UCLA

Lecture 1
Modeling and simulation for the growth of thin films

Russel Caflisch
Mathematics Department
Materials Science and Engineering Department
UCLA
&
IPAM

www.math.ucla.edu/~material

Sapporo 2010

Outline

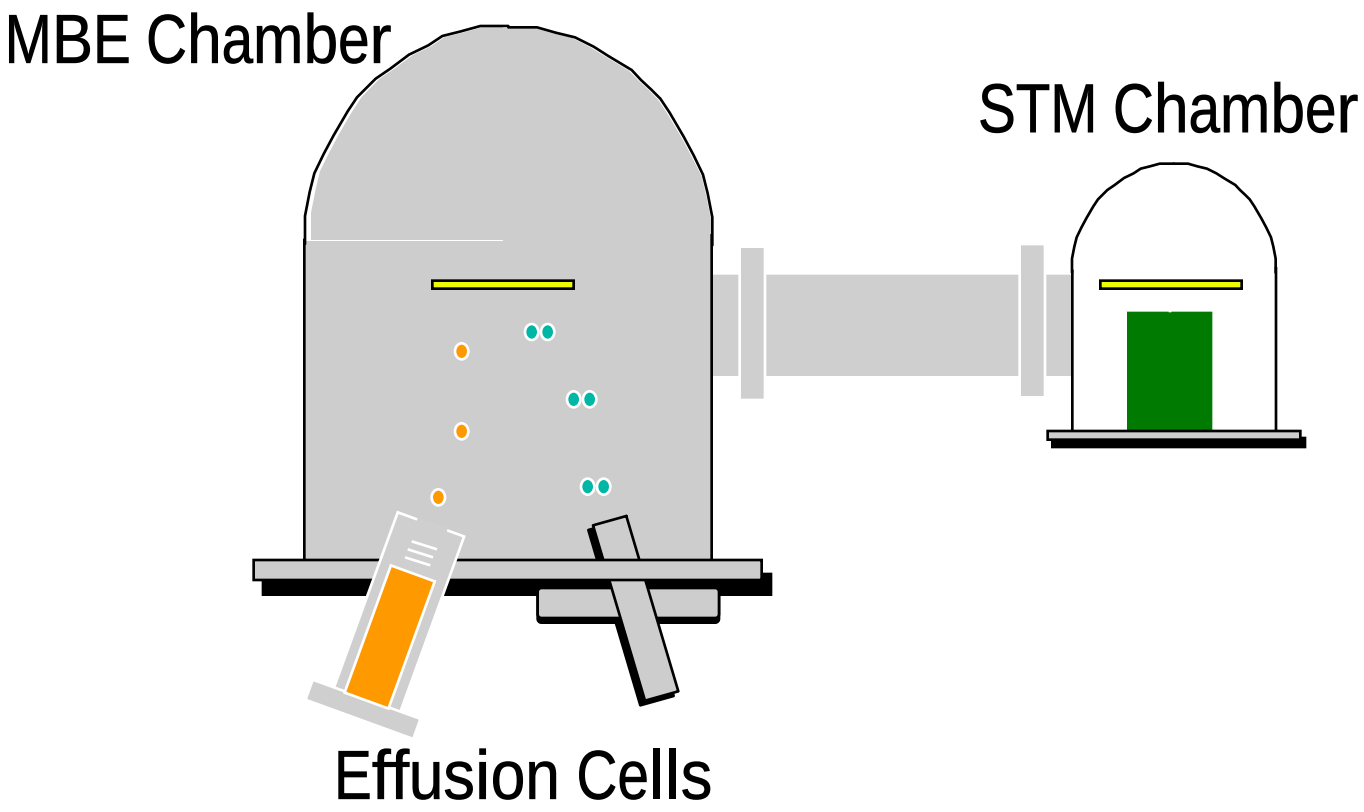
- Epitaxial Growth
  - molecular beam epitaxy (MBE)
  - Step edges and islands
- Solid-on-Solid using kinetic Monte Carlo
  - Atomistic, stochastic
- Island dynamics model
  - Continuum in lateral directions/atomistic in growth direction
  - Level set implementation
  - Kinetic step edge model
- Conclusions

Outline

- Epitaxial Growth
  - molecular beam epitaxy (MBE)
  - Step edges and islands
- Solid-on-Solid using kinetic Monte Carlo
  - Atomistic, stochastic
- Island dynamics model
  - Continuum in lateral directions/atomistic in growth direction
  - Level set implementation
  - Kinetic step edge model
- Conclusions

