Dynamics of Step Edges in Thin Film Growth

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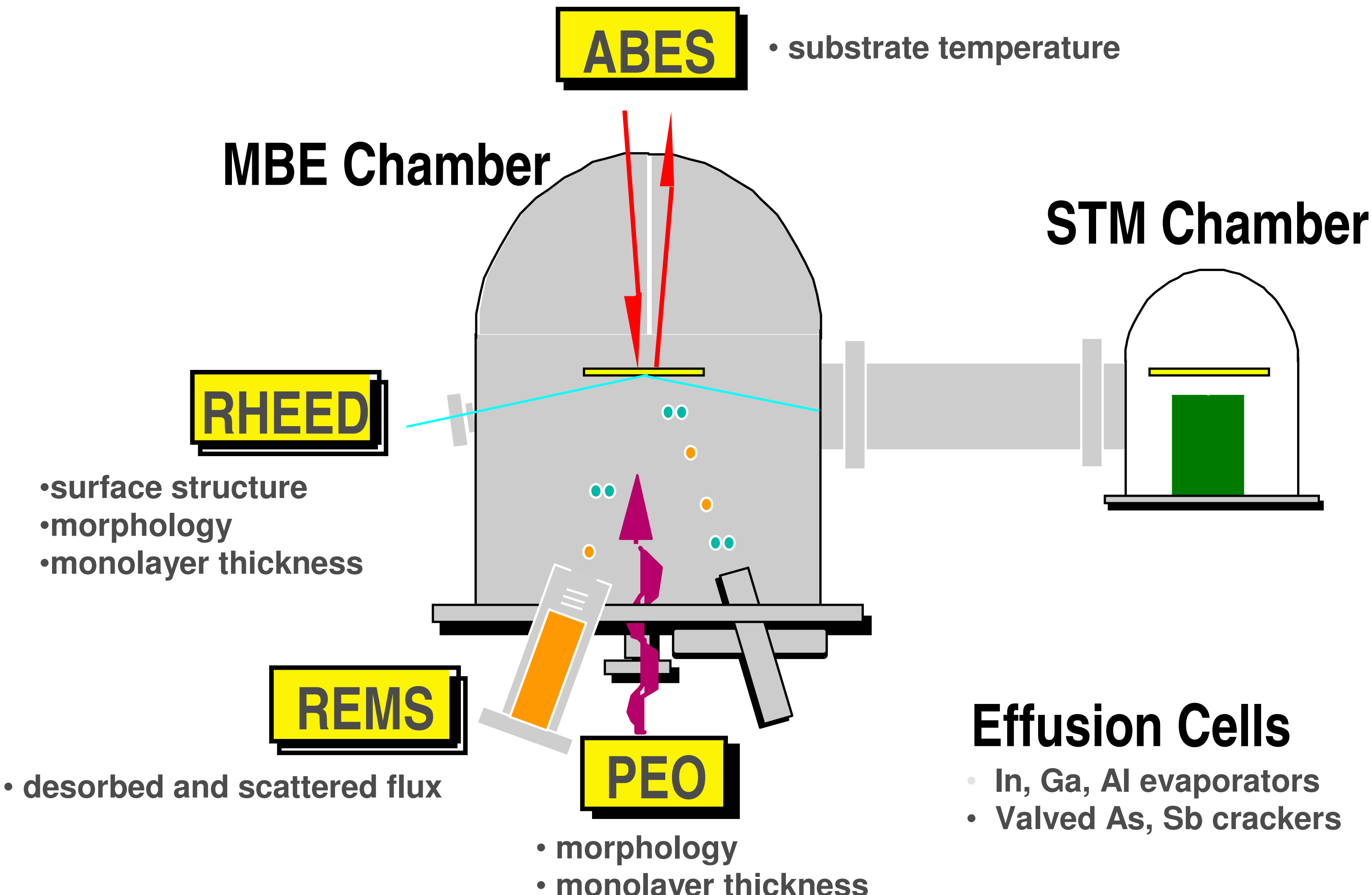
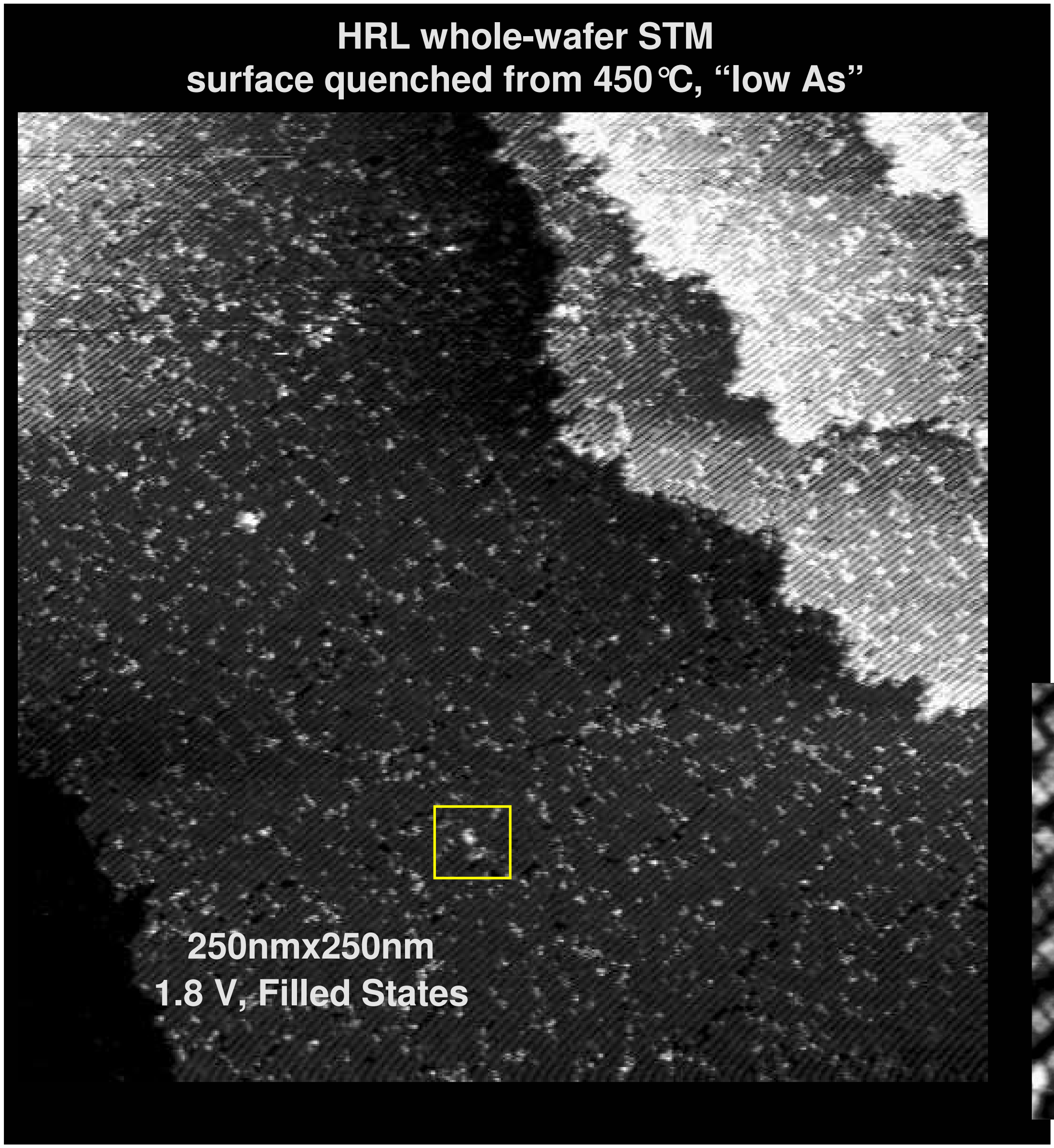
Outline

- Epitaxial Growth
  - molecular beam epitaxy (MBE)
  - Step edges and islands
- Mathematical models for epitaxial growth
  - atomistic: Solid-on-Solid using kinetic Monte Carlo
  - continuum: Villain equation
  - island dynamics: BCF theory
- Kinetic model for step edge
- Asymptotics
  - edge diffusion and line tension (Gibbs-Thomson) boundary conditions
- Conclusions

