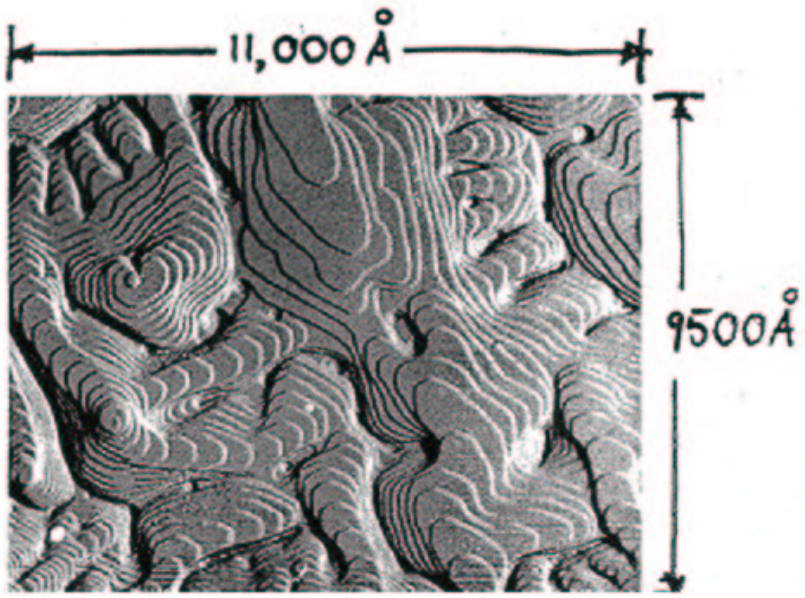
Accuracy

- Errors inherent to BCF model:
  - Errors resulting from interactions
  - Errors from neglected events
- Errors relative to "adatom" KMC:
  - Discretization error $\sim M^2 \equiv (\Delta x)^2$
  - Variance reduction
  - Coupling error



Step edge instability

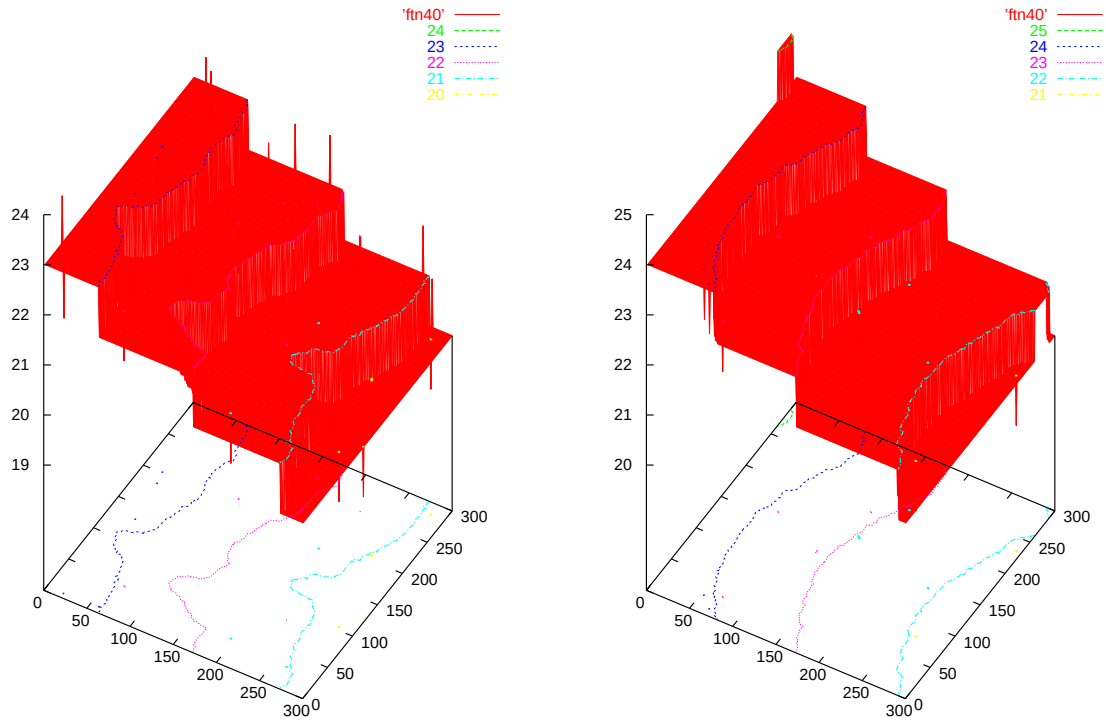
Experiment: Behm, *et. al.* Phys. Rev. Lett.(1994)