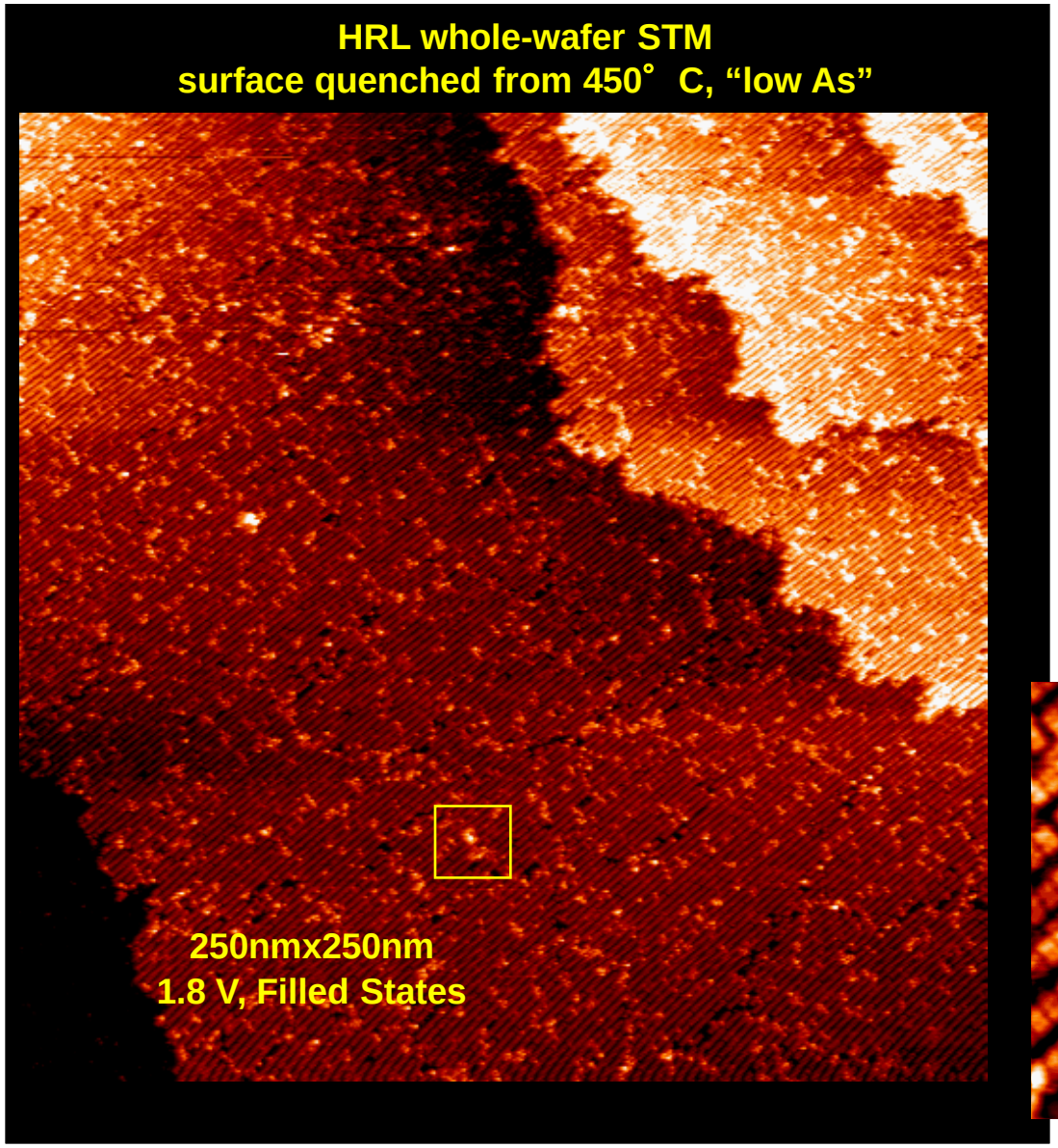
UCLA

Molecular Beam Epitaxy (MBE) Growth and Analysis Facility

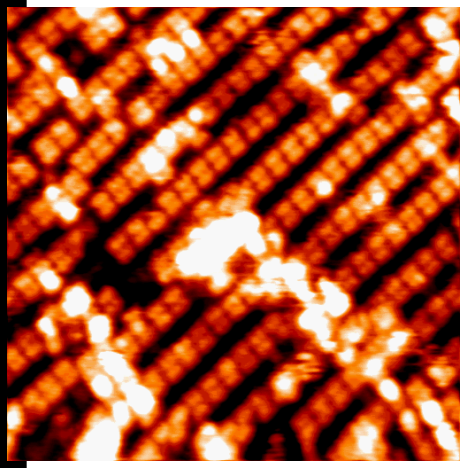


UCLA

STM Image of InAs



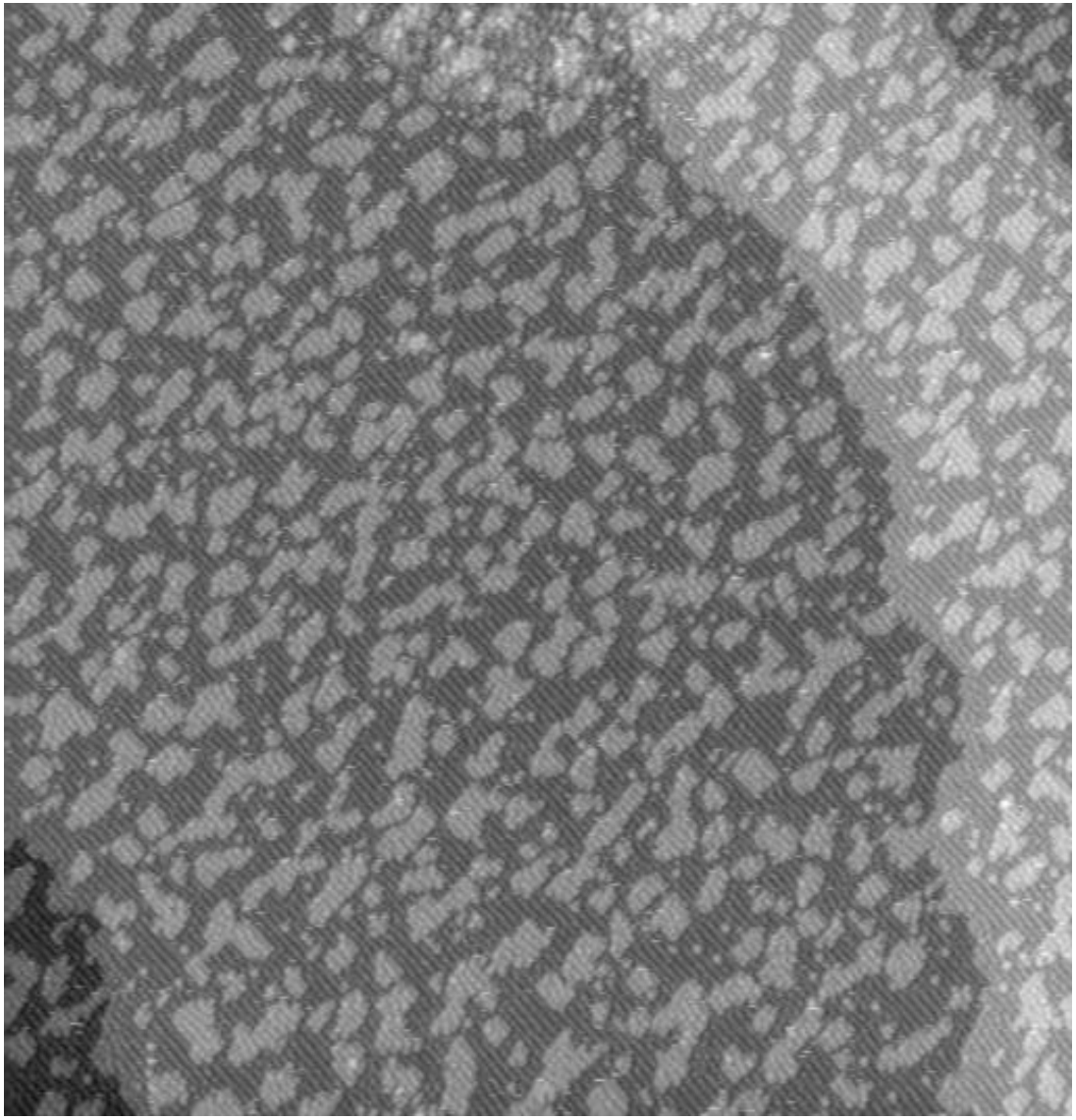
20nmx20nm



Barvosa-Carter, Owen, Zinck (HRL Labs)

UCLA

AlSb Growth by MBE

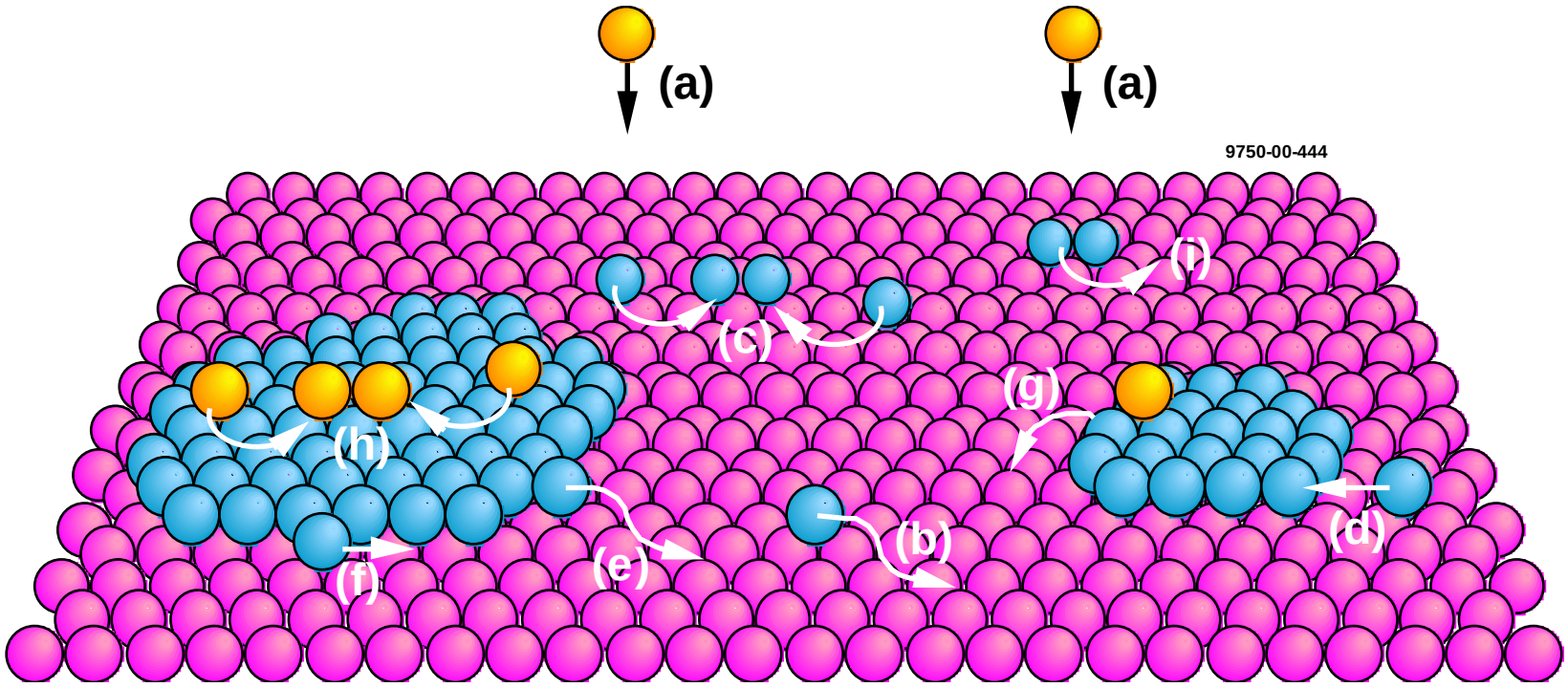


Barvosa-Carter and Whitman, NRL

Sapporo 2010

UCLA

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

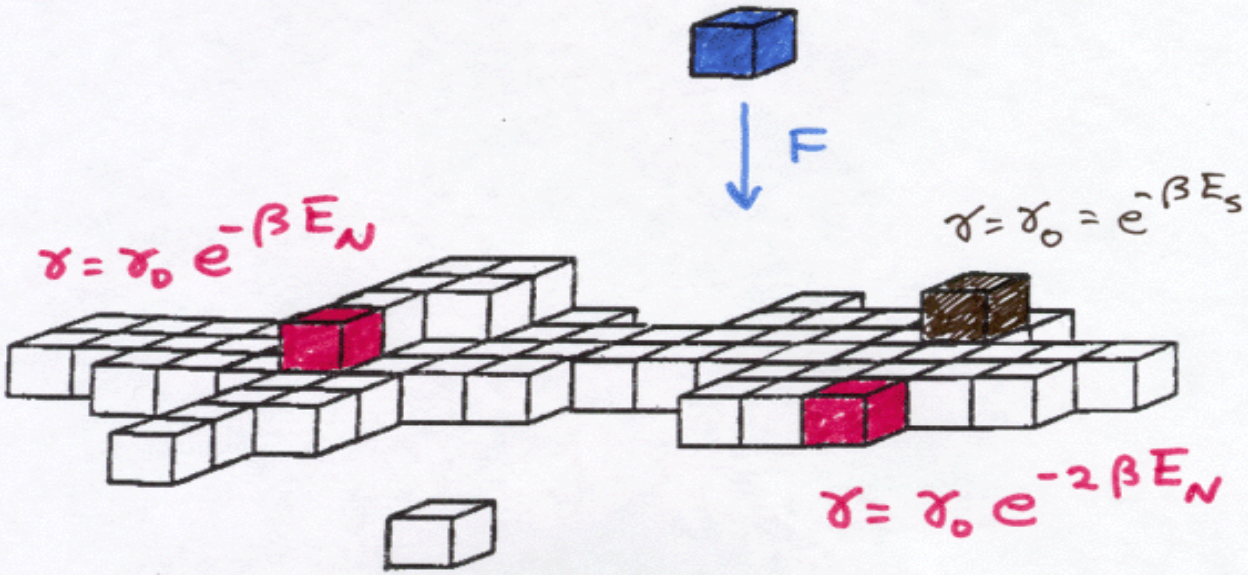
Outline

- Epitaxial Growth
  - molecular beam epitaxy (MBE)
  - Step edges and islands
- Solid-on-Solid using kinetic Monte Carlo
  - Atomistic, stochastic
- Island dynamics model
  - Continuum in lateral directions/atomistic in growth direction
  - Level set implementation
  - Kinetic step edge model
- Conclusions

Solid-on-Solid Model

- Interacting particle system
  - Stack of particles above each lattice point
- Particles hop to neighboring points
  - random hopping times
  - Arrhenius 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