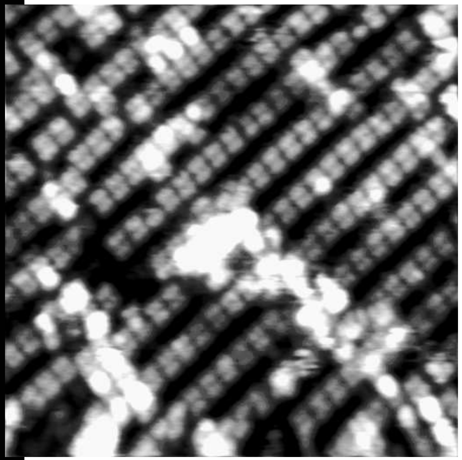
Growth and Analysis Facility at HRL



STM Image of InAs

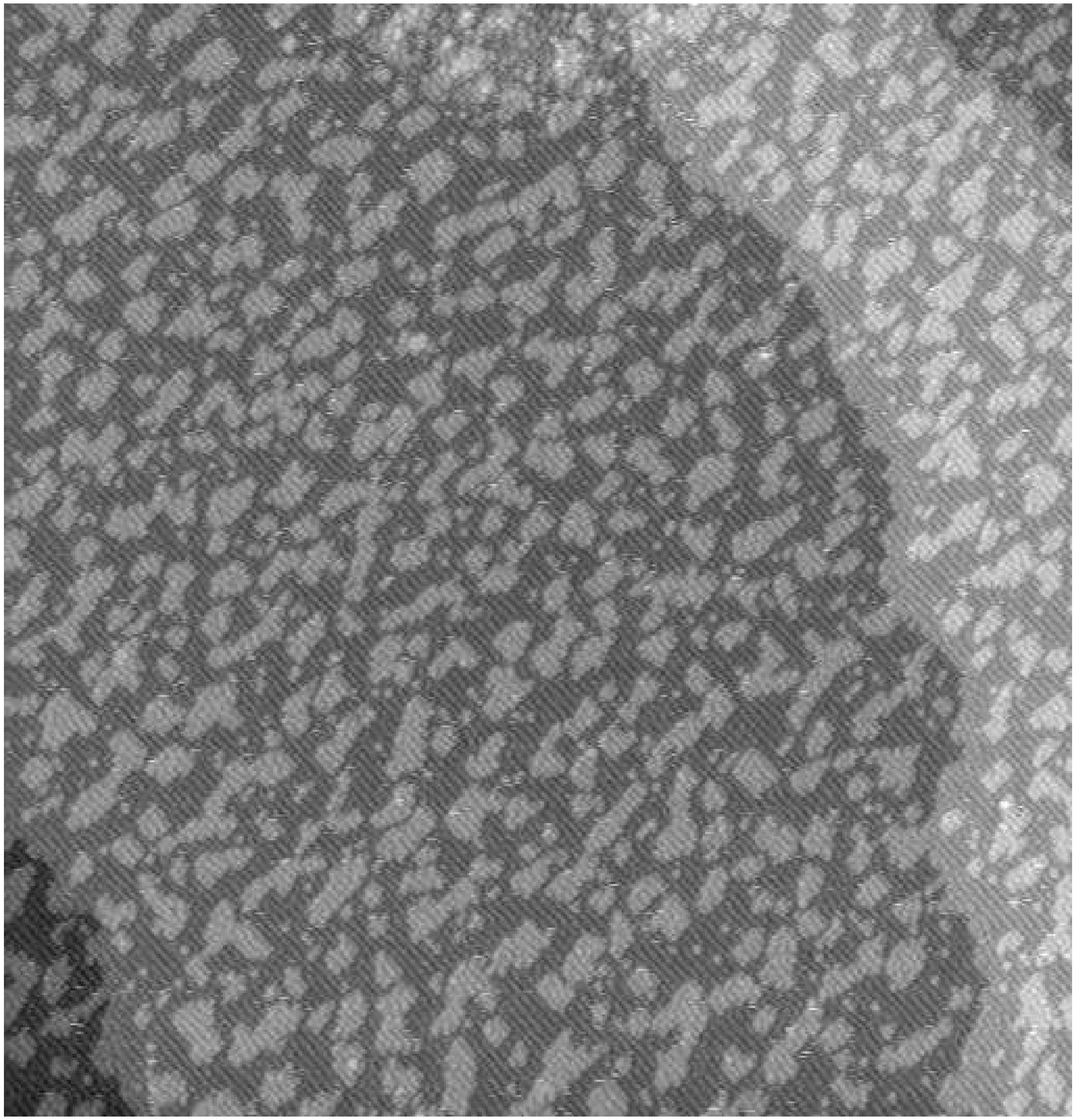


20nmx20nm



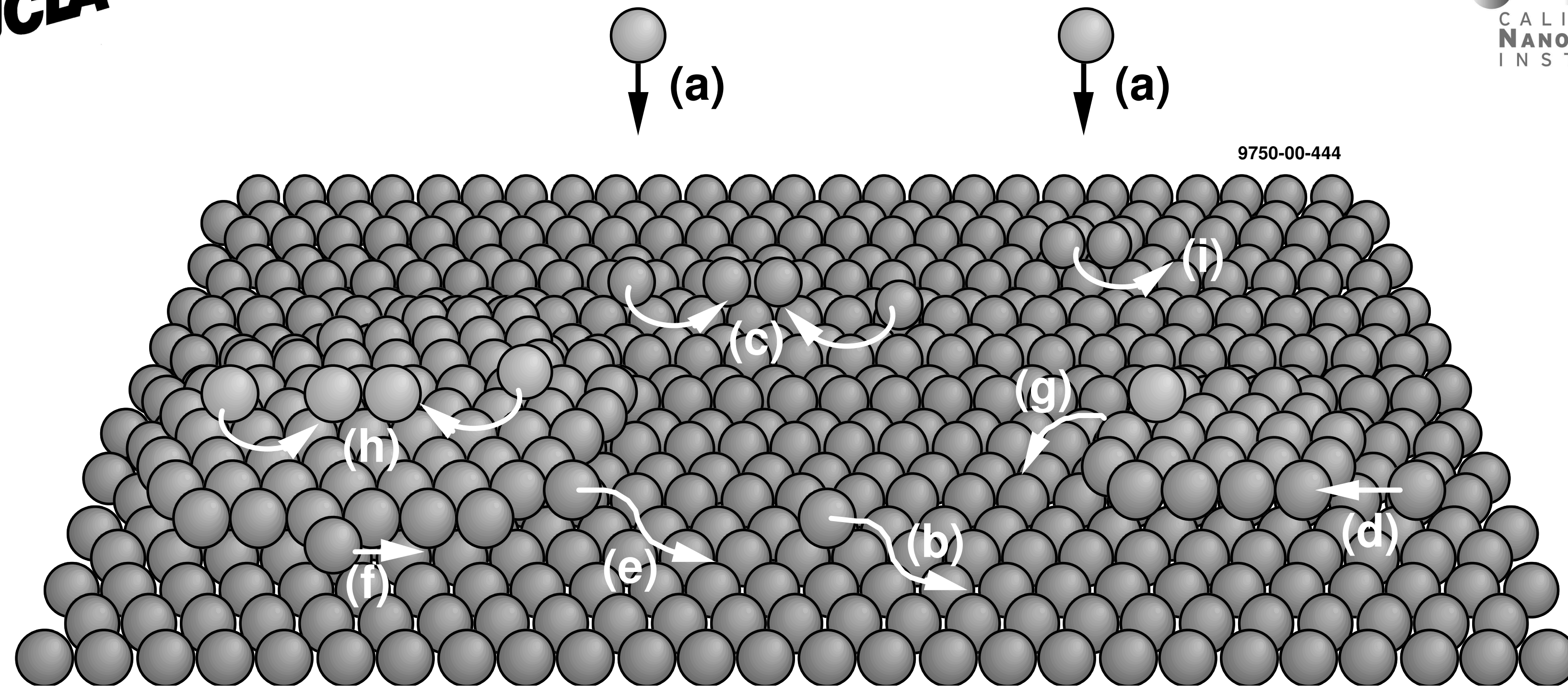
Barvosa-Carter, Owen, Zinck (HRL)

AlSb Growth by MBE



Barvosa-Carter and Whitman, NRL

Basic Processes in Epitaxial Growth

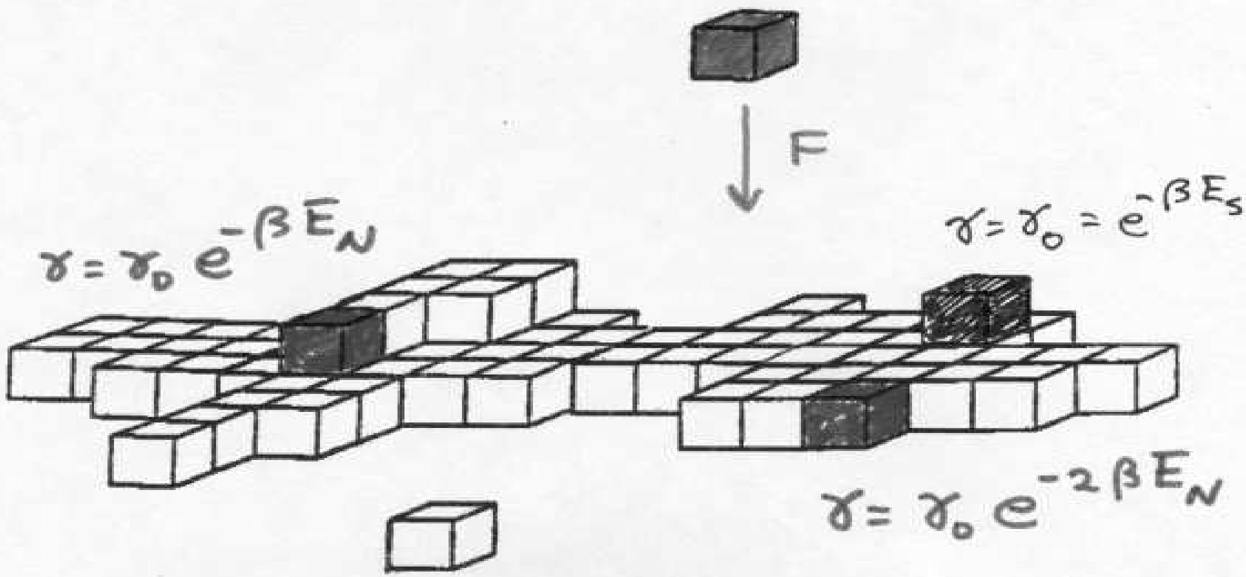


(a) deposition
(b) diffusion
(c) nucleation
(d) attachment
(e) detachment
(f) edge diffusion
(g) diffusion down step
(h) nucleation on top of islands
(i) dimer diffusion

Solid-on-Solid Model

- Interacting particle system
  - Stack of particles above each lattice point
- Particles hop to neighboring points
  - random hopping times
  - hopping rate $D = D_0 \exp(-E/T)$,
  - E = energy barrier, depends on nearest neighbors
- Deposition of new particles
  - random position
  - arrival frequency from deposition rate
- Simulation using kinetic Monte Carlo method
  - Gilmer & Weeks (1979), Smilauer & Vvedensky, …

Pair–bond solid–on–solid model

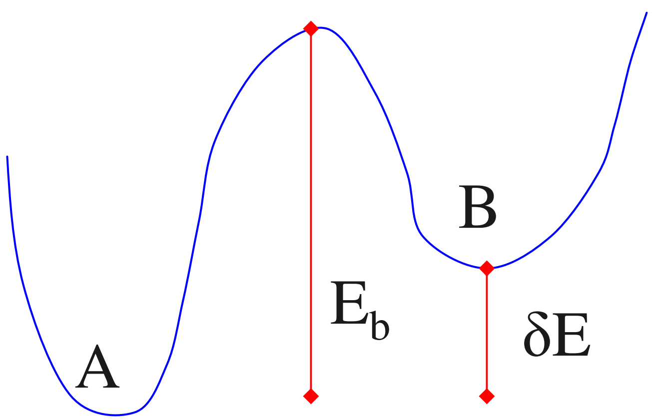


E_S : Substrate Bond Energy

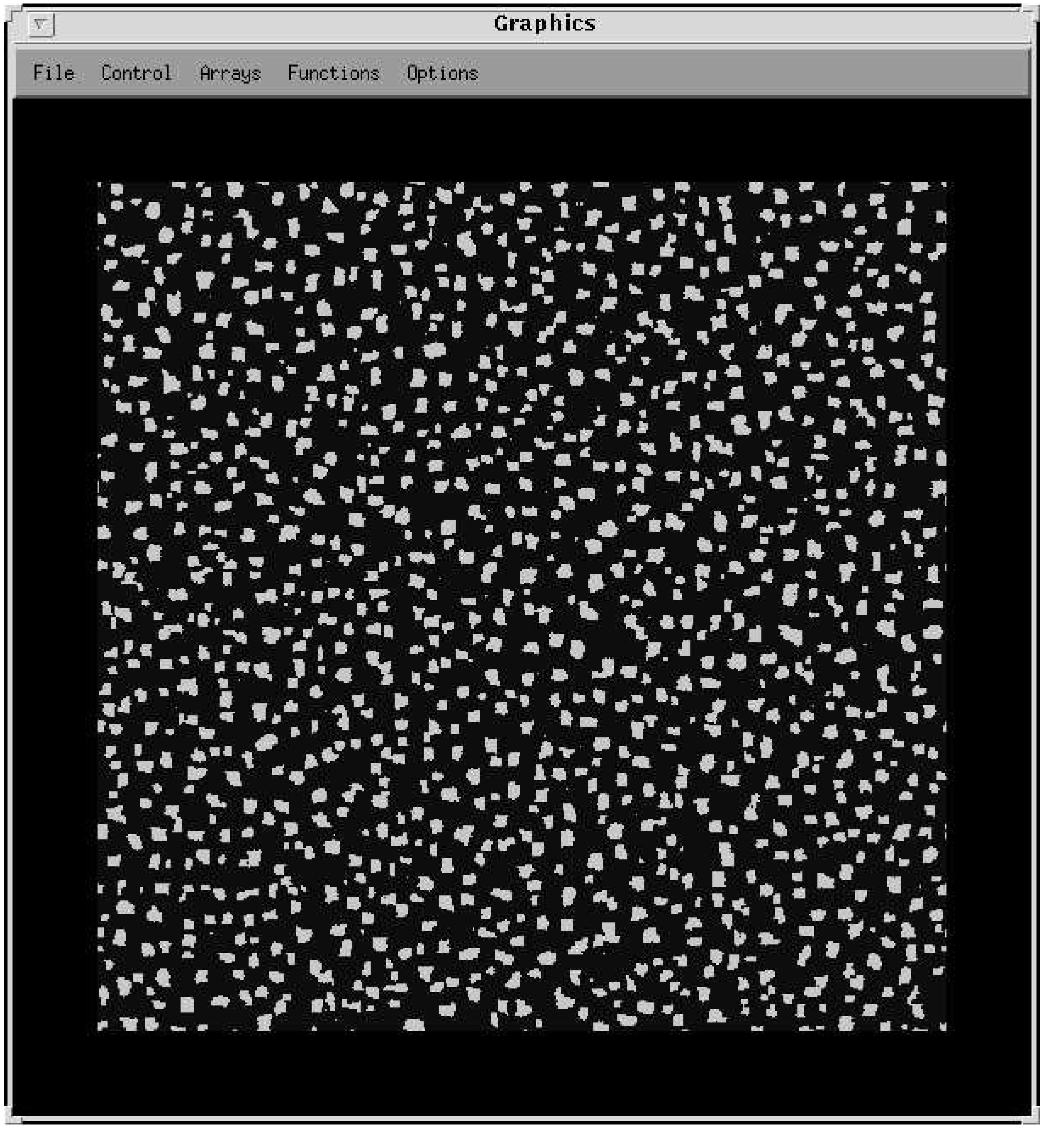
E_N : Nearest Neighbor Bond Energy

Kinetic Monte Carlo

- Random hopping from site A→ B
- hopping rate $D_0 \exp(-E/T)$,
  - $E = E_b$ = energy barrier between sites
  - not δE = energy difference between sites