Theory: Bales & Zangwill, Phys. Rev. B (1990)

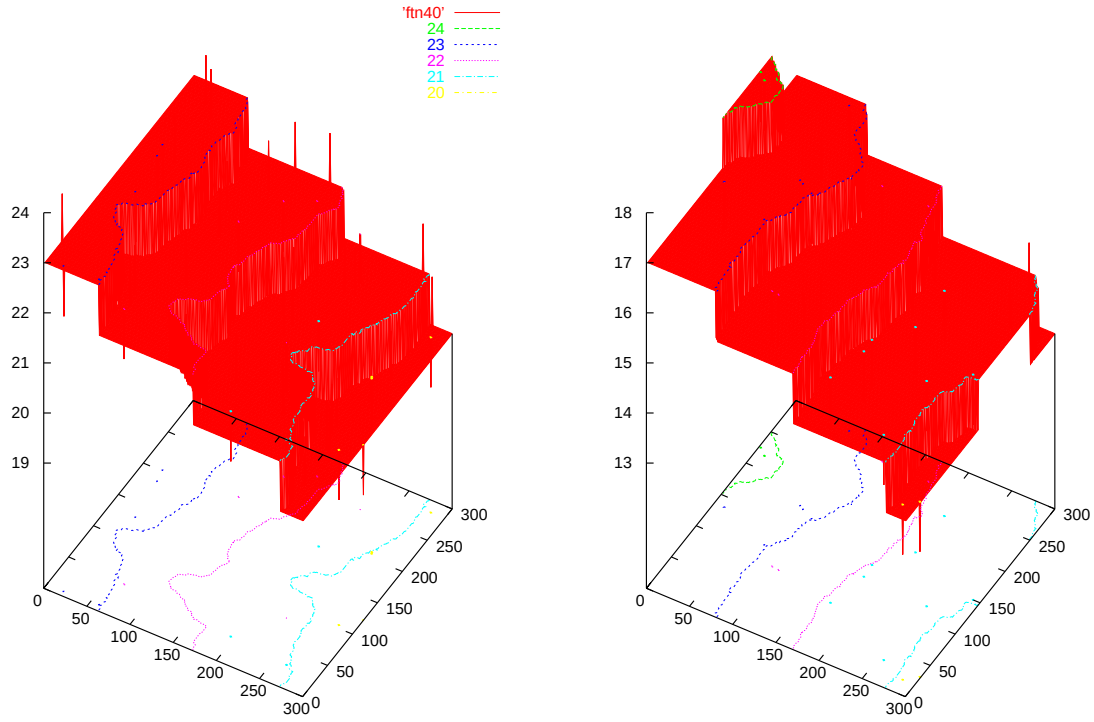
Simulation: Rost, Smilauer & Krug, Surf. Science (1996).