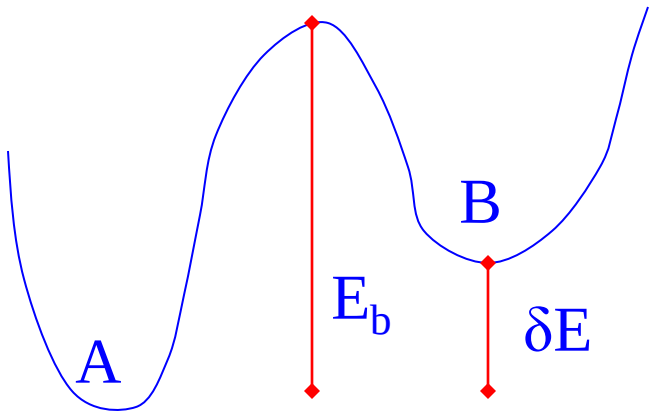


E_S : Substrate Bond Energy

E_N : Nearest Neighbor Bond Energy

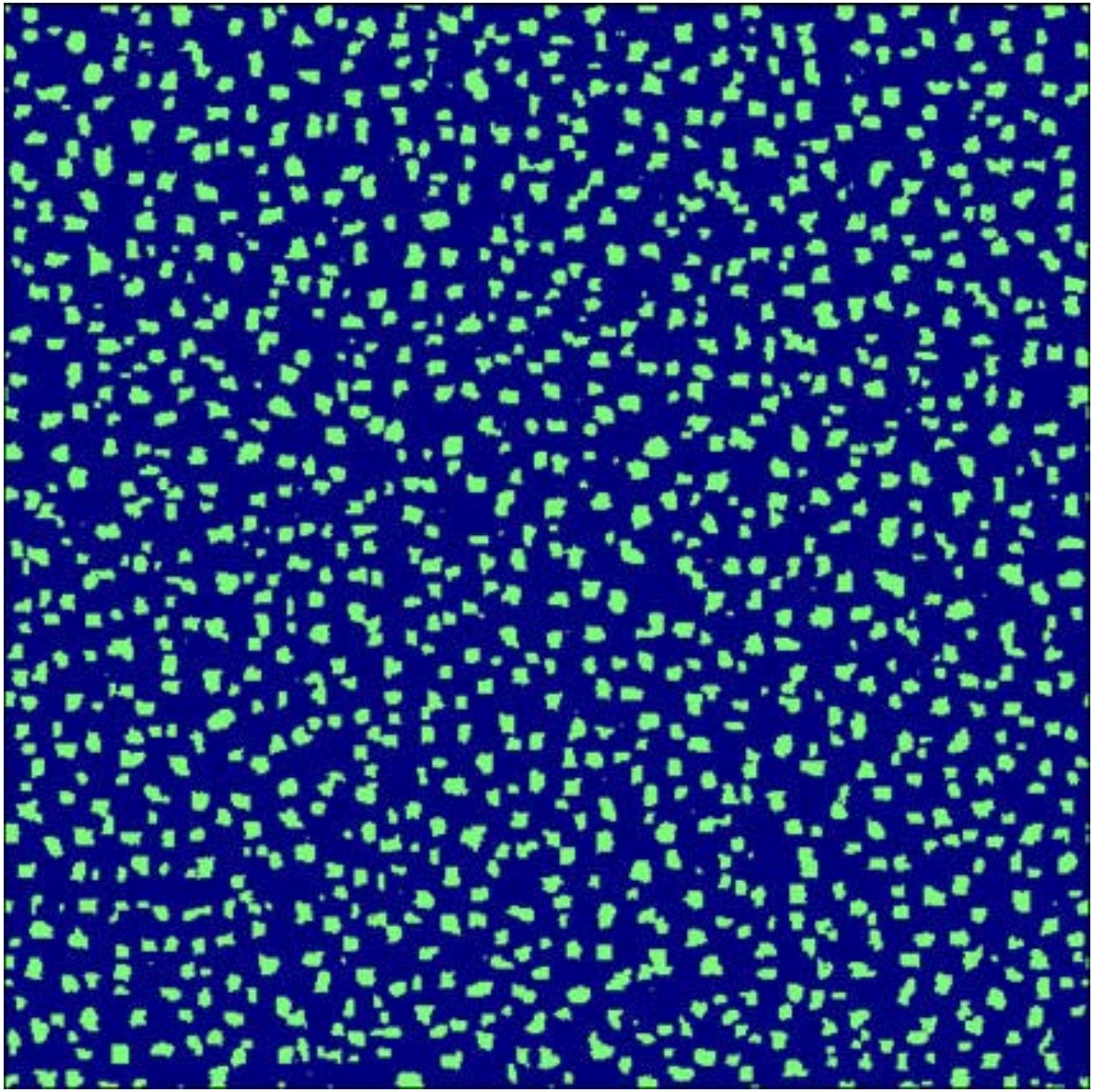
Kinetic Monte Carlo

- 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
- Transition state theory