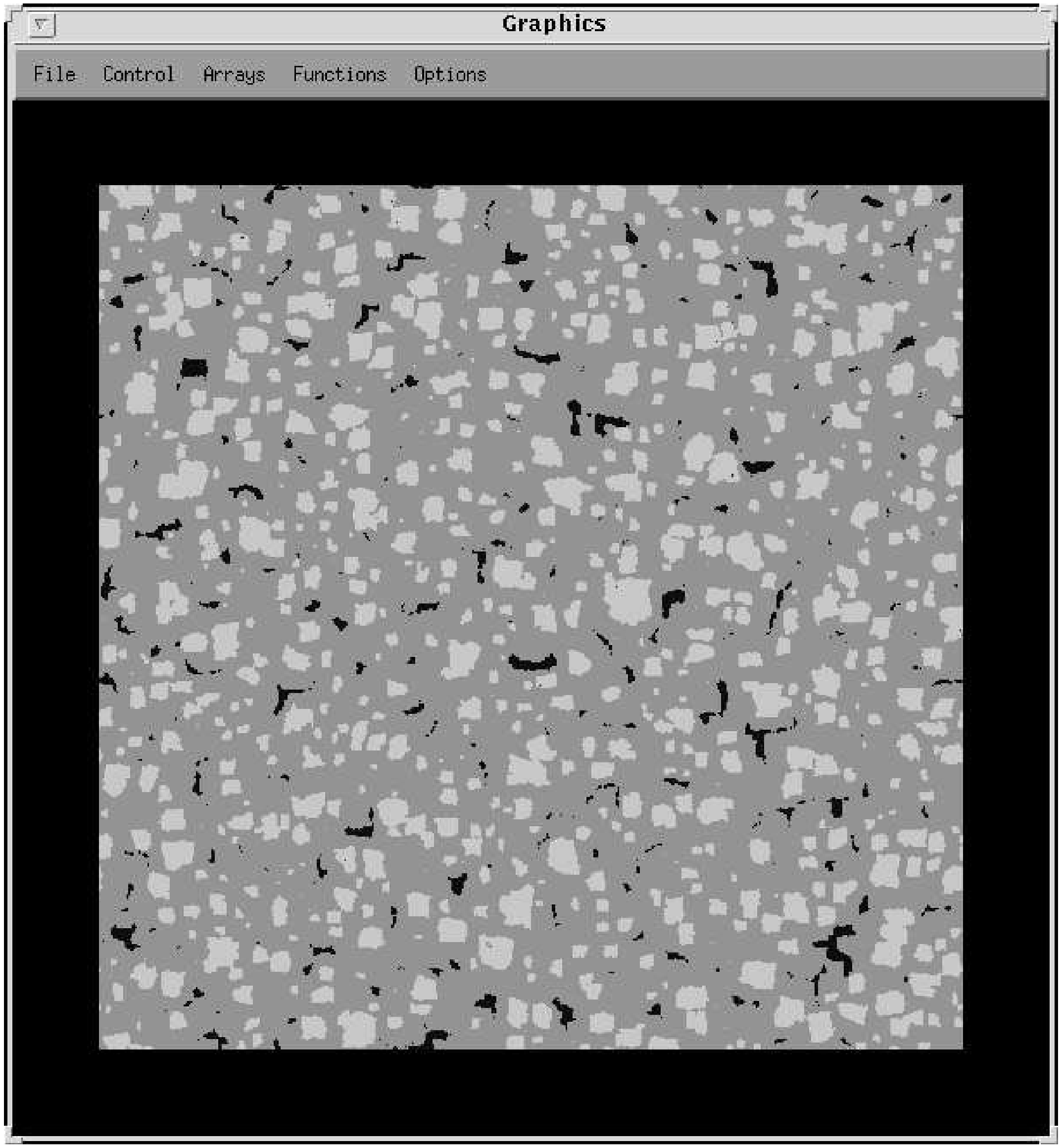


SOS Simulation for coverage=.2

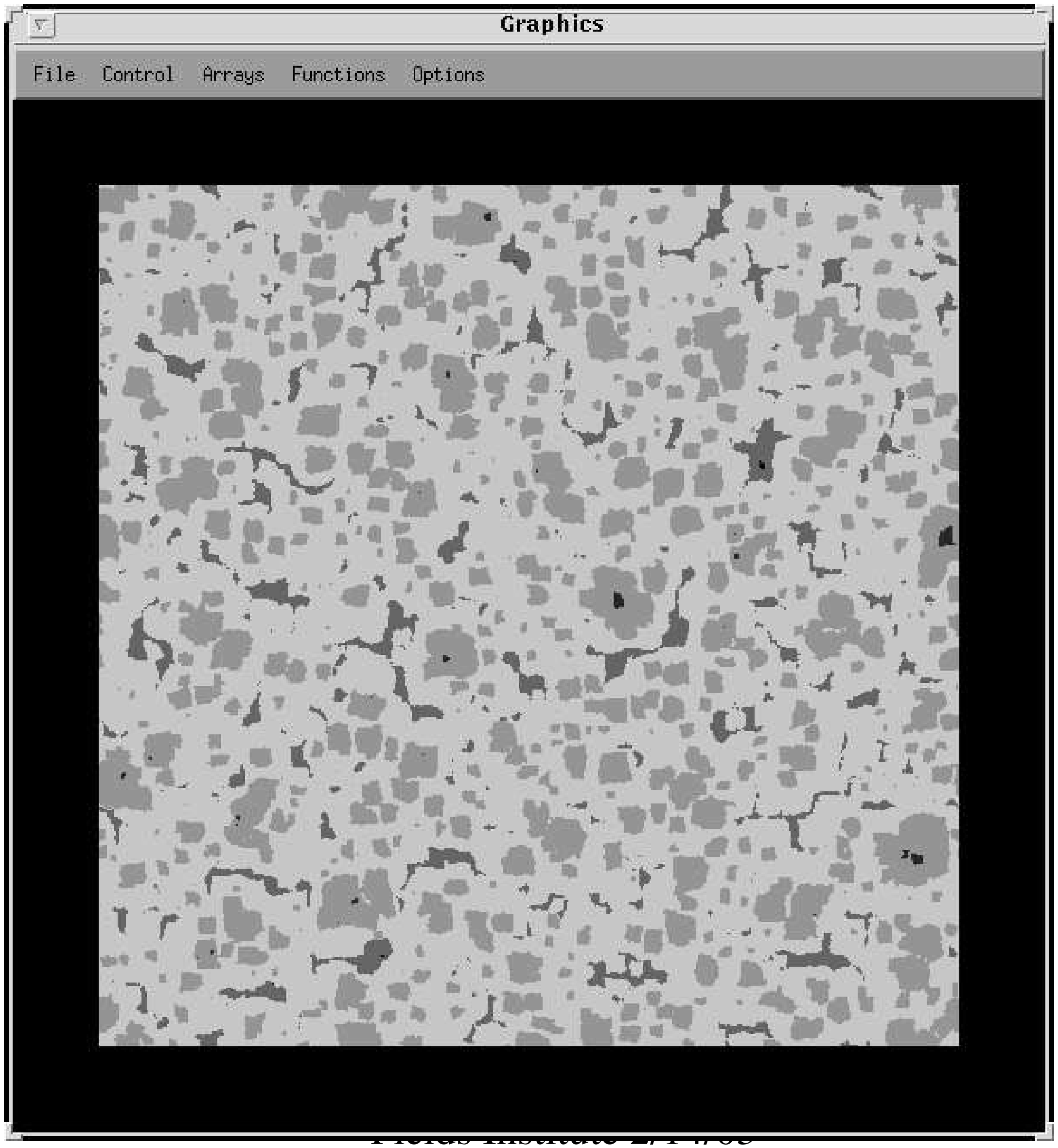


Gyure and Ross, HRL

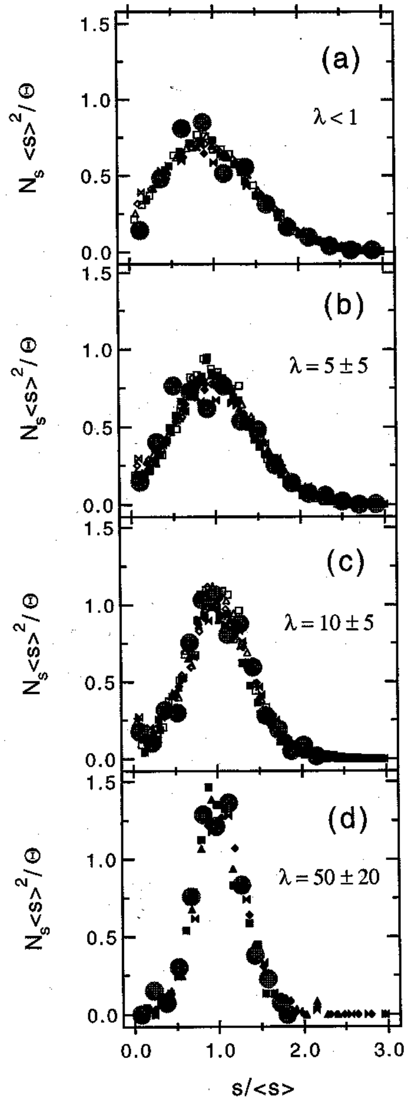
SOS Simulation for coverage=10.2

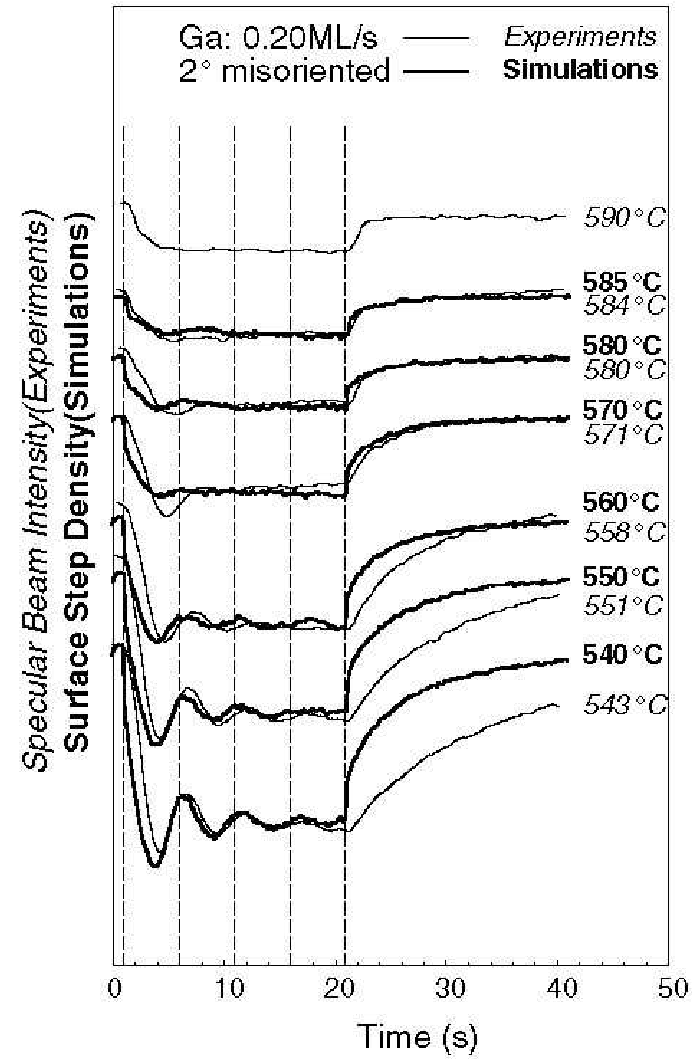


SOS Simulation for coverage=30.2



Validation of SOS Model: Comparison of Experiment and KMC Simulation
(Vvedensky & Smilauer)





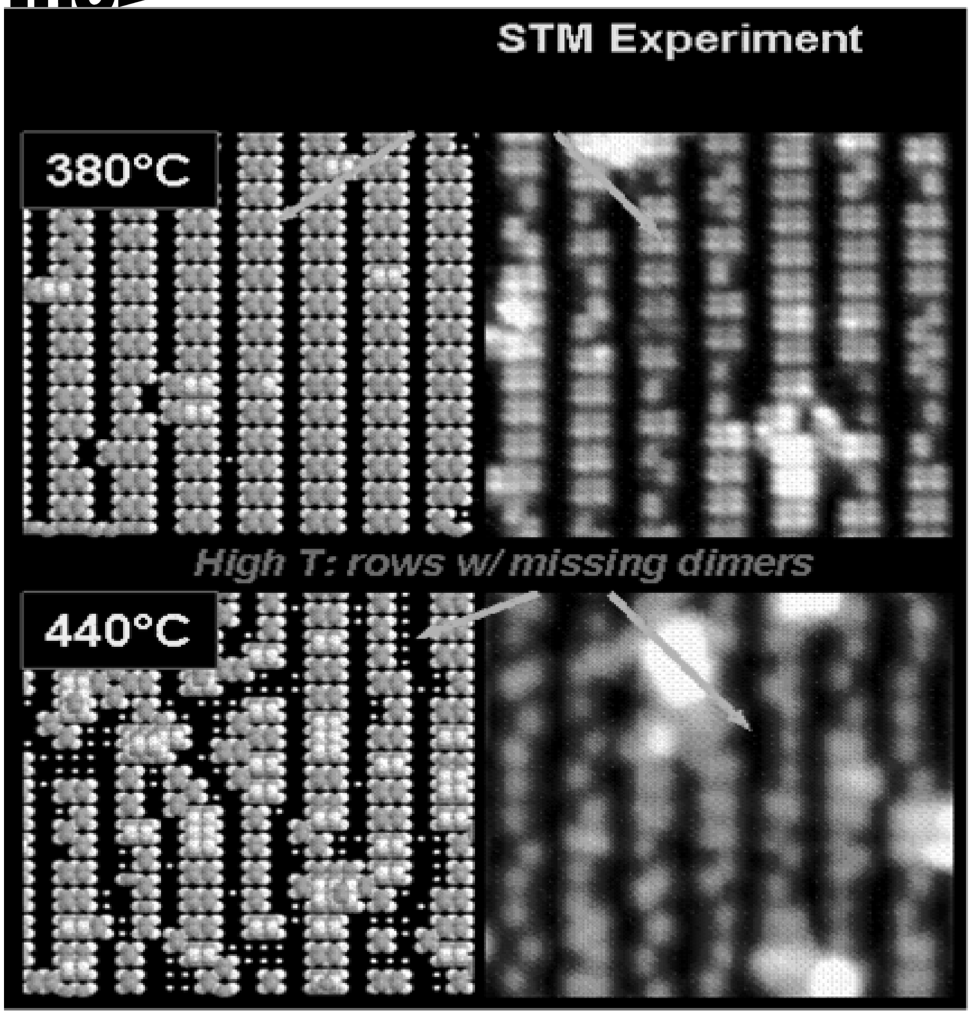
Island size density

Step Edge Density (RHEED)