KMC and Hybrid surface



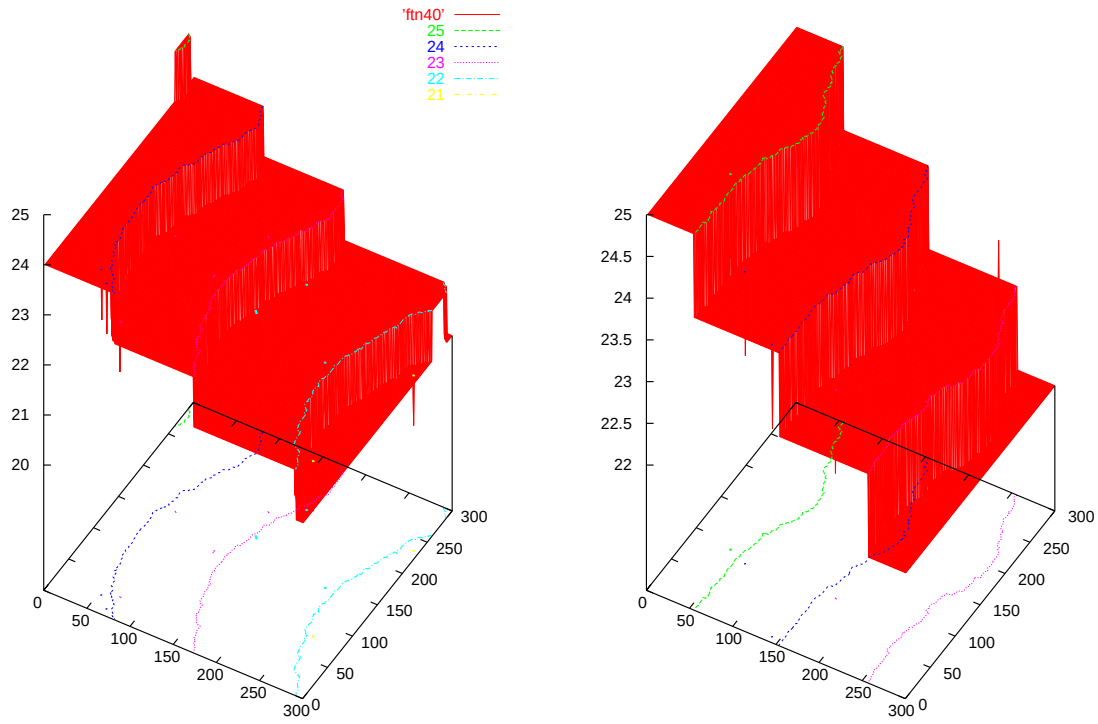
- KMC (left) took about 12 days to simiulate.
- Hybrid (right) took about 56 hours with cell width 10

KMC and Hybrid surface



- KMC (left) took about 12 days to simiulate.
- Hybrid (right) took about 70 hours with cell width 15

Hybrid and Adaptive KMC surface



The simulaion on the right uses a crude, coarse-grained KMC instead of solving a discretized diffusion equation.

It was slightly faster.

Off-lattice KMC

Collaborators:

Weidong Guo (post-doc, UTK)
Weinan E (Princeton)

- In all KMC models, transition state theory predicts rates of the form $R \sim \exp[-\Delta\Phi]$
- In lattice-based models, the energy landscape Φ is prescribed.
- In off-lattice KMC, we wish to allow an arbitrary set of atom positions $\{\mathbf{r}_i\}$.
- The potential energy of such a collection is often modeled as a sum of pair-wise interactions, *e.g.* the Lennard-Jones potential:

$$\Phi = \sum_{ij} \Phi_{ij} = \sum_{ij} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

Off-lattice KMC Algorithm

1. Identify the set of likely transitions $\mathbf{x}_{ik}$ (*i.e.* new local minima) for each particle

$$\mathbf{x}_{ik} = \min_{x \in S_{ik}} \Phi(\mathbf{x}, \{\mathbf{r}_{j \neq i}\})$$