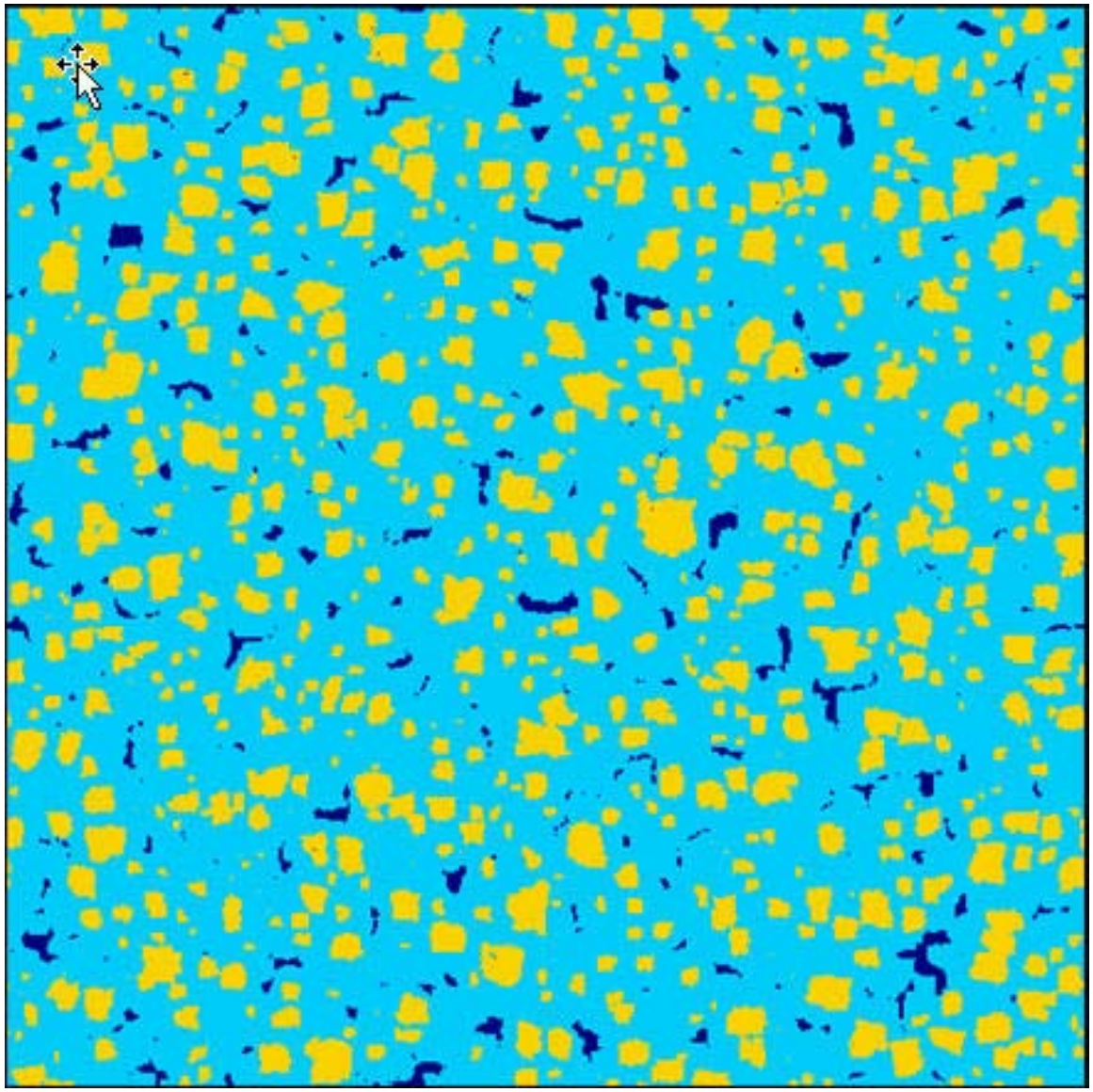


UCLA

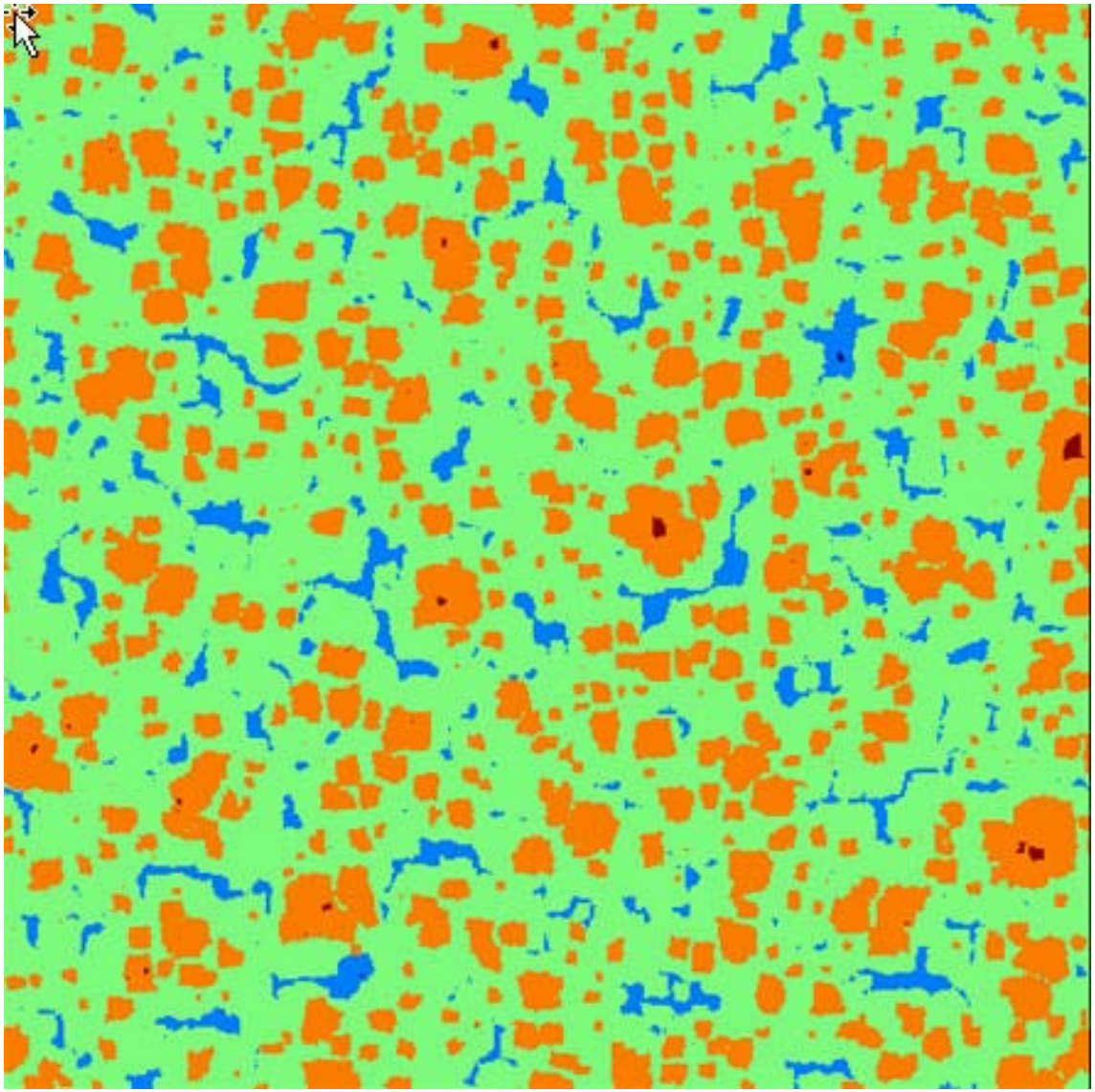
SOS Simulation for coverage=.2



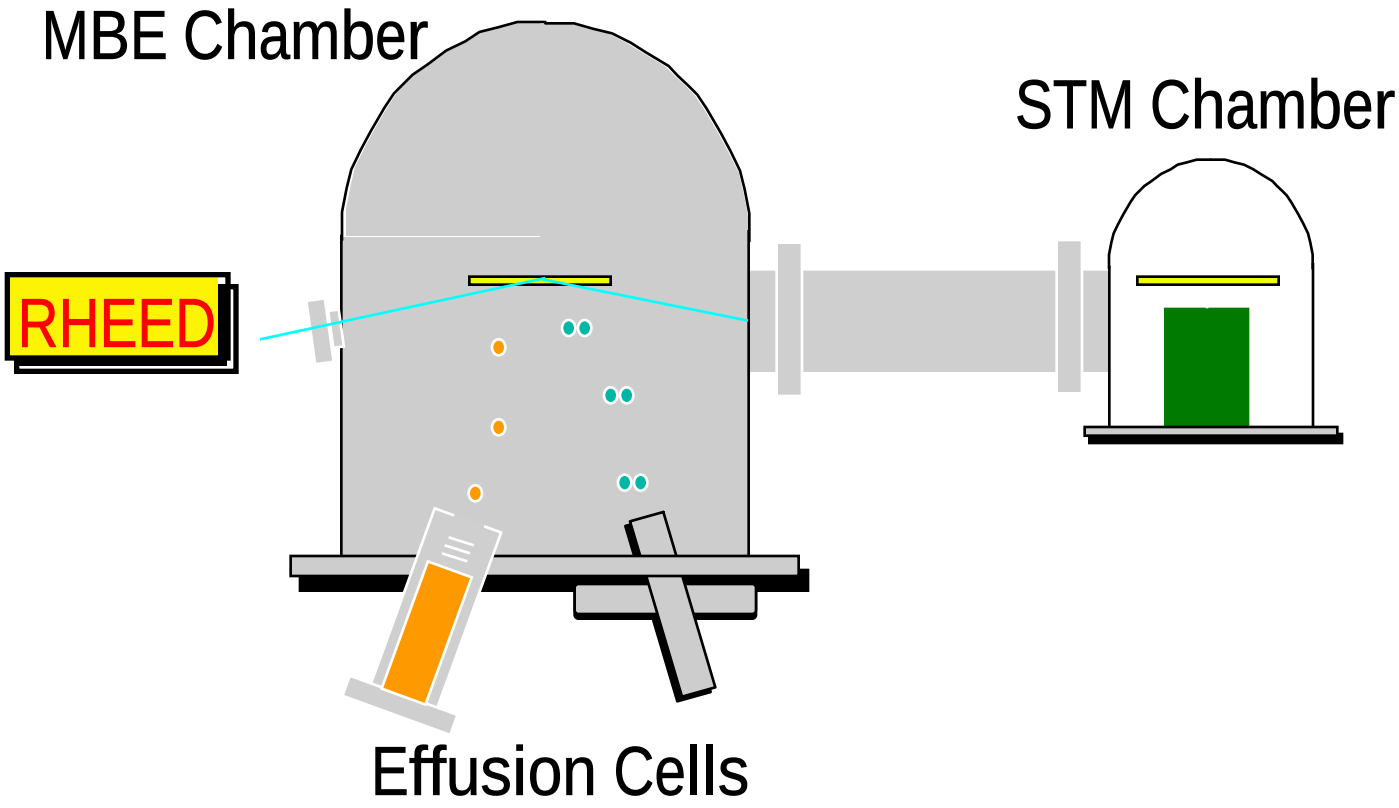
SOS Simulation for coverage=10.2



SOS Simulation for coverage=30.2



Molecular Beam Epitaxy (MBE) Growth and Analysis Facility



UCLA

Validation of SOS Model: Comparison of Experiment and KMC Simulation

(Vvedensky & Smilauer)

$E_S - E_N$ model

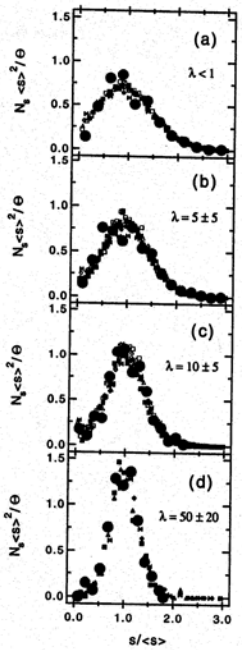
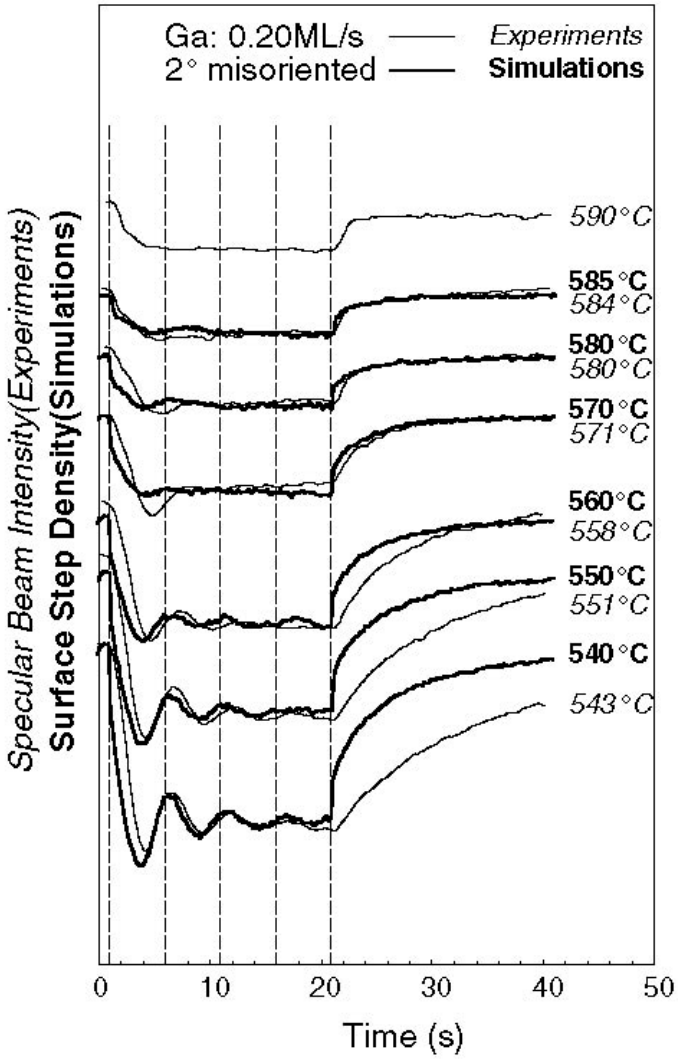


Fig. 4. Island size distributions for Fe/Fe(001) from Ref. [20] (large circles) compared to pair-bond model simulation results: (a) experiment at $T = 20°C$, simulation for $0.10 \le \theta \le 0.25$ with $E_N = 1.0$ eV and $F = 0.1$, s^{-1} (open symbols) and rm $E_N = 0.3$ eV and $F = 0.5$ s^{-1} (closed symbols); (b) experiment at $T = 163°C$, simulation for $0.10 \le \theta \le 0.25$ with $E_N = 0.7$ eV and $F = 0.001$ s^{-1} (open symbols) and $E_N = 0.3$ eV and $F = 0.2$ s^{-1} (closed symbols); (c) experiment at $T = 250°C$, simulation for $0.12 \le \theta \le 0.25$ with $E_N = 0.6$ eV and $F = 0.001$ s^{-1} (open symbols) and $E_N = 0.3$ eV and $F = 0.03$ s^{-1} (closed symbols); (d) experiment at $T = 356°C$, simulation for $0.12 \le \theta \le 0.25$ with $E_N = 0.3$ eV and $F = 0.001$ s^{-1}.

Vvedensky et al.

Island size density

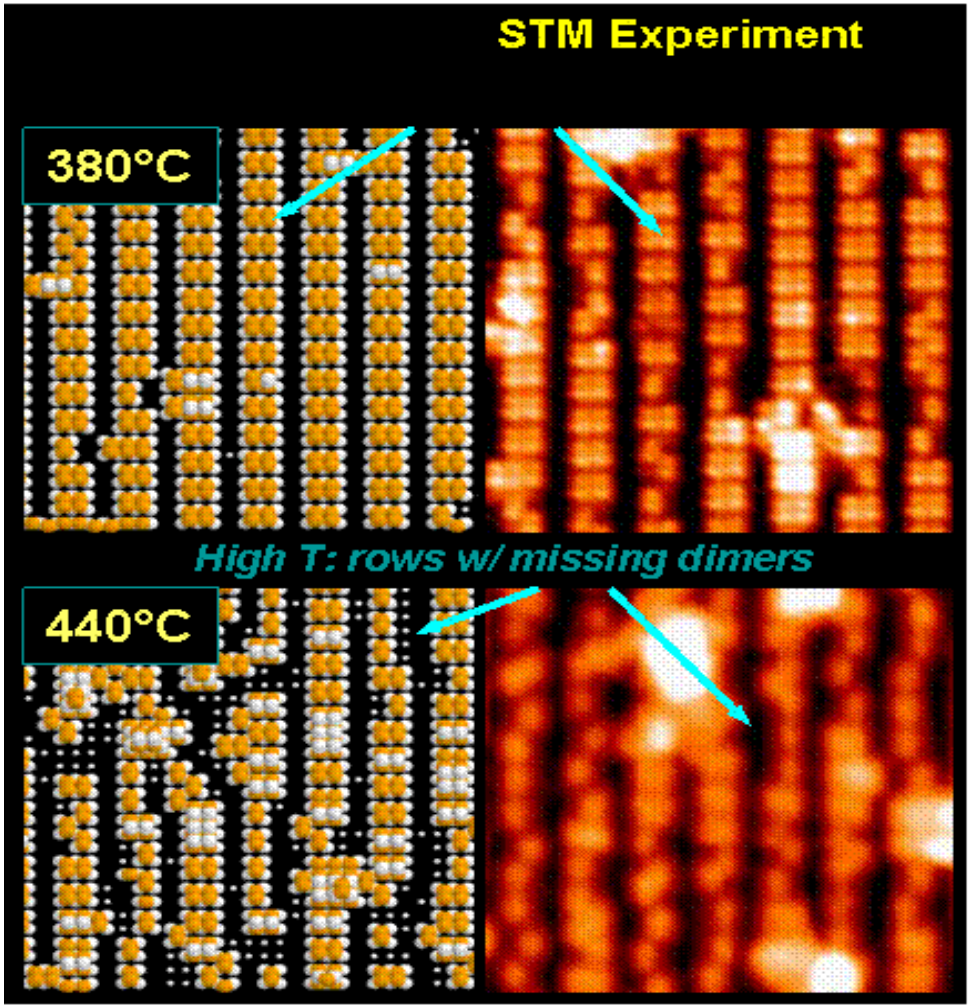


Step Edge Density (RHEED)

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)

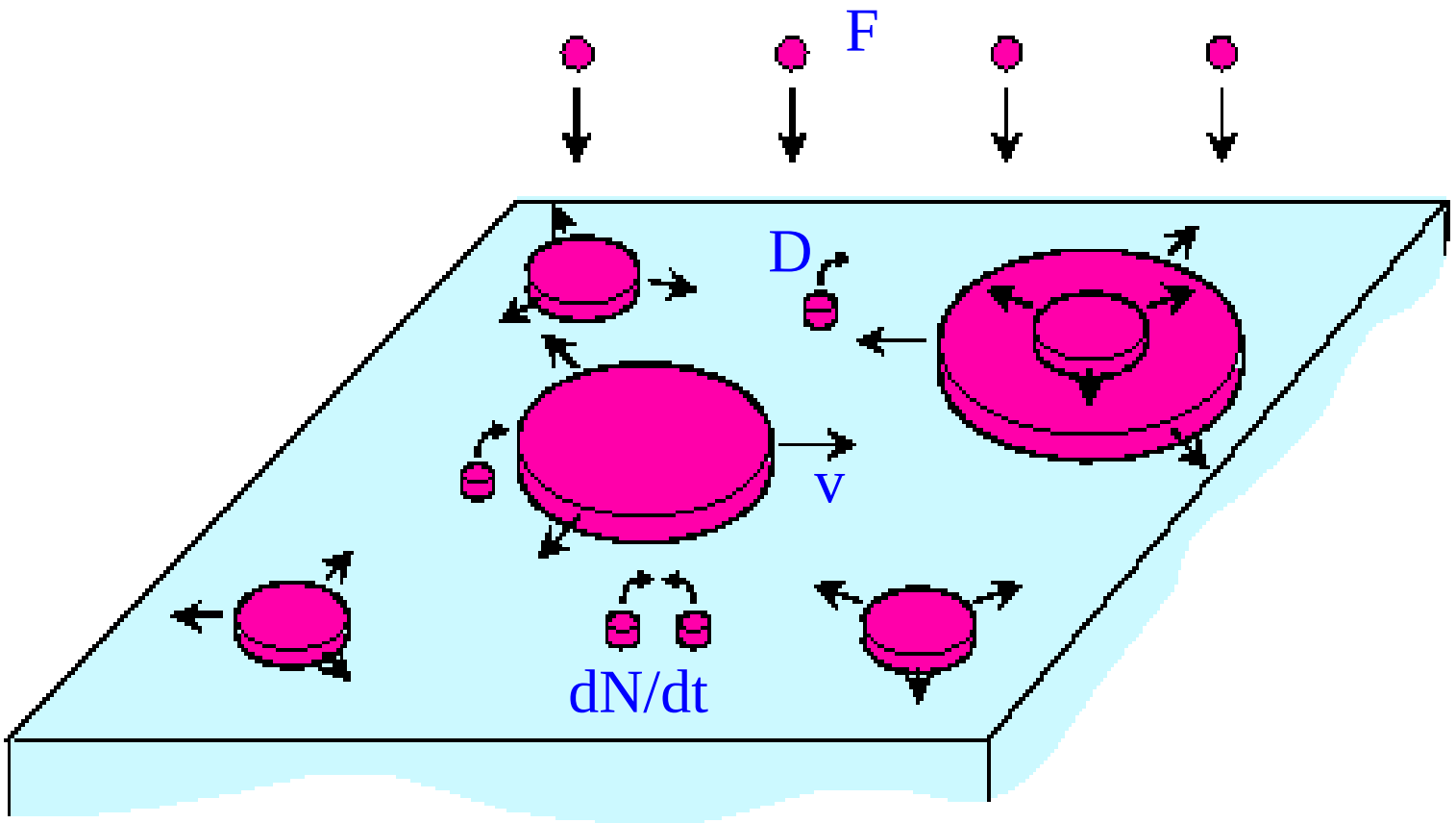
High resolution KMC (left); STM images (right)