Difficulties with SOS/KMC

- Difficult to analyze
- Computationally slow
  - adatom hopping rate must be resolved
  - difficult to include additional physics, e.g. strain
- Rates are empirical
  - idealized geometry of cubic SOS
  - cf. “high resolution” KMC

High Resolution KMC Simulations



- InAs
- zinc-blende lattice, dimers
- rates from ab initio computations
- computationally intensive
  - many processes
- describes dynamical info (cf. STM)
- similar work
  - Vvedensky (Imperial)
  - Kratzer (FHI)

High resolution KMC (left); STM images (right)

Gyure, Barvosa-Carter (HRL), Grosse (UCLA,HRL)

Continuum Theory for Epitaxial Growth

- Villain equation (1991) h(x,y,t)= height

$$h_t = -\underbrace{\Delta^2 h}_{\text{surface diffusion}} + \underbrace{\Delta h}_{\text{desorption}} + \underbrace{\Delta(|\nabla h|^2)}_{\text{nonlinearity}} + \underbrace{F}_{\text{mean deposition}} + \underbrace{\eta}_{\text{deposition noise}}$$

- Related work: Ortiz; Kohn; …
- Describes rough growth
  - inapplicable to morphology of very thin layers (h=h(t))
- Range of validity is uncertain
  - incomplete derivation (dynamic vs. thermodynamic)
  - surface diffusion: $E[h] = \int \kappa^2 \, ds$, no atomistic derivation

Island Dynamics

- Burton, Cabrera, Frank (1951)
- Epitaxial surface
  - adatom density ρ
  - continuum in lateral direction, atomistic in growth direction
- Adatom diffusion equation, equilibrium BC, step edge velocity

  $\rho_t = D\Delta \rho + F$

  $\rho = \rho_{eq}$

  $v = D [\partial \rho / \partial n]$

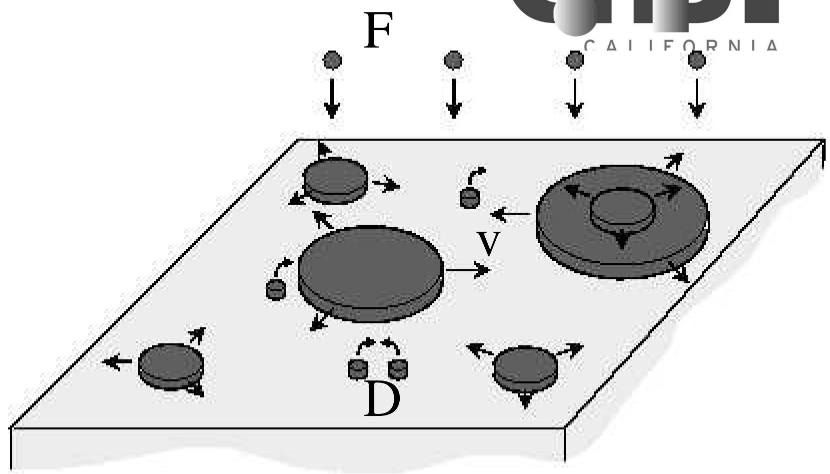
- Line tension (Gibbs-Thomson) in BC and velocity

  $D \partial \rho / \partial n = c(\rho - \rho_{eq}) + c \kappa$

  $v = D [\partial \rho / \partial n] + c \kappa_{ss}$

  - similar to surface diffusion, since $\kappa_{ss} \sim x_{ssss}$

Island Dynamics/Level Set Equations



- Variables
  - N=number density of islands
  - Γ_k = island boundaries of height k represented by "level set function" ω

    $$\Gamma_k(t) = \{ x : \omega(x,t)=k \}$$
  - adatom density $\theta(x,y,t)$
- Adatom diffusion equation

$$\rho_t - D \, \Delta \rho = F - dN/dt$$

- Island nucleation rate

$$dN/dt = \int D \, \sigma_1 \, \rho^2 \, dx$$

σ_1 = capture number for nucleation

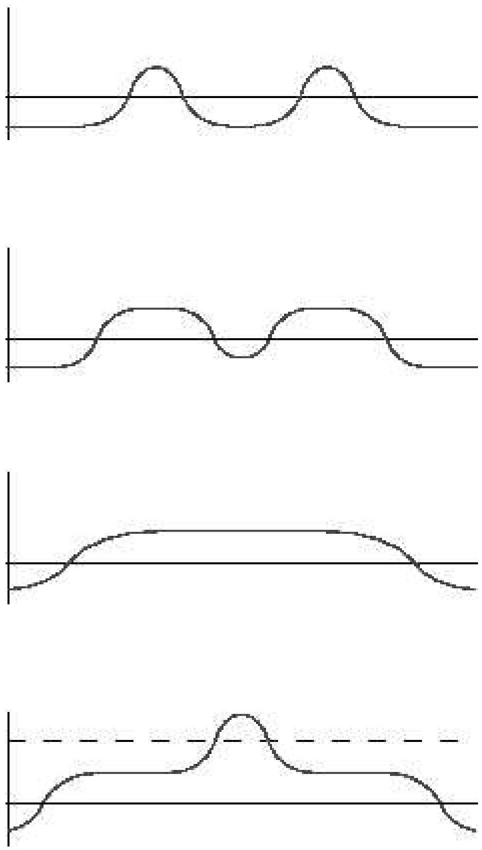
- Level set equation (motion of Γ)

$$\varphi_t + v \text{ grad } \varphi = 0$$

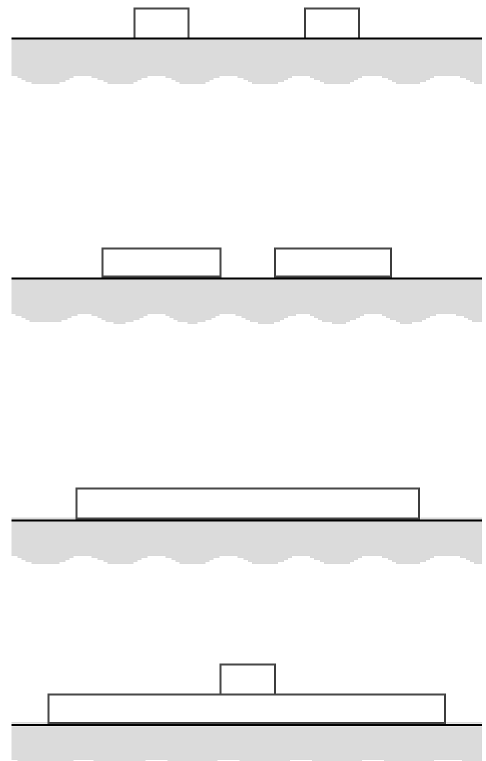
v = normal velocity of boundary Γ

The Levelset Method

Level Set Function φ

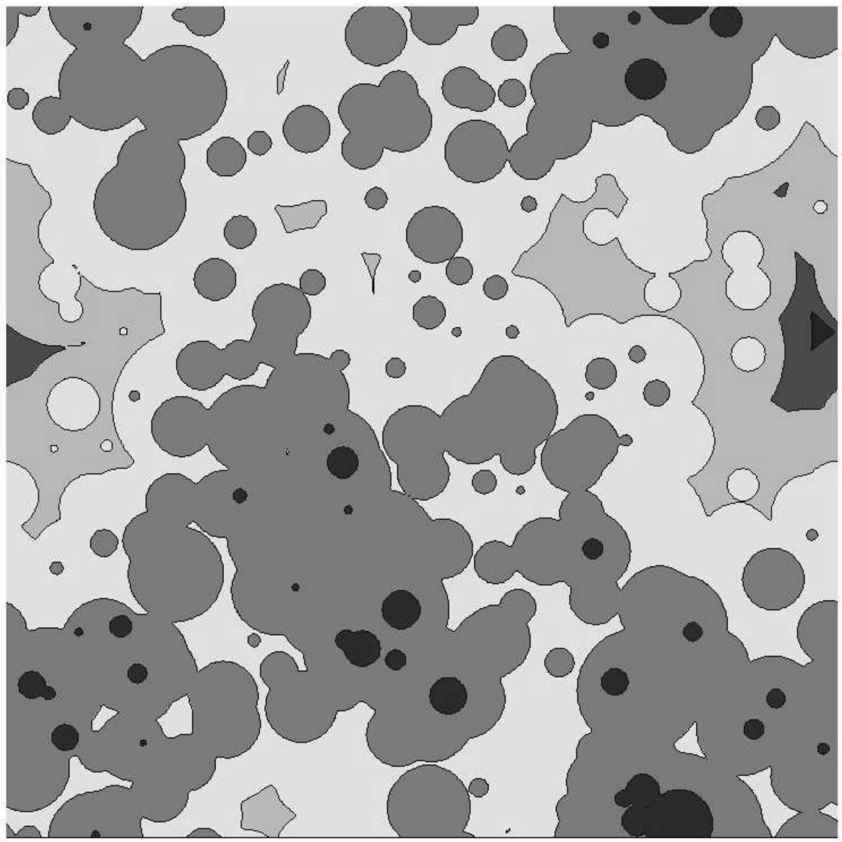


Surface Morphology



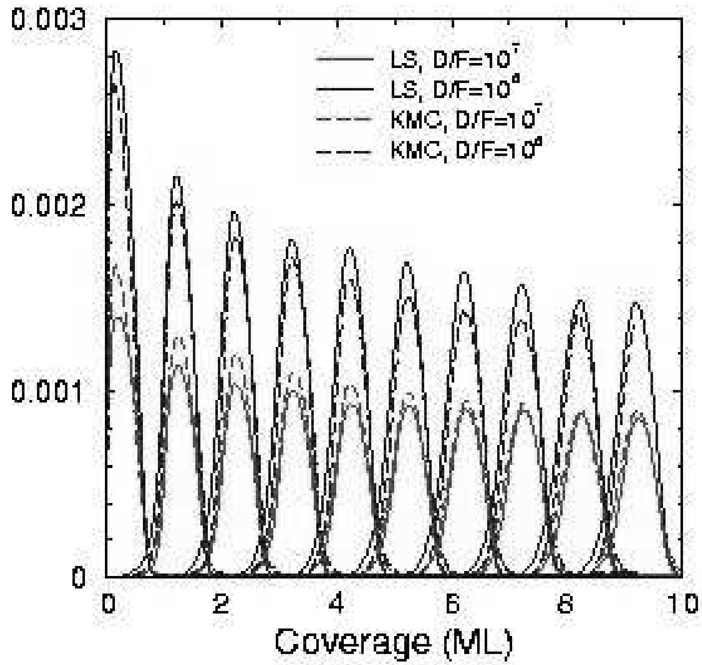
Level Contours after 40 layers

In the multilayer regime, the level set method produces results that are qualitatively similar to KMC methods.