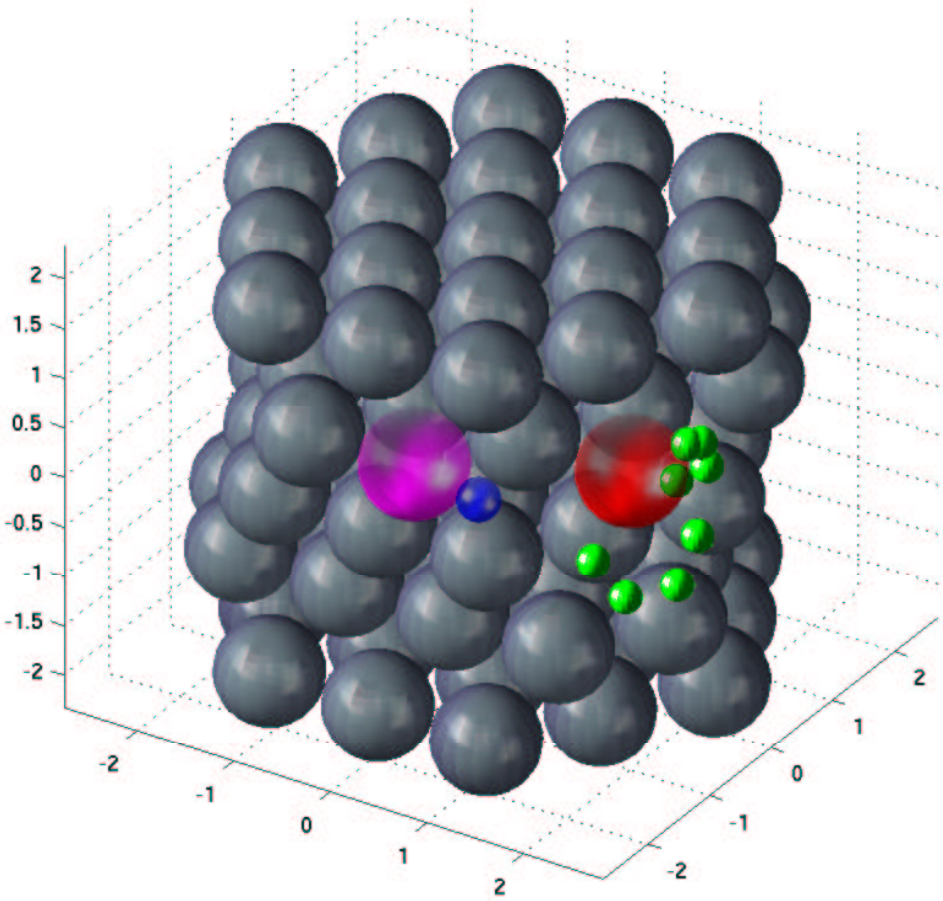
2. Identify the barrier $\Delta\Phi = \Phi_* - \Phi_0$ for each transition, where

$$\Phi_* = \min_{\mathbf{r}_i(s) \in \mathrm{P}} \max_{s \in [0,1]} \Phi(\mathbf{r}_i, \{\mathbf{r}_{j \neq i}\})$$

3. Use the BKL algorithm to randomly select and execute an event

4. Locally relax new configuration, with occasional global relaxation

Off-lattice KMC



- This is rather slow.
- Applications might include nano-tubes, wires, pipeflow, gears, levers...

Summary

- Cross-indexed lists
  - provides a minimal-search KMC algorithm
  - combine with rejection for arbitrary rate sets
- Hybrid scheme
  - significantly faster than KMC
  - many complications with respect to accuracy
- Work in progress
  - Off-lattice KMC
  - Adaptive/multi-grid KMC

For further details...

T.P. Schulze, "A Hybrid Method for Simulating Epitaxial Growth," *Journal of Crystal Growth* **263** (2004) 605-615.

T.P. Schulze, P. Smereka and Weinan E, "Coupling Kinetic Monte-Carlo and Continuum Models with Application to Epitaxial Growth," *J. Comp. Phys.* **189** (2003) 197-211.

T.P. Schulze, "Kinetic Monte-Carlo with Minimal Searching," *Phys. Rev. E* **65** (2002) 036704.

http://www.math.utk.edu/ schulze/publications.htm