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

Outline

- Epitaxial Growth
  - molecular beam epitaxy (MBE)
  - Step edges and islands
- Solid-on-Solid using kinetic Monte Carlo
  - Atomistic, stochastic
- Island dynamics model
  - Continuum in lateral directions/atomistic in growth direction
  - Level set implementation
  - Kinetic step edge model
- Conclusions

Island Dynamics



Island Dynamics

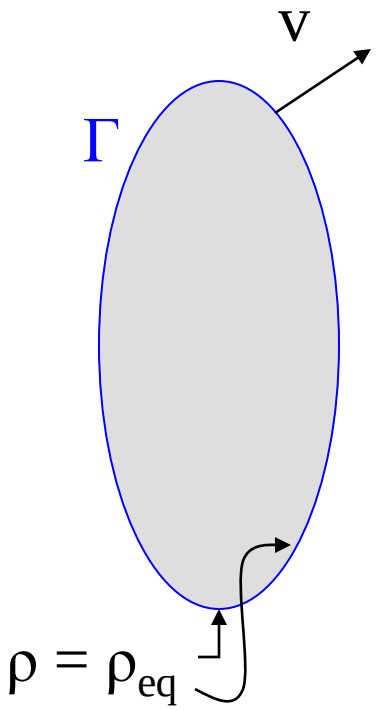
- BCF Theory: Burton, Cabrera, Frank (1951)
- Epitaxial surface
  - adatom density $\rho(x,t)$
  - Step edges = union of curves $\Gamma(t)$
  - continuum in lateral direction, atomistic in growth direction
- Evolution of ρ and Γ
  - Adatom diffusion equation with equilibrium BC

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

$$\rho = \rho_{eq} \quad \text{on } \Gamma(t)$$

  - F= deposition rate, D = diffusion coefficient
  - Step edge velocity: $\Gamma(t)$ moves at normal velocity

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



Additions to BCF Theory

- Nucleation and breakup of islands
- Step stiffness/line tension
- Strain effects (Lecture 2)
- Numerical implementation: Level set method

Nucleation (and Breakup)

- Islands nucleate due to collisions between adatoms
  - Rate = $D\ \sigma_1\ \rho^2$
  - σ_1 = capture number for nucleation
    - accounts for correlation between random walkers: they have not collided earlier
- Modification in ρ eqtn
  - Nucleation is a loss term

$$\rho_t = D\Delta\rho + F - dN/dt$$
$$dN/dt = \int D\ \sigma_1\ \rho^2\ dx$$

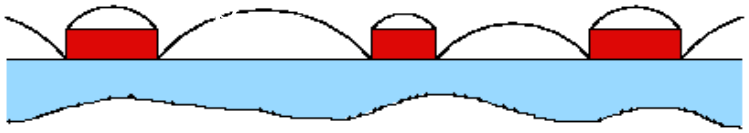
- Choice of nucleation time and position
  - Deterministic time, stochastic position
  - When N crosses an integer, nucleate a new island
    - $N(t) \approx$ # islands at time t
  - Choose position at random with probability density proportional to

$$D\ \sigma_1\ \rho^2$$

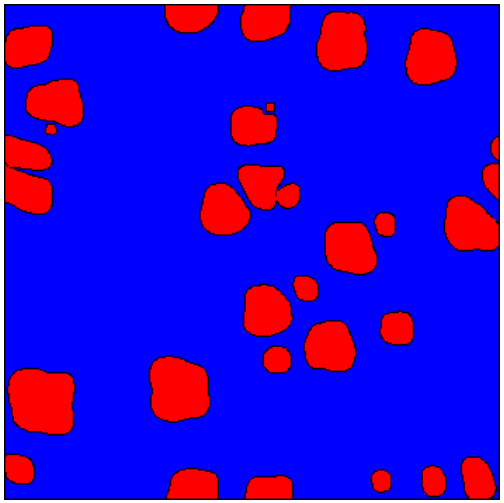
  - Alternatives to this choice of position were not successful
  - Ratsch et al. (2000)
- Similar method for adatom detachment and breakup of small islands

Nucleation:
Deterministic Time, Random Position

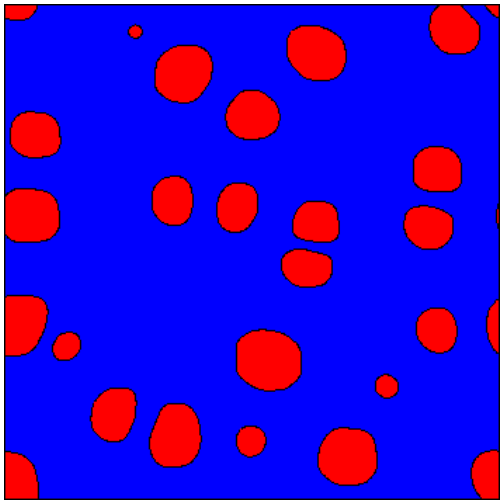
$$\frac{dN}{dt} = D\left\langle \rho(\mathbf{x},t)^2 \right\rangle$$



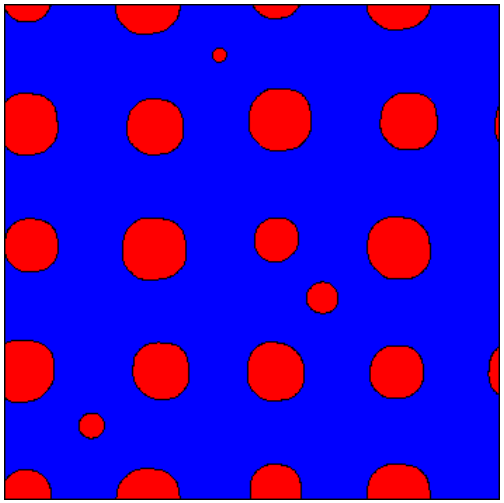
Random Seeding
independent of ρ



Probabilistic Seeding
weight by local ρ^2



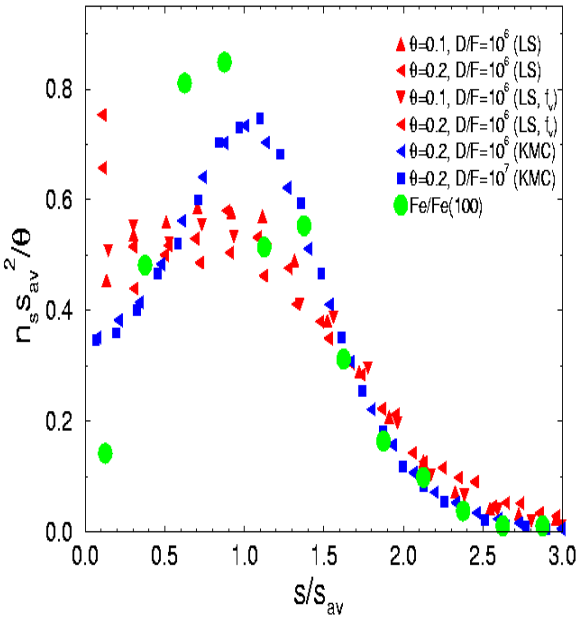
Deterministic Seeding
seed at maximum ρ^2

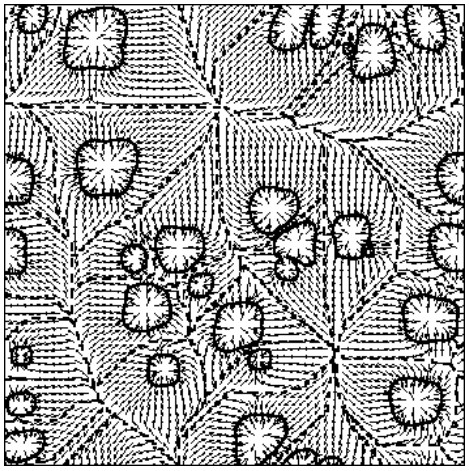


UCLA

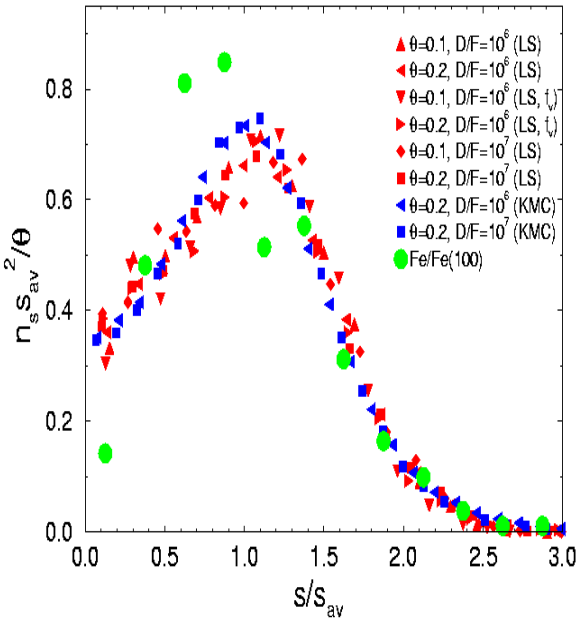
Effect of Seeding Style on Scaled Island Size Distribution