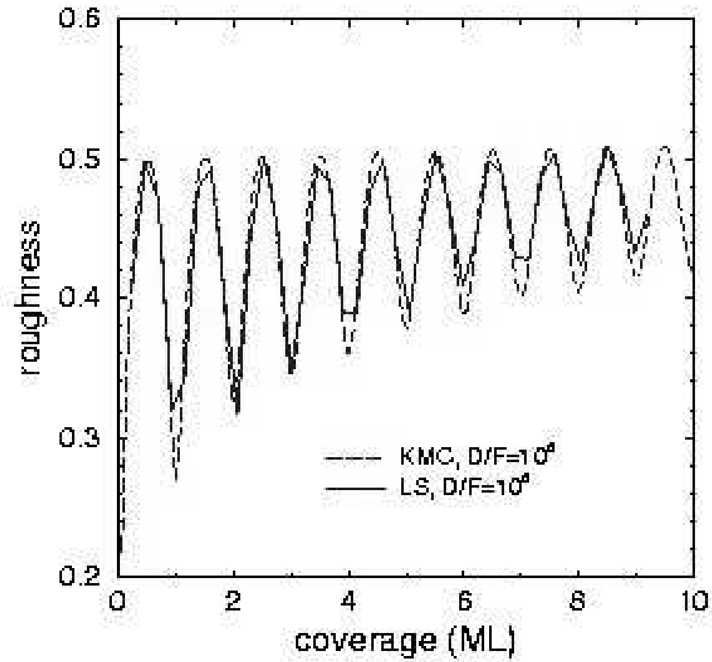


Multilayer Comparison Levelset - KMC

Island Densities



Surface Roughness



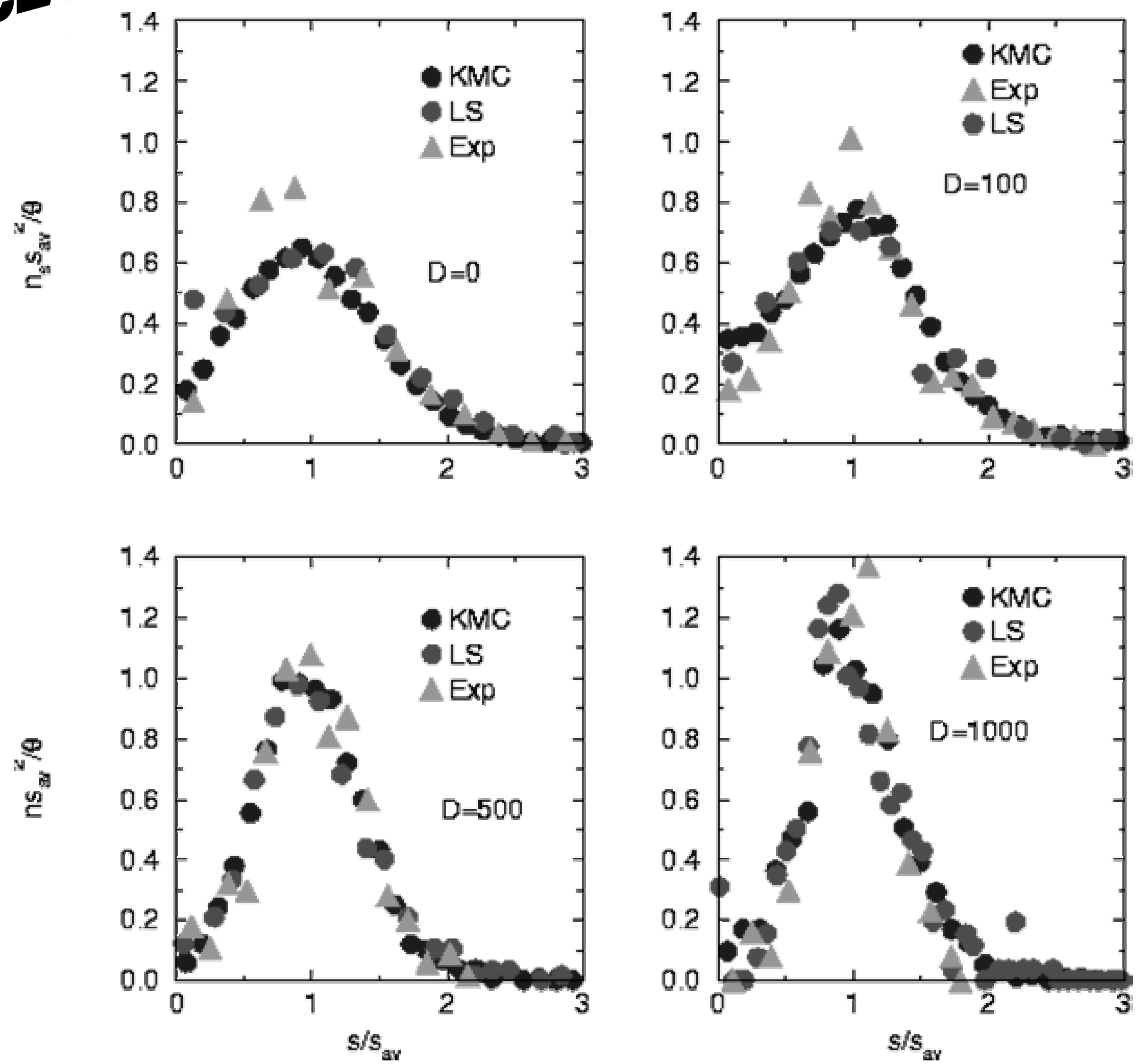
We choose edge diffusion in KMC as $D_{\text{edge}}/D = 0.01$.

LS = level set implementation of island dynamics

UCLA/HRL/Imperial group,

Chopp, Smereka

Island size distributions



Experimental Data for Fe/Fe(001),
Stroscio and Pierce,
Phys. Rev. B 49 (1994)

Stochastic nucleation and breakup of islands

Kinetic Theory for Step Edge Dynamics and Adatom Boundary Conditions

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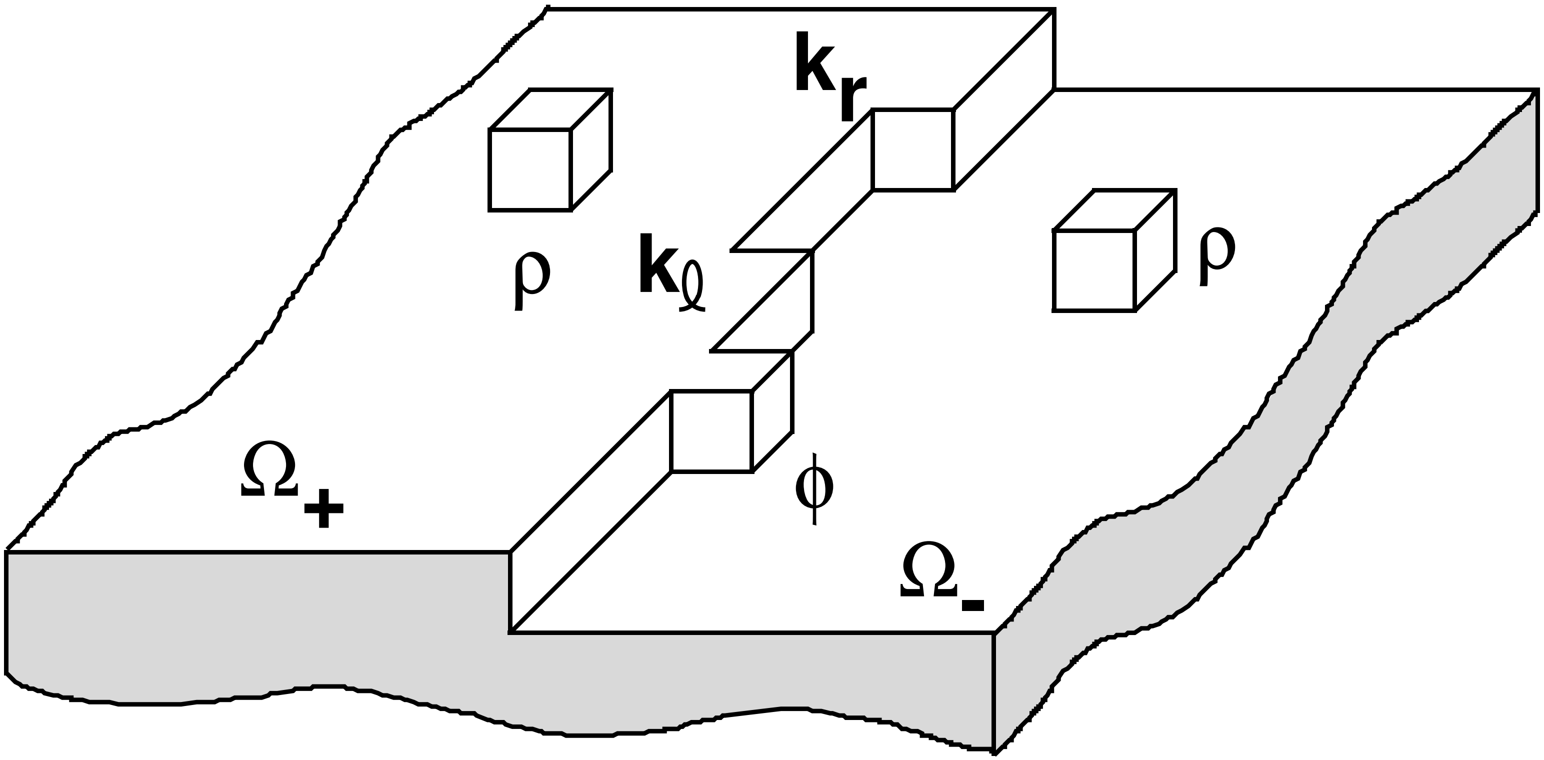
Step Edge Components

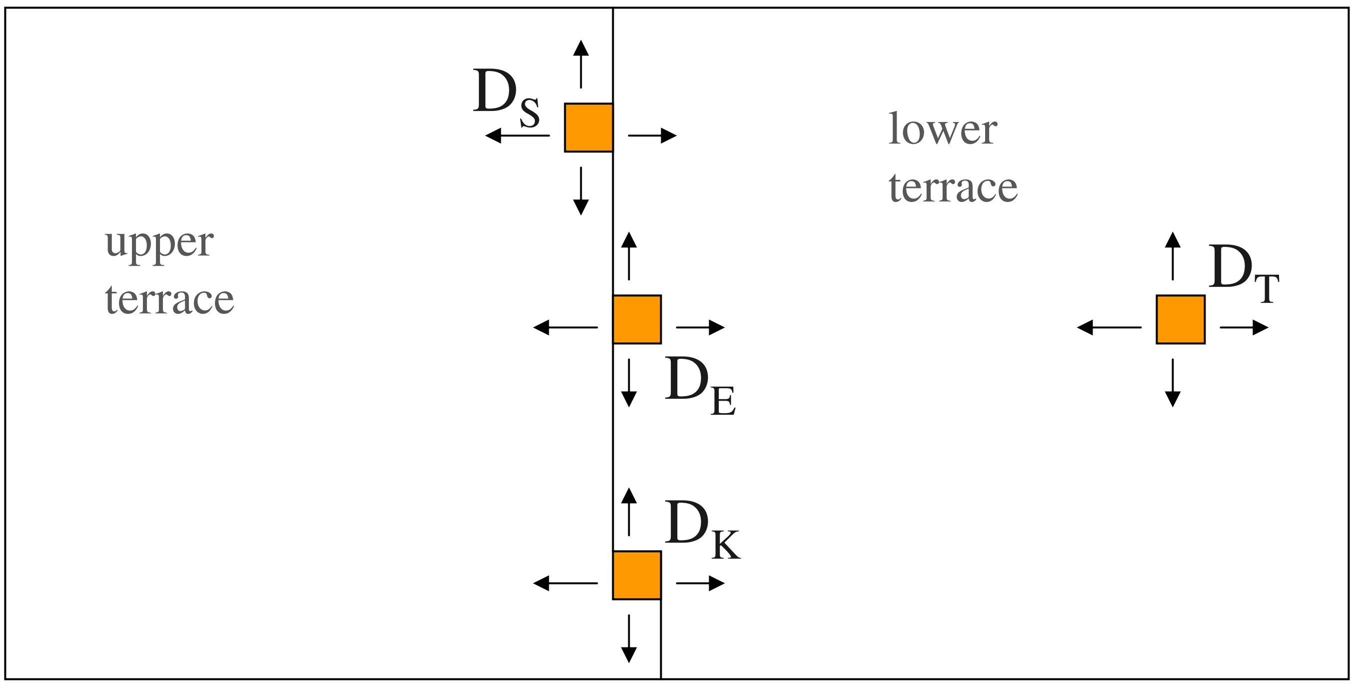


- adatom density θ
- edge atom density ρ
- kink density (left, right) k
- terraces (upper and lower) Ω

Diffusion Coefficients

Hopping rate = diffusion coefficient, for bond energy E

D_T	hopping rate on terrace
$D_E = D_T\, e^{-E/T}$	hopping rate along and off of edge
$D_K = D_T\, e^{-2E/T}$	hopping rate from kink
$D_S = D_T\, e^{-3E/T}$	hopping rate out of a uniform edge



BCF Theory

- Equilibrium of step edge with terrace
- Gibbs distributions

$$\rho = e^{-2E/T}$$

$$\varphi = e^{-E/T}$$

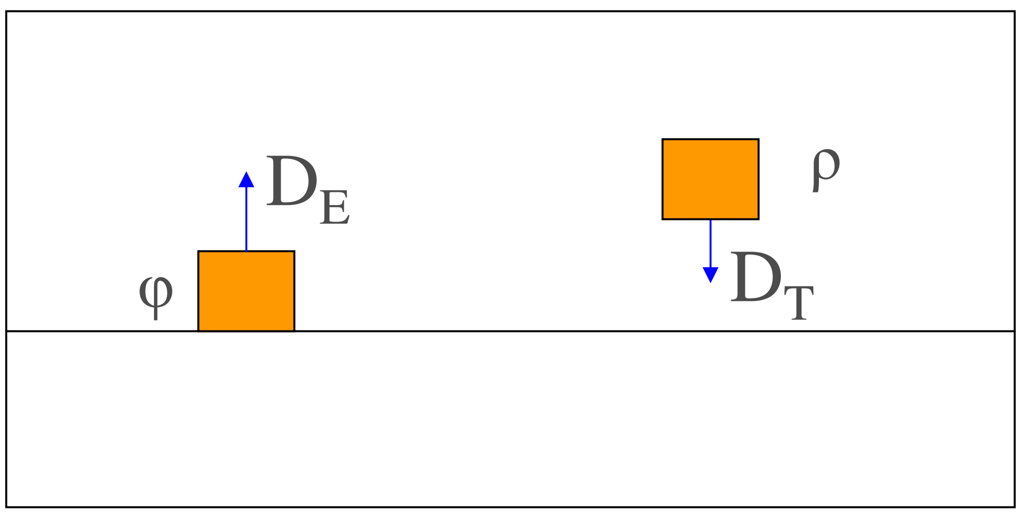
$$k = 2e^{-E/2T}$$

- Derivation from detailed balance
- BCF includes kinks of multi-heights

Detailed Balance: Attachment/Detachment at Edge

edge atom ↔ terrace adatom:

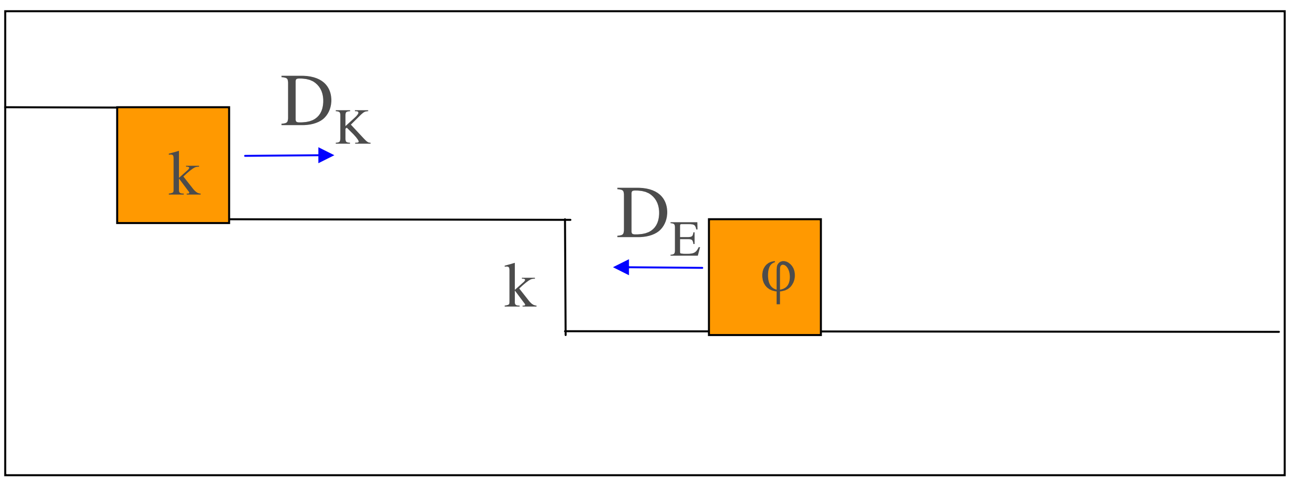
$$D_E \varphi = D_T \rho$$



Detailed Balance: Attachment/Detachment at Kinks

kink ↔ edge atom:

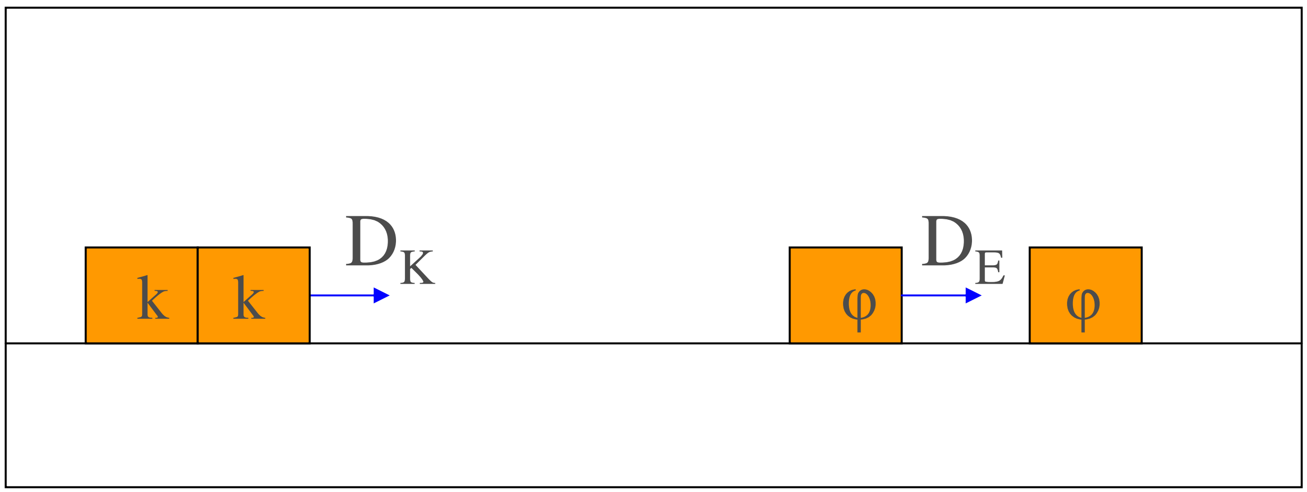
$$D_K \, k = D_E \, k \, \varphi$$



Detailed Balance: Nucleation/Breakup of Kink Pairs

kink pair ("island") ↔ edge atom pair

$$D_K\ (1/4)\ k^2 = D_E\ \varphi^2$$



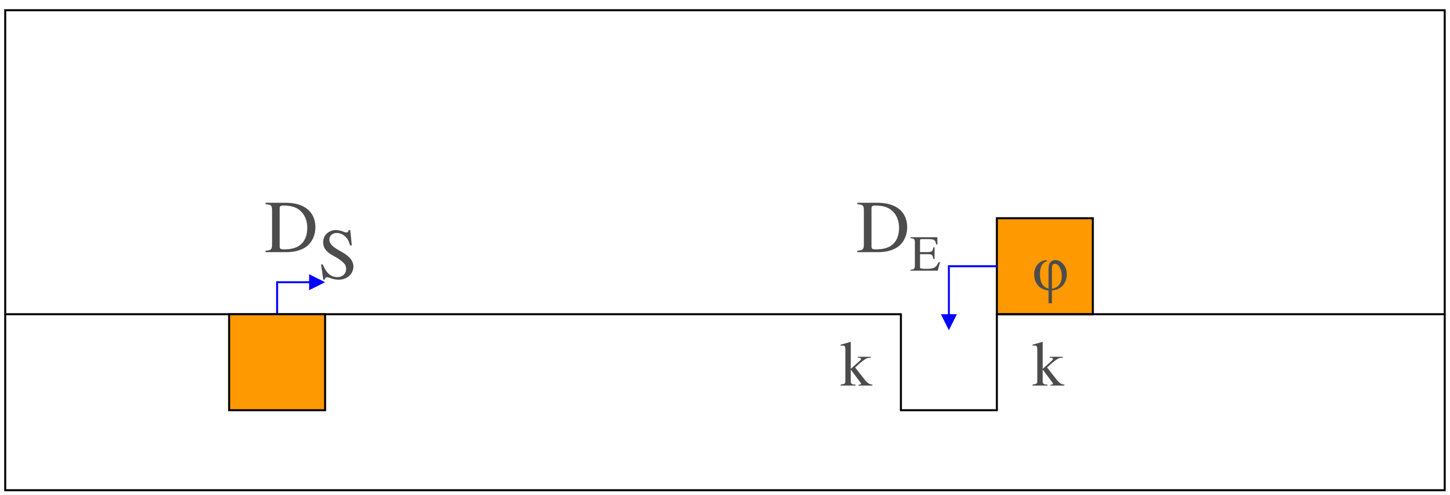
Detailed Balance: Creation/Filling of Holes along Edge

kink pair (“hole”) + edge atom

$\leftrightarrow$ straight step:

$D_E\ (1/4)\ k^2\ \varphi = D_S$

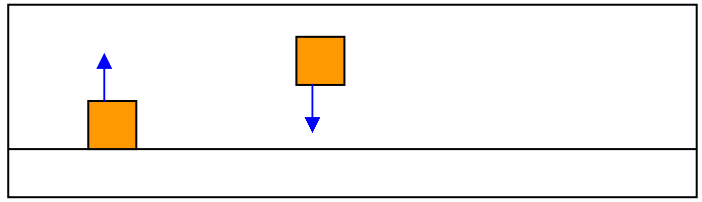
Filling in hole is key step: completion of a row



Detailed Balance

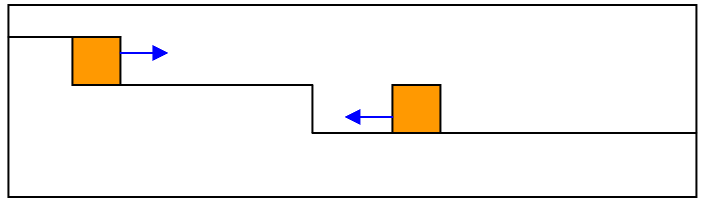
edge atom ↔ terrace adatom:

$$D_E\, \varphi = D_T\, \rho$$



kink ↔ edge atom:

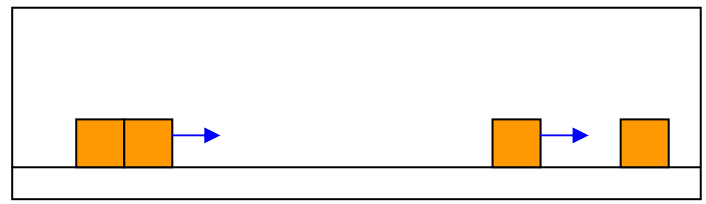
$$D_K\, k = D_E\, k\, \varphi$$



kink pair (“island”)

↔ edge atom pair:

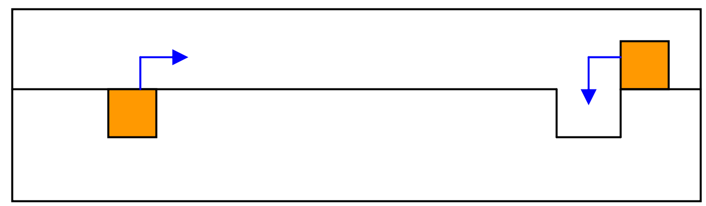
$$D_K\, (1/4)\, k^2 = D_E\, \varphi^2$$



kink pair (“hole”) + edge atom

↔ straight step:

$$D_E\, (1/4)\, k^2\, \varphi = D_S$$



Conclusions:

$$\rho = D_K / D_T = e^{-2E/T}$$

$$\varphi = D_K / D_E = e^{-E/T}$$

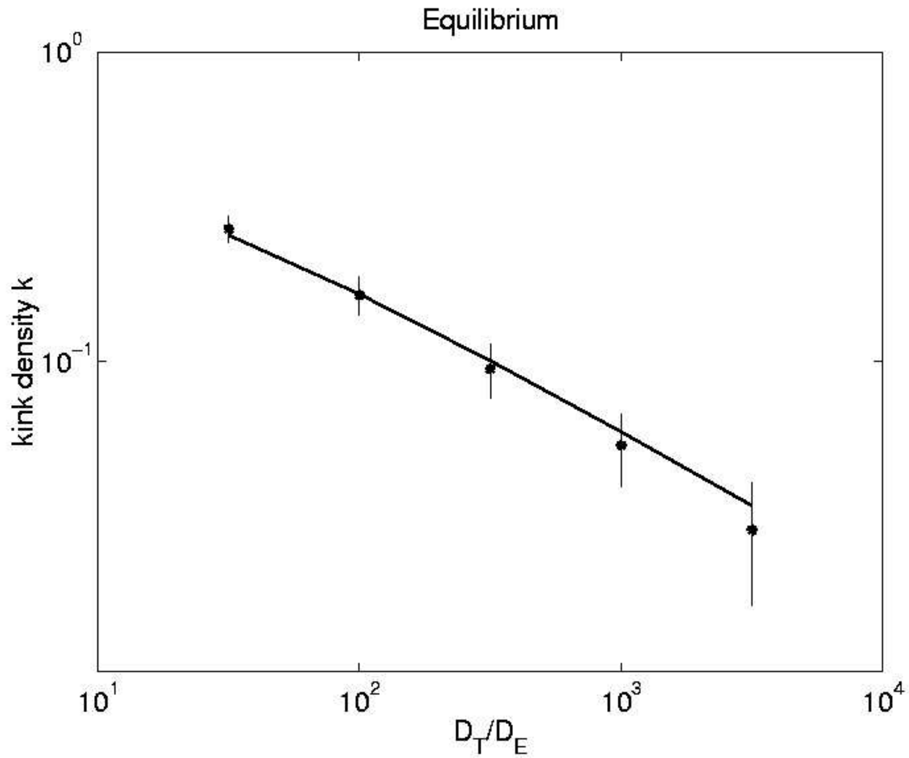
$$k = 2(D_S / D_K)^{1/2} = 2e^{-E/2T}$$

$$D_S\, D_E = D_K^{\,2}$$

Equilibrium Solution

$$\rho = (D_E/D_T)\varphi$$
$$\varphi = k^2/4$$
$$k = 2\sqrt{D_K/D_E}$$

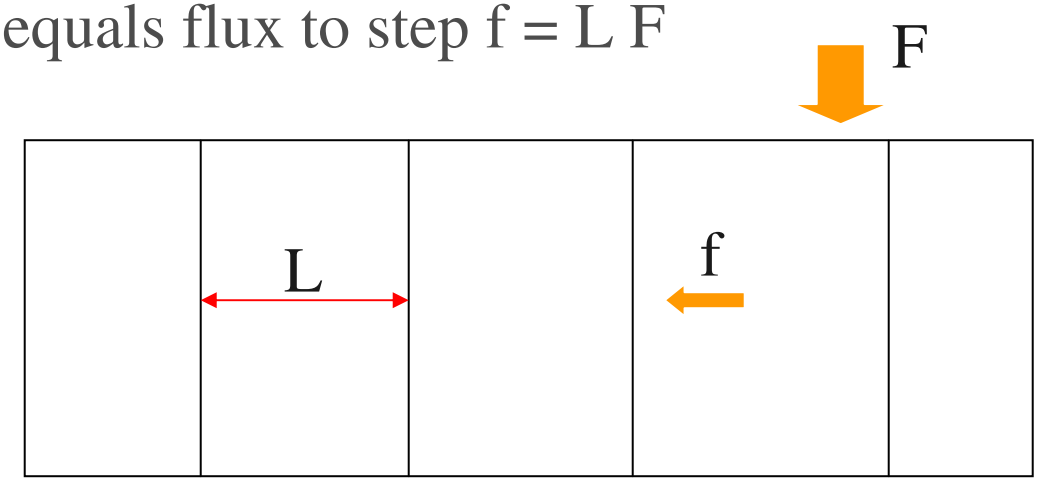
- Solution for F=0 (no growth)
- Same as BCF theory
- D_T, D_E, D_K are diffusion coefficients (hopping rates) on Terrace, Edge, Kink in SOS model