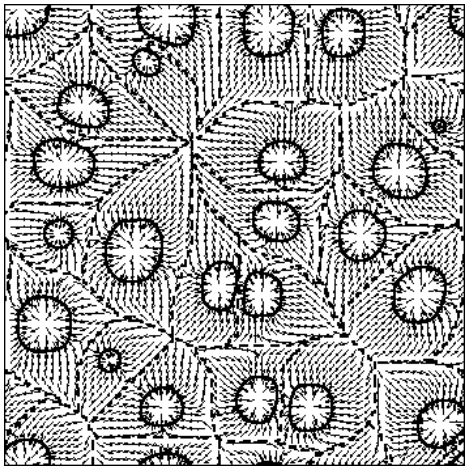
Random Seeding



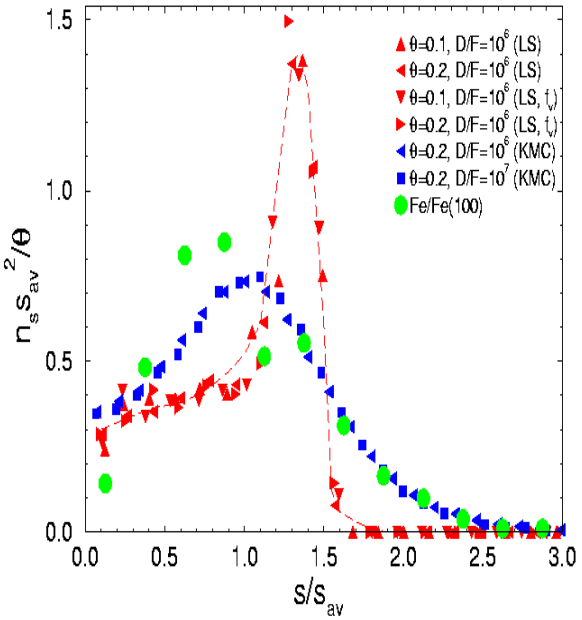


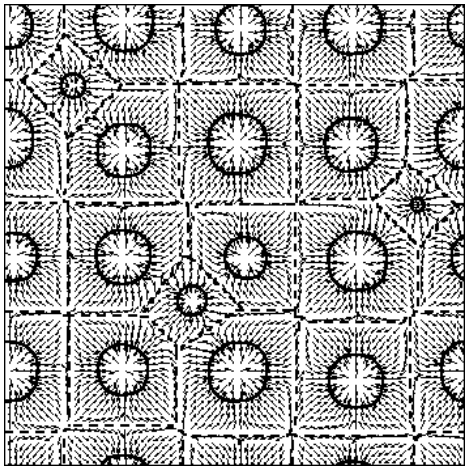
Probabilistic Seeding





Deterministic Seeding





C. Ratsch et al., Phys. Rev. B (2000)

Line Tension/Step Stiffness

- Gibbs-Thomson terms: boundary condition for ρ and island velocity v

$$D\,\partial\rho/\partial n = D(\rho - \rho_*) - \tilde{\mu}\,\kappa$$

$$v = D\,[\partial\rho/\partial n] - \tilde{\mu}\,\kappa_{ss}$$

  - Line tension γ and step stiffness $\tilde{\gamma}$ satisfy

$$\tilde{\gamma} = (T / D\rho_*)\tilde{\mu}$$ = free energy per unit length

$$\tilde{\gamma} = \gamma + \gamma_{ss}$$

- Asymptotic analysis of detailed step edge model for $|\kappa| < O(P_{edge}) << 1$
  - First derivation of Gibbs-Thomson from kinetics rather than energetics
    - Previous derivations use equilibrium or thermodynamic driving forces
  - ρ_* from kinetic steady state RC & Li (2003)
  - Anisotropy of $\tilde{\gamma}$ RC & Margetis (2007)

Anisotropy of step stiffness $\tilde{\gamma}$

$$\tilde{\gamma} = \begin{cases} c\,\theta^{-1} & \text{for } P_E^{1/2} << \theta << 1 \\ O(1) & \text{for } 0 < \theta << P_E^{1/2} \end{cases}$$

$$c = \bar{c}\,\left(f_+ + f_-\right)_\theta$$

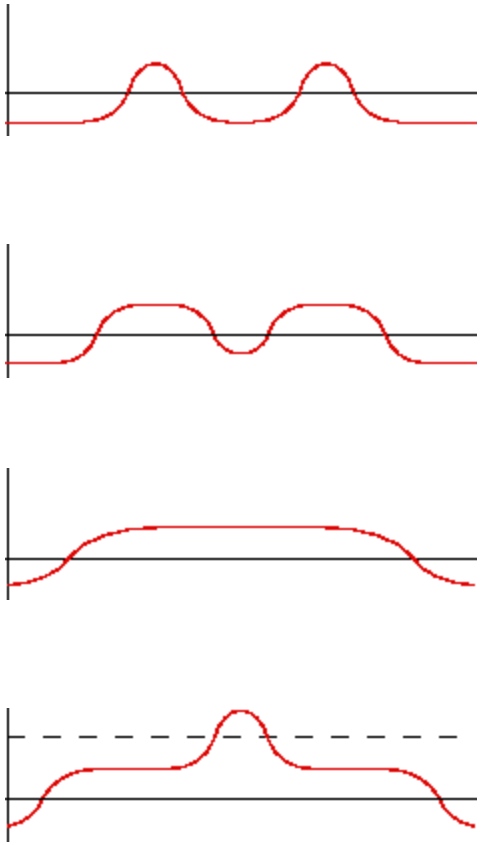
- θ = angle of step edge
- f_+, f_- are flux from upper, lower terrace
- θ^{-1} similar to results for Ising model, near-equilibrium by Einstein and Stasevich (2005)

Level Set Method

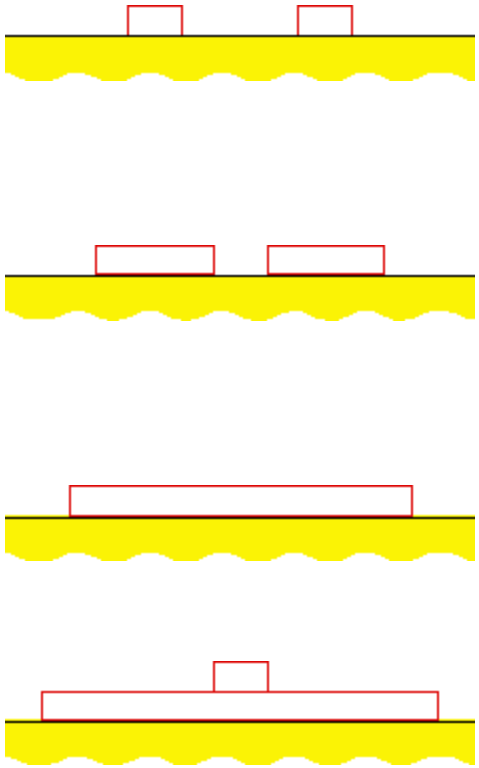
- Level set equation for description and motion of 
  -  (t) =boundary for islands of height n = { x : φ(x,t) = n }
  - $\varphi_t + v\,|\text{grad}\,\varphi| = 0$
  - v = normal velocity of 
  - Nucleation of new islands performed by "manual" raising of level set function. Requires minimal size (4 atoms) for new islands
- Implementation
  - REC, Gyure, Merriman, Ratsch, Osher, Zinck (1999)
  - Chopp (2000)
  - Smereka (2000)
- Choice of grid
  - Numerical grid needed for diffusion and LS equations
  - Physical (atomistic) grid needed for nucleation and breakup
  - We use a single atomistic grid, which we consider to be a numerical grid when needed

The Levelset Method

Level Set Function φ

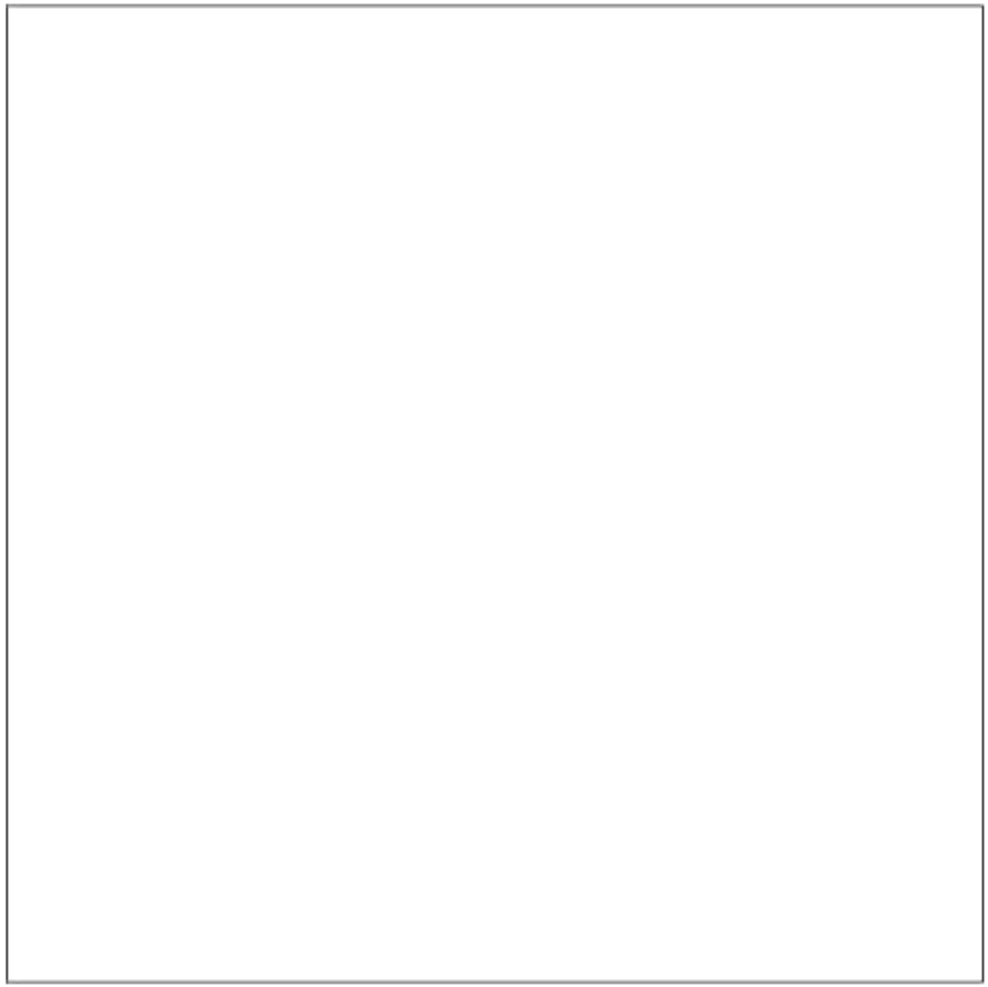


Surface Morphology



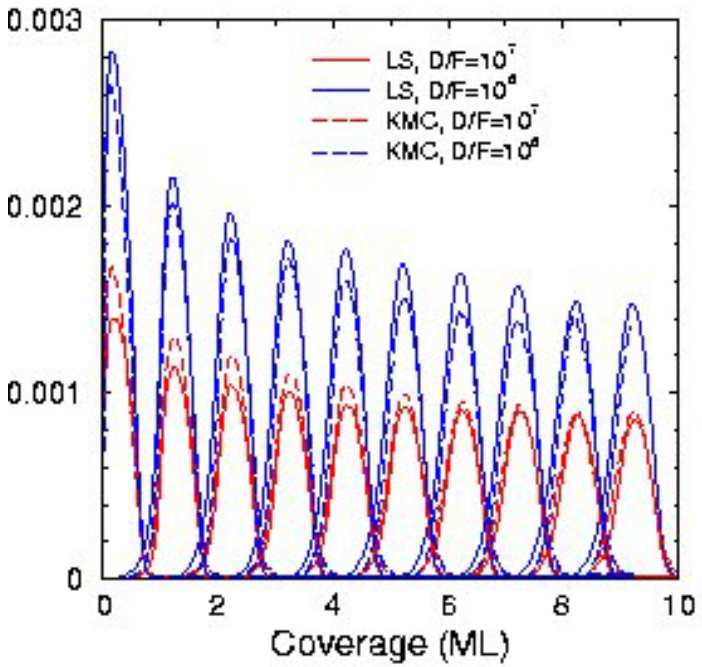
UCLA

Simulated Growth by the Island Dynamics/Level Set Method

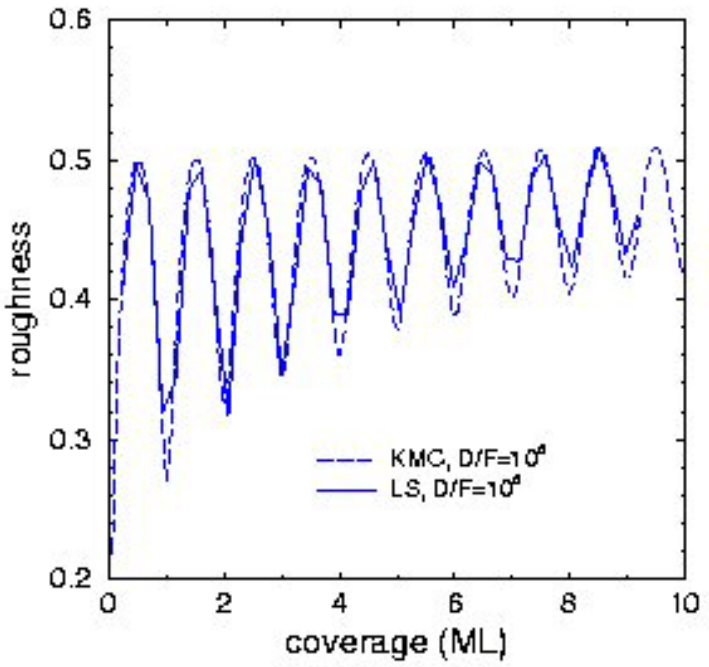


Multilayer Comparison Levelset - KMC

Island Densities



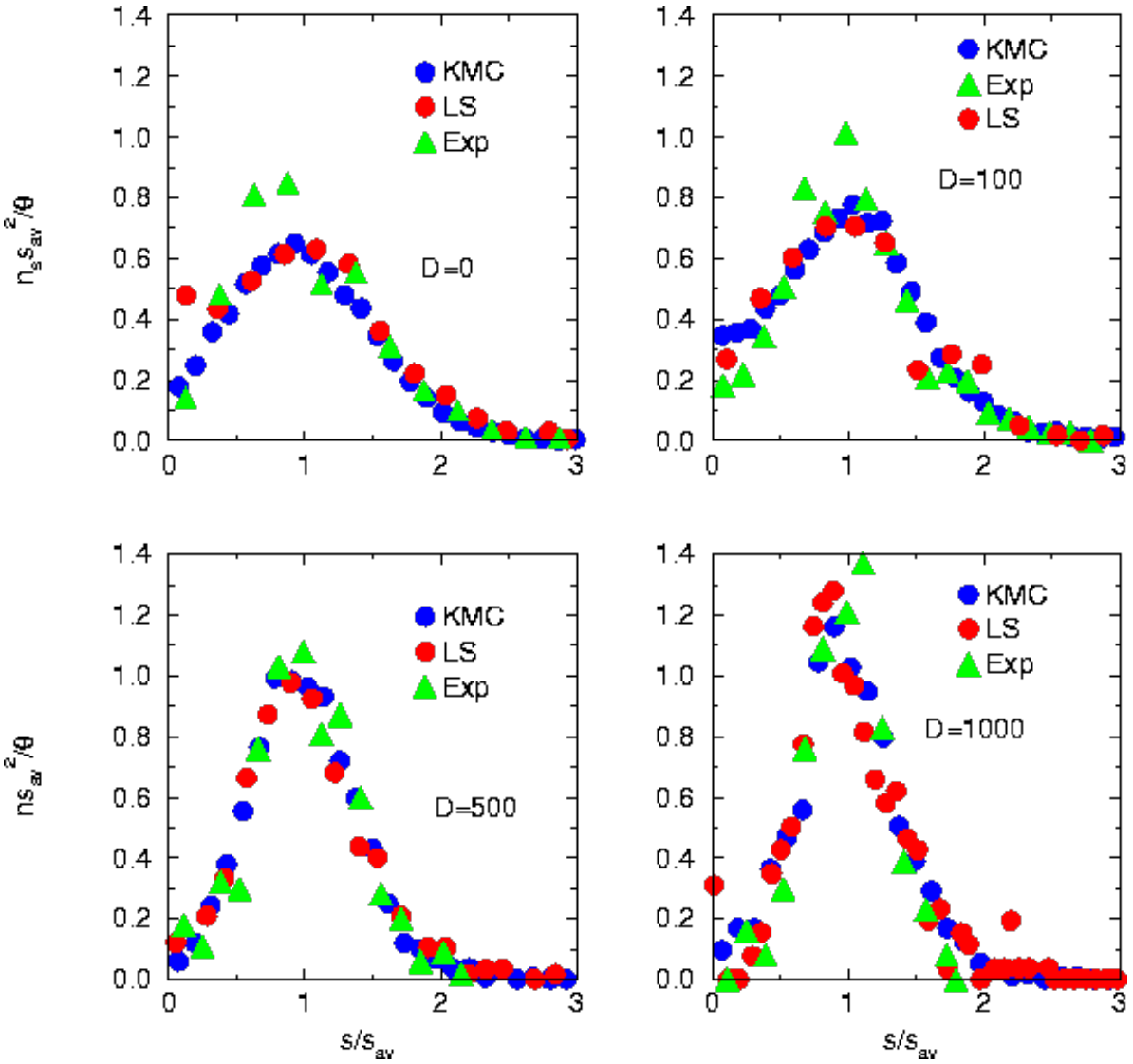
Surface Roughness



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

LS = level set implementation of island dynamics

Island size distributions



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

D = detachment rate

Stochastic nucleation and breakup of islands

Petersen, Ratsch, REC, Zangwill (2001)

Computational Speed: Level Set vs. KMC

- LS ≈ KMC for nucleation dominated growth
  - Diffusion computation on atomistic lattice is slow
- LS >> KMC for attachment/detachment dominated
  - Frequent attachment/detachment events represented by single effective detachment

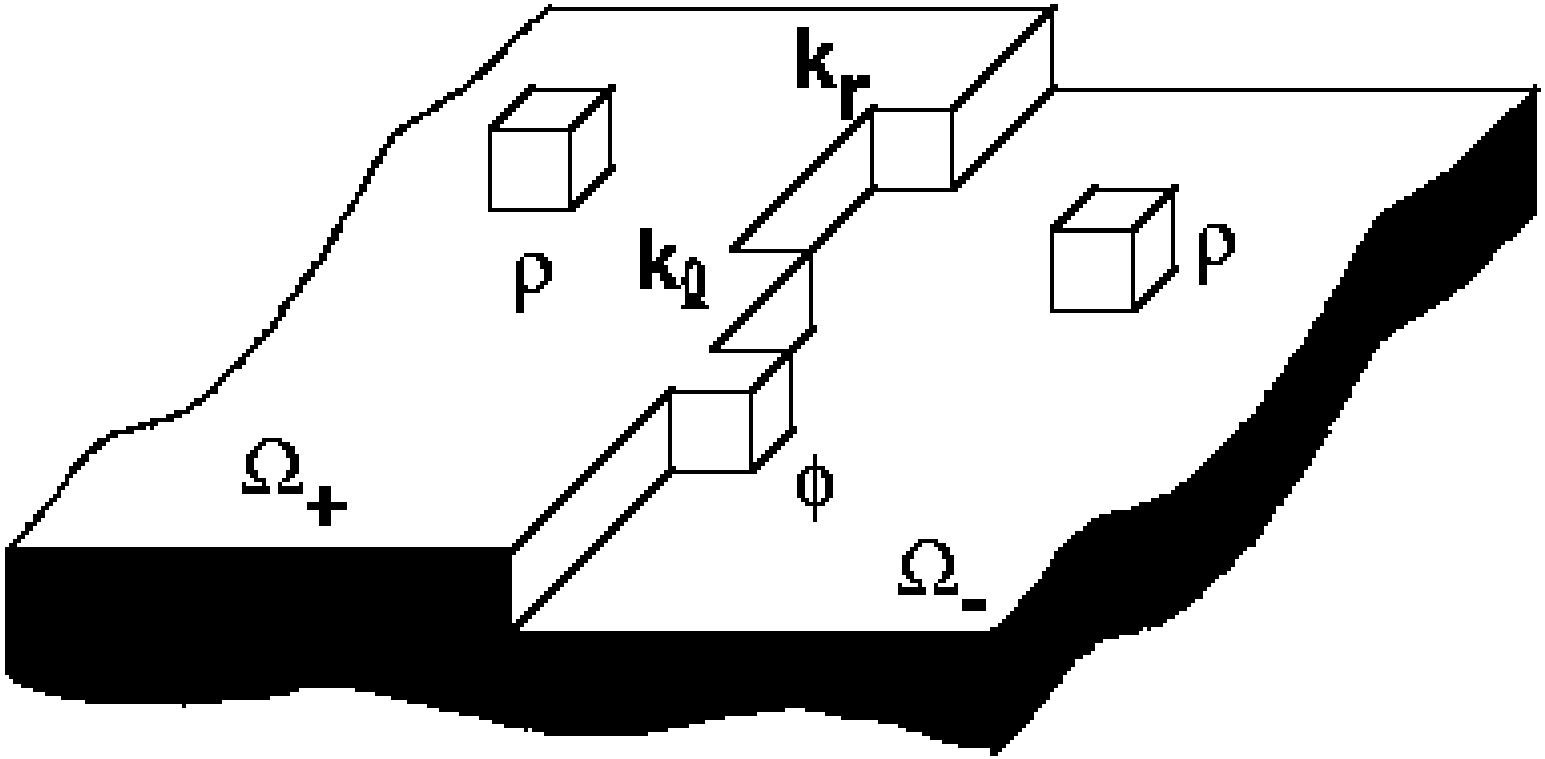
Outline

- Epitaxial Growth
  - molecular beam epitaxy (MBE)
  - Step edges and islands
- Solid-on-Solid using kinetic Monte Carlo
  - Atomistic, stochastic
- Island dynamics model
  - Continuum in lateral directions/atomistic in growth direction
  - Level set implementation
  - Kinetic step edge model
- Conclusions

Kinetic Theory for Step Edge Dynamics

- Theory for structure and evolution of a step edge
  - Mean-field assumption for edge atoms and kinks
  - Dynamics of corners are neglected
- Equilibrium solution (BCF)
  - Gibbs distribution $e^{-E/kT}$ for kinks and edge atoms
  - Detailed balance at edge between each process and the reverse process
- Kinetic steady state
  - Based on balance between unrelated processes
- Applications of detailed model
  - Estimate of roughness of step edge, which contributes to detachment rate
  - Starting point for kinetic derivation of Gibbs-Thomson
- References
  - REC, E, Gyure, Merriman & Ratsch (1999)
  - Similar model by Balykov & Voigt (2006), Filimonov & Hervieu (2004)
  - Related models by Evans & collaborators