Comparison of results from theory(-) and KMC/SOS (●)

Kinetic Steady State

- Deposition flux F
- Vicinal surface with terrace width L
- No detachment from kinks or step edges, on growth time scale
  - detailed balance not possible
- Advance of steps is due to attachment at kinks
  - equals flux to step f = L F



Detailed Balance

edge atom ↔ terrace adatom:

$$D_E \, \varphi = D_T \, \rho$$

kink ↔ edge atom:

$$D_K \, k = D_E \, k \, \varphi$$

kink pair (“island”)

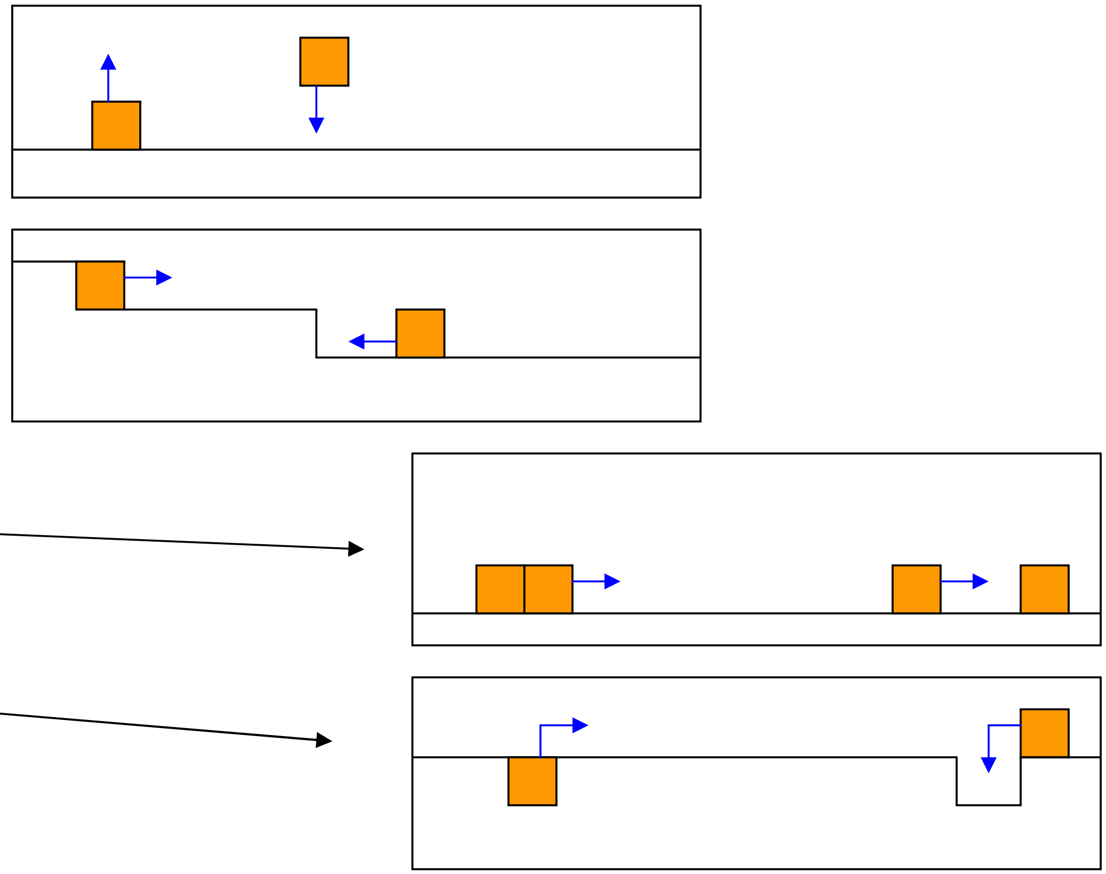
↔ edge atom pair:

$$D_K \, (1/4) \, k^2 = D_E \, \varphi^2$$

kink pair (“hole”) + edge atom

↔ straight step:

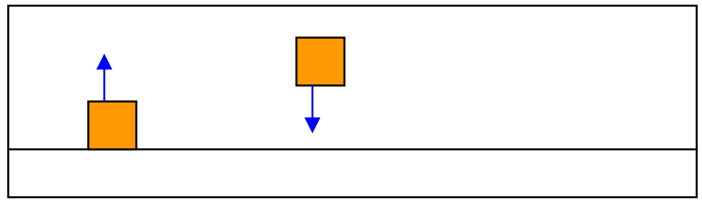
$$D_S = D_E \, (1/4) \, k^2 \, \varphi$$



Kinetic ~~Detailed~~ Balance

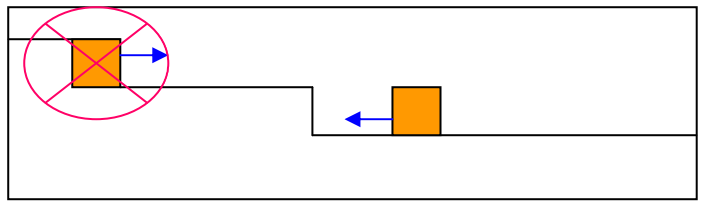
edge atom ↔ terrace adatom:

$$D_E \varphi = D_T \rho$$



kink ↔ edge atom:

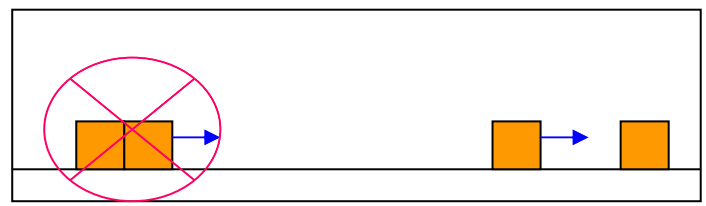
$$\cancel{D_K}\, k = D_E\, k\, \varphi$$



kink pair ("island")

↔ edge atom pair:

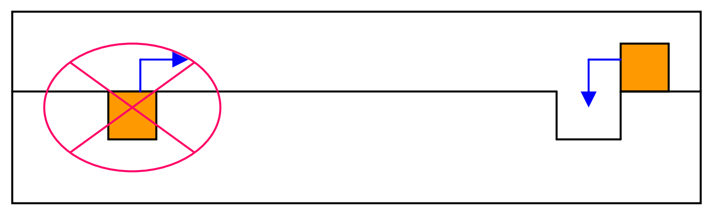
$$\cancel{D_K\, (1/4)\, k^2} = D_E\, \varphi^2$$



kink pair ("hole") + edge atom

↔ straight step:

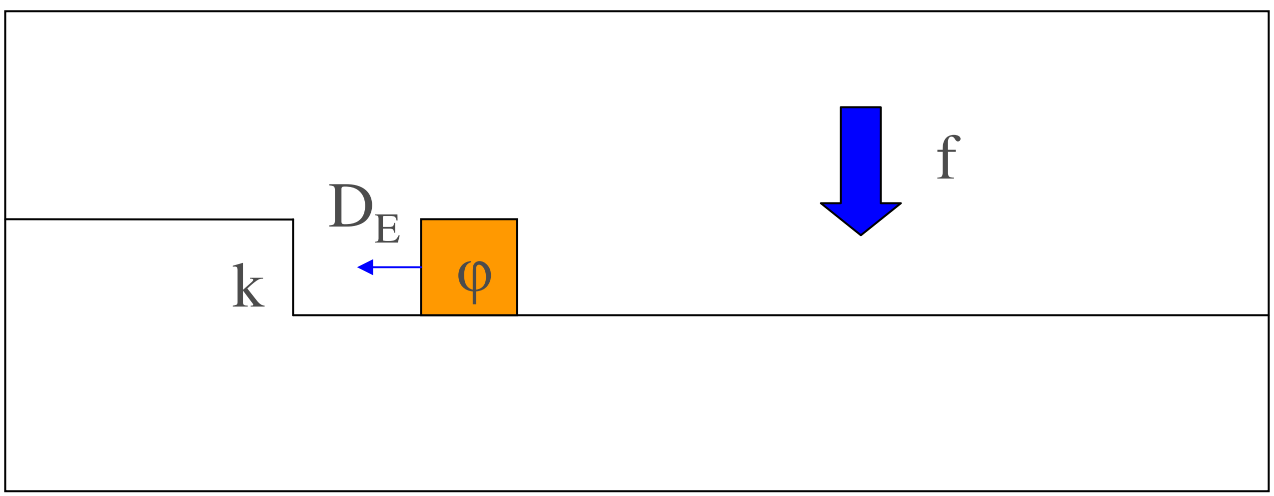
$$\cancel{D_S} = D_E\, (1/4)\, k^2\, \varphi$$



Kinetic Steady State: Flux to Step = Flux to Kinks

flux to kinks ↔ flux to edge :

$$D_E \, k \, \varphi = f = L \, F$$

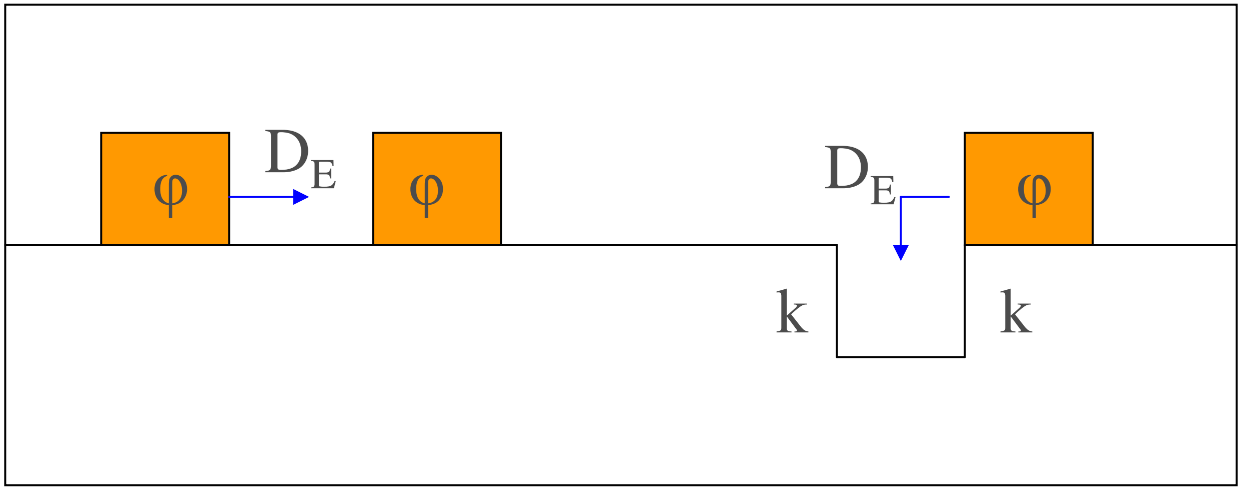


Kinetic Steady State: Kink Nucleation Rate = Hole Fill-in Rate

creation of kink pairs (“island”)

↔ filling in holes:

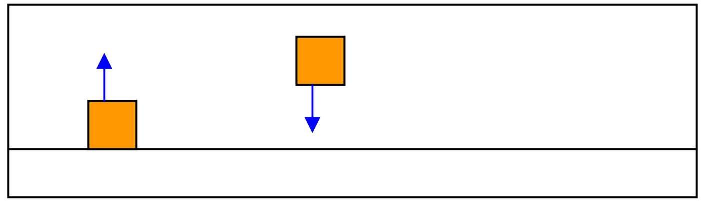
$D_E \, \varphi^2 = D_E \, (1/4) \, k^2 \, \varphi$



Kinetic Steady State

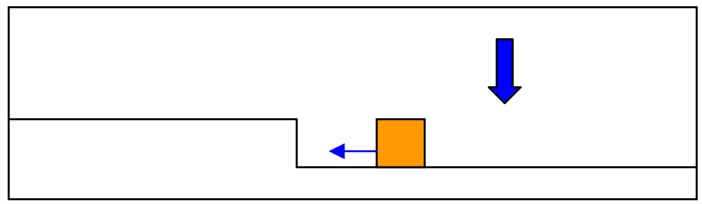
edge atom ↔ terrace adatom:

$D_E\ \varphi = D_T\ \rho$



flux to kinks ↔ flux to edge :