Step Edge Model



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

- Evolution equations for φ, ρ, k

$$\partial_t \rho - D_T \Delta \rho = F \qquad \text{on terrace}$$

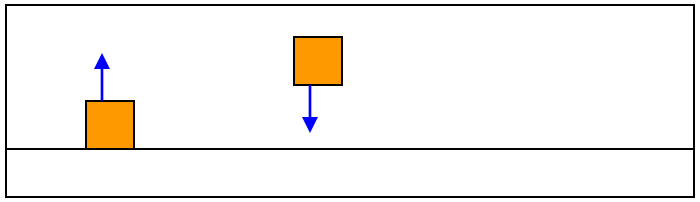
$$\partial_t \varphi - D_E \partial_s^2 \varphi = f_+ + f_- - f_0 \qquad \text{on edge}$$

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

Equilibrium from Detailed Balance

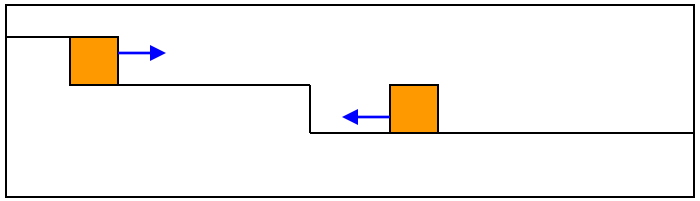
edge atom ↔ terrace adatom:

$D_E \varphi = D_T \rho$



kink ↔ edge atom:

$D_K k = D_E k \varphi$

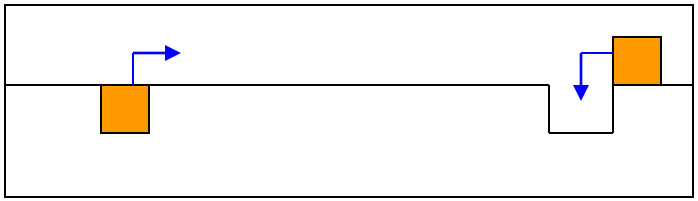


kink pair ("island")
↔ edge atom pair:

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

kink pair ("hole") + edge atom
↔ straight step:

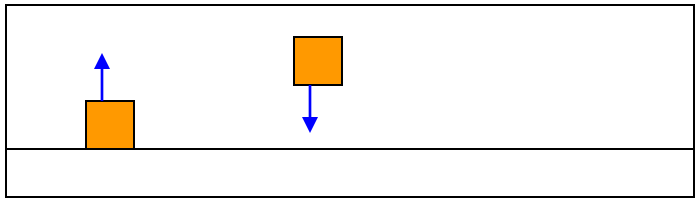
$D_S = D_E (1/4) k^2 \varphi$



Steady state Equilibrium from Kinetic Detailed Balance

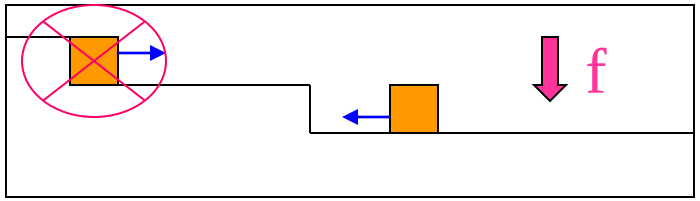
edge atom ↔ terrace adatom:

$D_E \varphi = D_T \rho$



kink ↔ edge atom:

$D_K k = D_E k \varphi$

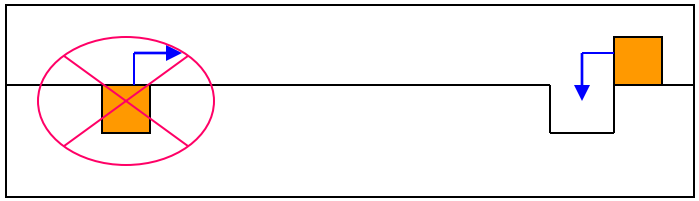


kink pair ("island")
↔ edge atom pair:

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

kink pair ("hole") + edge atom
↔ straight step:

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

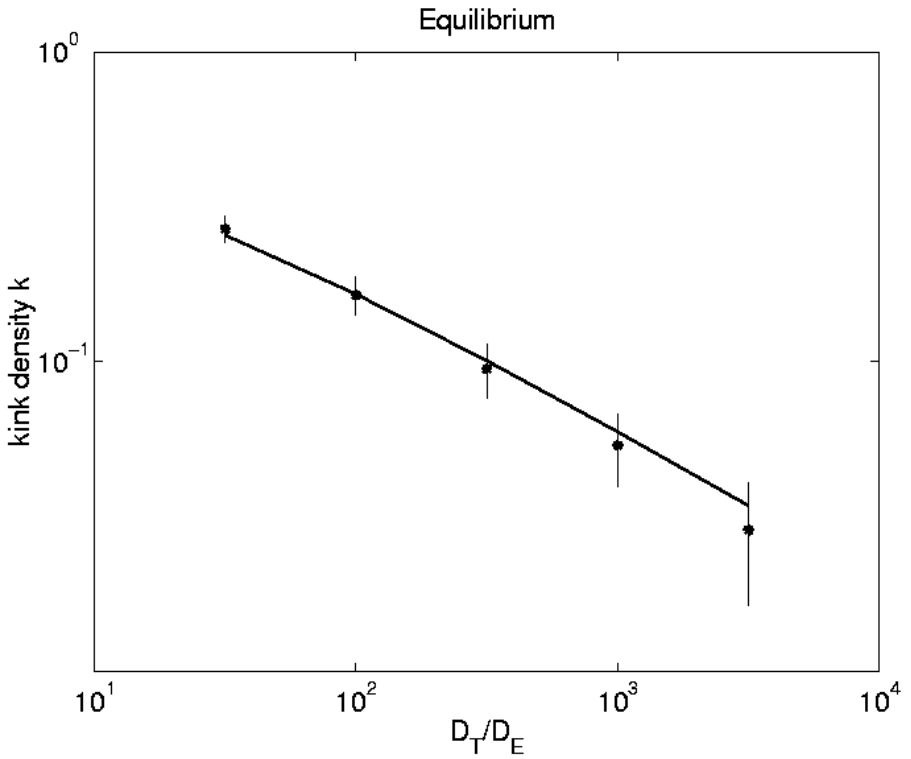


f= net flux to step edge

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)
- Derived from detailed balance
- D_T, D_E, D_K are diffusion coefficients (hopping rates) on Terrace, Edge, Kink in SOS model



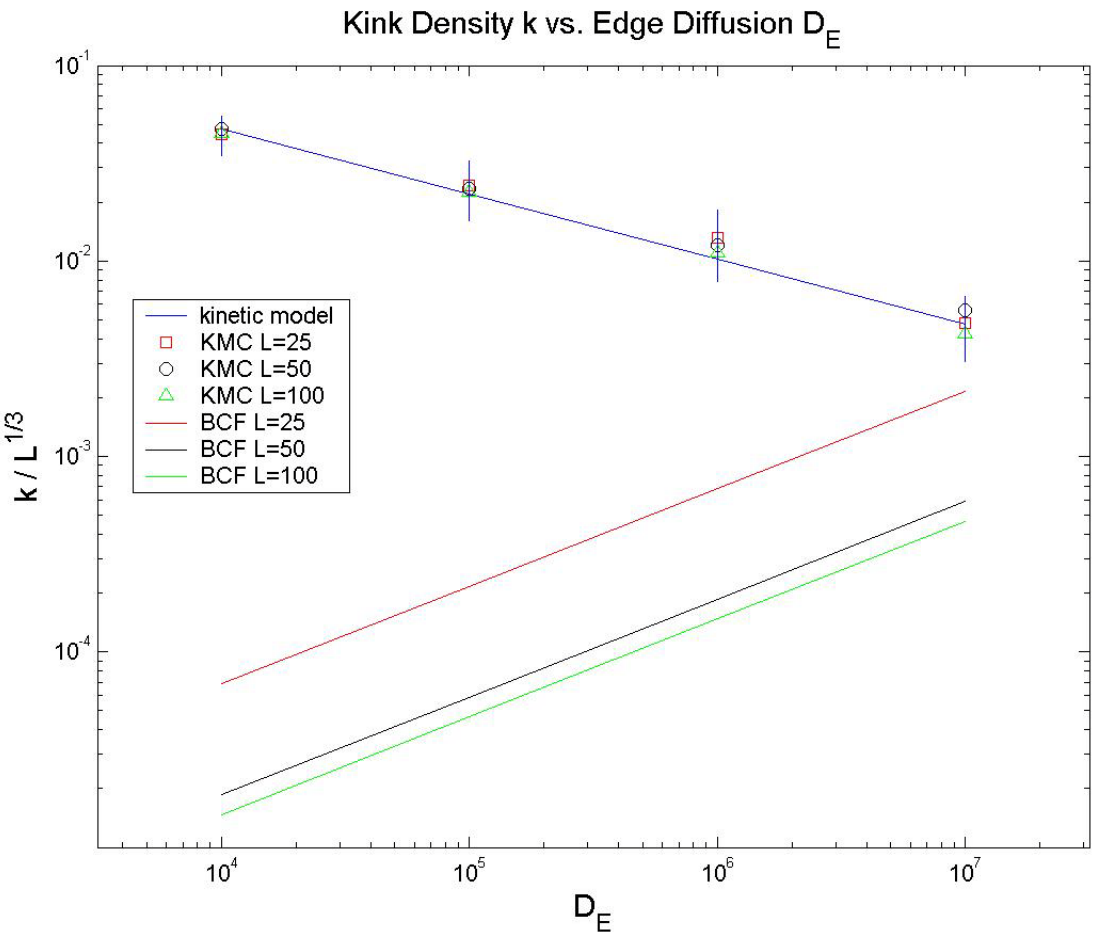
Comparison of results from theory(-) and KMC/SOS (●)

Kinetic Steady State vs. Equilibrium

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
- Derived from kinetic balance, not detailed balance
- $k >> k_{eq}$
- $P_{edge}=f/D_E$ "edge Peclet #"



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

Hybrid and Accelerated Methods: Island Dynamics and KMC

- Schulze, Smereka, E (2003)
- Russo, Sander, Smereka (2004)
- Schulze (2004)
- DeVita, Sander, Smereka (2006)
- Sun, Engquist, REC, Ratsch (2007)

Outline

- Epitaxial Growth
  - molecular beam epitaxy (MBE)
  - Step edges and islands
- Solid-on-Solid using kinetic Monte Carlo
  - Atomistic, stochastic
- Island dynamics model
  - Continuum in lateral directions/atomistic in growth direction
  - Level set implementation
  - Kinetic step edge model
- Conclusions

Summary

- Island dynamics method for epitaxial growth
  - Coarse-graining of KMC
  - Stochastic nucleation
- Kinetic model for step edge
  - kinetic steady state ≠ BCF equilibrium
  - validated by comparison to SOS/KMC
- Next lectures
  - Inclusion of strain in epitaxial systems
  - Strain leads to geometric structure (e.g. quantum dots) and alloy segregation