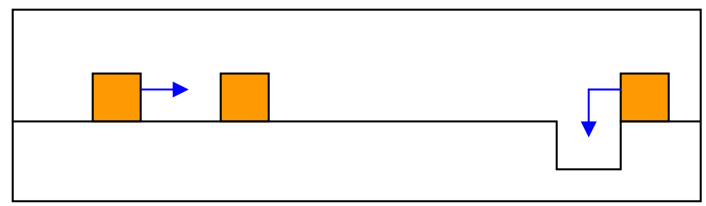
$D_E\ k\ \varphi = f = L\ F$



creation of kink pairs (“island”)

↔ filling in holes:

$D_E\ \varphi^2 = D_E\ k^2\ \varphi$



Conclusions:

$$\rho = (D_E / D_T)\ \varphi$$

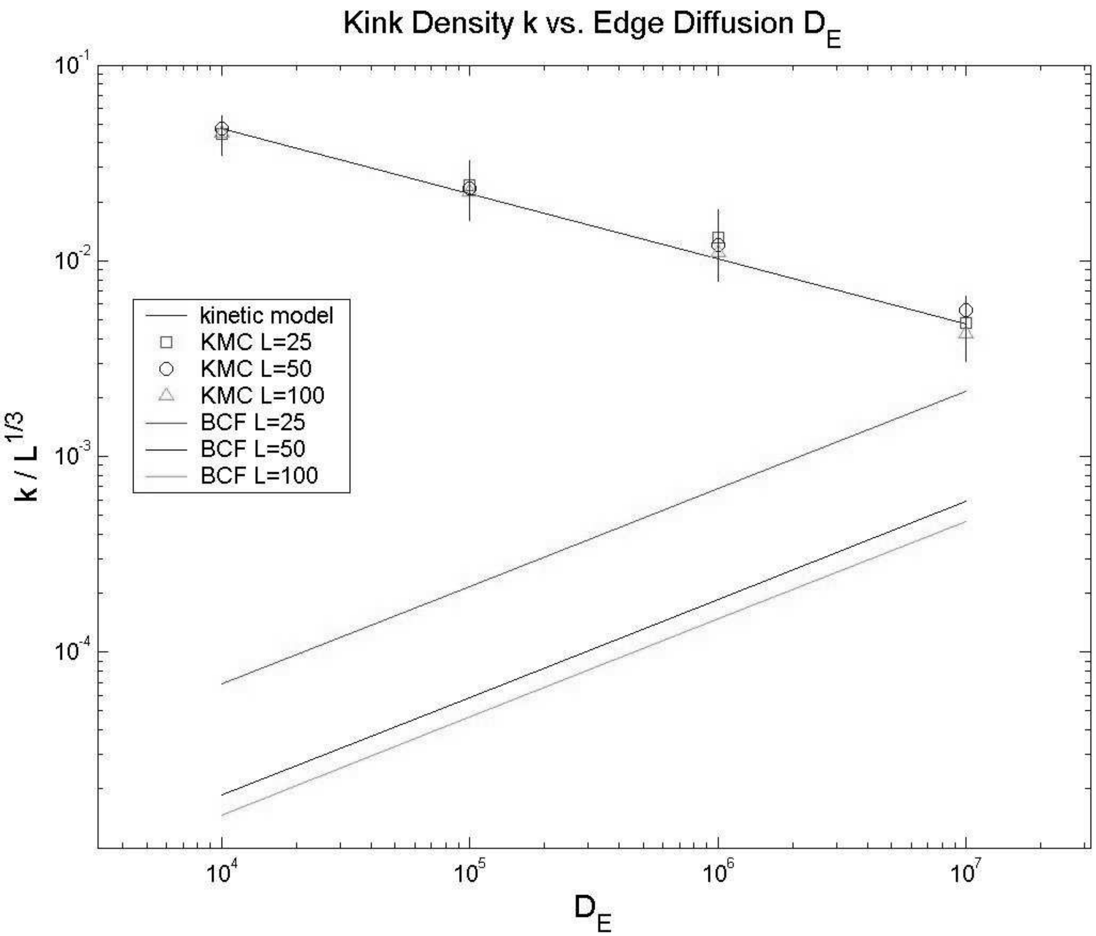
$$\varphi = k^2$$

$$k = (L\ F / D_E)^{1/3}$$

F= deposition flux, L= terrace width

Kinetic Steady State

$$\rho_{\pm} = (D_E/D_T)\varphi$$
$$\varphi = k^2/4$$
$$k = (\frac{16}{15}P_{\text{edge}})^{\frac{1}{3}}$$



- Solution for F>0
- $k >> k_{eq}$
- $P_{edge}=F_{edge}/D_E$ "edge Peclet #"
  $= F\ L\ /\ D_E$

Comparison of scaled results from steady state (-), BCF(- - -), and KMC/SOS (□○△) for L=25,50,100, with F=1, $D_T=10^{12}$

Unsteady Edge Model from Atomistic Kinetics

- Evolution equations for φ, ρ, k

  $\partial_t \rho - D_T \nabla^2 \rho = F$ on terrace

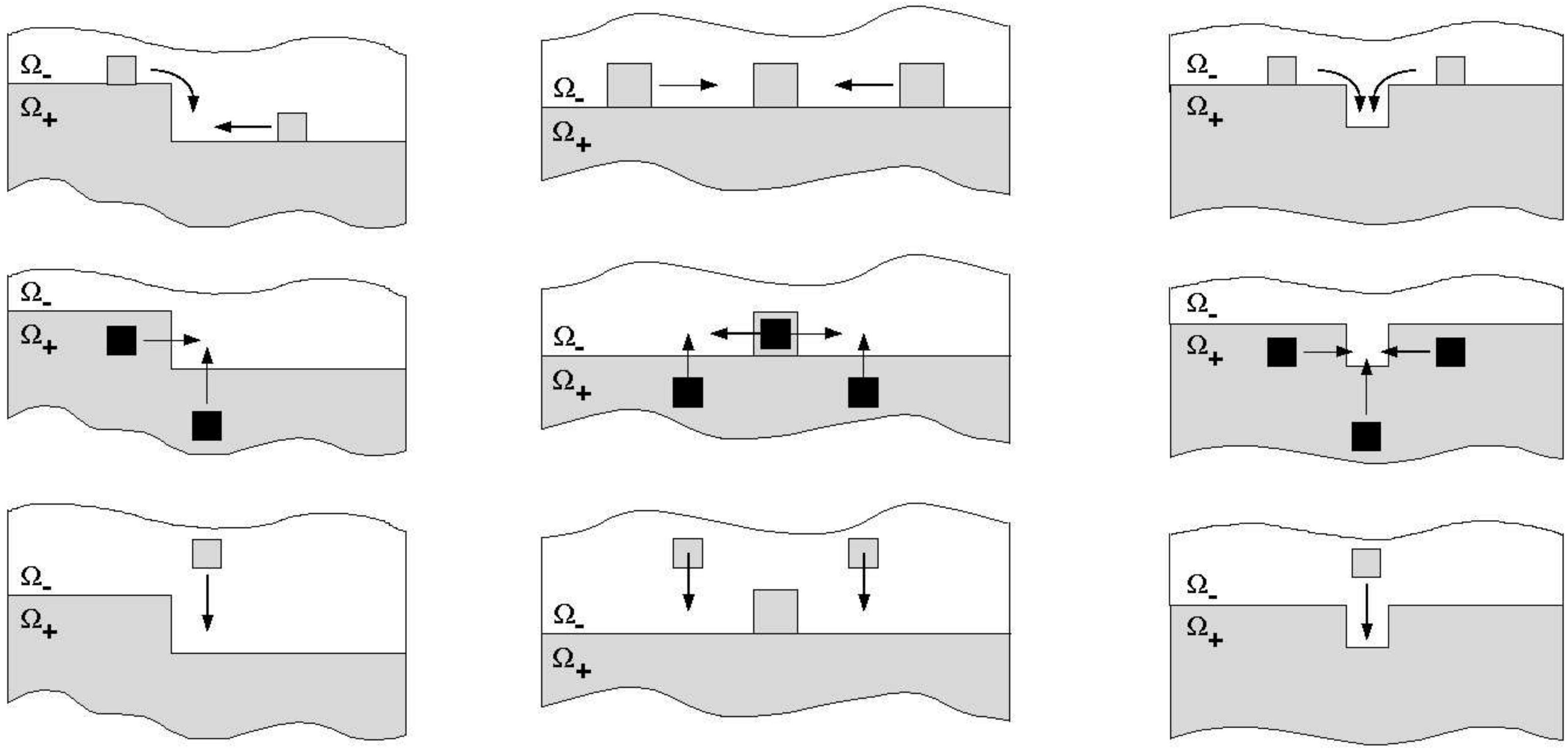
  $\partial_t \varphi - D_E \partial_s^2 \varphi = f_+ + f_- - f_0$ on edge

  $\partial_t k - \partial_s (w (k_r - k_\ell))= 2 (g - h)$ on edge

- Boundary conditions for ρ on edge from left (+) and right (-)
  - $v \rho_+ + D_T \mathbf{n}\cdot\nabla \rho = - f_+$
  - $v \rho_+ + D_T \mathbf{n}\cdot\nabla \rho = f_-$
- Variables
  - ρ = adatom density on terrace
  - φ = edge atom density
  - k = kink density
- Parameters
  - D_T, D_E, D_K, D_S = diffusion coefficients for terrace, edge, kink, solid
- Interaction terms
  - v,w = velocity of kink, step edge
  - F, $f_{\pm}$, f_0 = flux to surface, to edge, to kinks
  - g,h = creation, annihilation of kinks

Adatom and Kink Dynamics on a Step Edge

top view of step edge



Attachment at kinks
♏ kink velocity w

Kink pair creation
♏ kink creation rate g

Kink pair collision
♏ kink loss rate h

Reverse processes do not occur in typical MBE growth
♏ no detailed balance ♏ nonequilibrium

Constitutive relations

- Geometric conditions for kink density
  - $k_r + k_\ell = k$
  - $k_r - k_\ell = -\tan\theta$
- Velocity of step
  - $v = w\, k \cos\theta$
- Flux from terrace to edge,
  - $f_+ = D_T\, \rho_+ - D_E\, \varphi$
  - $f_- = D_T\, \rho_- - D_E\, \varphi$
- Flux from edge to kinks
  - $f_0 = v(\varphi\, \kappa + 1)$
- Microscopic equations for velocity w, creation rate g and annihilation rate h for kinks
  - $w = 2\, D_E\, \varphi + D_T\, (2\rho_+ + \rho_-) - 5\, D_K$
  - $g = 2\, (D_E\, \varphi + D_T\, (2\rho_+ + \rho_-))\, \varphi - 8\, D_K\, k_r\, k_\ell$
  - $h = (2D_E\, \varphi + D_T\, (3\rho_+ + \rho_-))\, k_r\, k_\ell - 8\, D_S$

Asymptotics for Large D/F

- Assume slowly varying kinetic steady state along island boundaries
  - expansion for small "Peclet number" $f / D_E = \varepsilon^3$
  - f is flux to edge from terrace
- Distinguished scaling limit
  - $k = O(\varepsilon)$
  - $\varphi = O(\varepsilon^2)$
  - $\varphi = O(\varepsilon^2)$ = curvature of island boundary = X_{yy}
  - $Y = O(\varepsilon^{-1/2})$ = wavelength of disurbances
- Results at leading order
  - $v = (f_+ + f_-) + \underbrace{D_E \varphi_{yy}}$ edge diffusion
  - $k = c_3 v / \varphi$
  - $c_1 \varphi^2 - c_2 \varphi^{-1} v = \underbrace{(\varphi X_y)_y}$ curvature
- Linearized formula for φ
  - $\varphi = c_3 (f_+ + f_-)^{2/3} - c_4 \varphi$

Macroscopic Boundary Conditions

- Island dynamics model
  - $\rho_t - D_T \quad \rho = F$ adatom diffusion between step edges
  - $X_{\ t} = v$ velocity of step edges
- Microscopic BCs for ρ

$$D_T\, \mathbf{n}\cdot \mathrm{grad}\, \rho = D_T\, \overbrace{\rho - D_E}^{\text{detachment}}\, \varphi \equiv f$$

- From asymptotics
  - θ_{*}= reference density = $(D_E / D_T)\, c_1((f_+ + f_-)/ D_E)^{2/3}$
  - γ = line tension = $c_4 D_E$
- BCs for ρ on edge from left (+) and right (-), step edge velocity

$$\pm D_T\, \mathbf{n}\cdot \mathrm{grad}\, \rho = D_T\, (\rho - \theta_{*}) + \gamma\, \kappa$$

$$v = (f_+ + f_-) + c\, (f_+ + f_-)_{ss} + \gamma\, \kappa_{ss}$$

Conclusions

- Kinetic model for step edge
  - kinetic steady state ≠ BCF equilibrium
  - validated by comparison to SOS/KMC
- Atomistic derivation of Gibbs-Thomson
  - includes effects of edge diffusion, curvature, detachment
- Open problems
  - derivation based on distinguished limit, rather than physical regime
  - derivation of surface diffusion