PREDICTIVE MODELING of EPITAXIAL THIN FILM GROWTH: ATOMISTIC and CONTINUUM APPROACHES

CSCAMM 10/03

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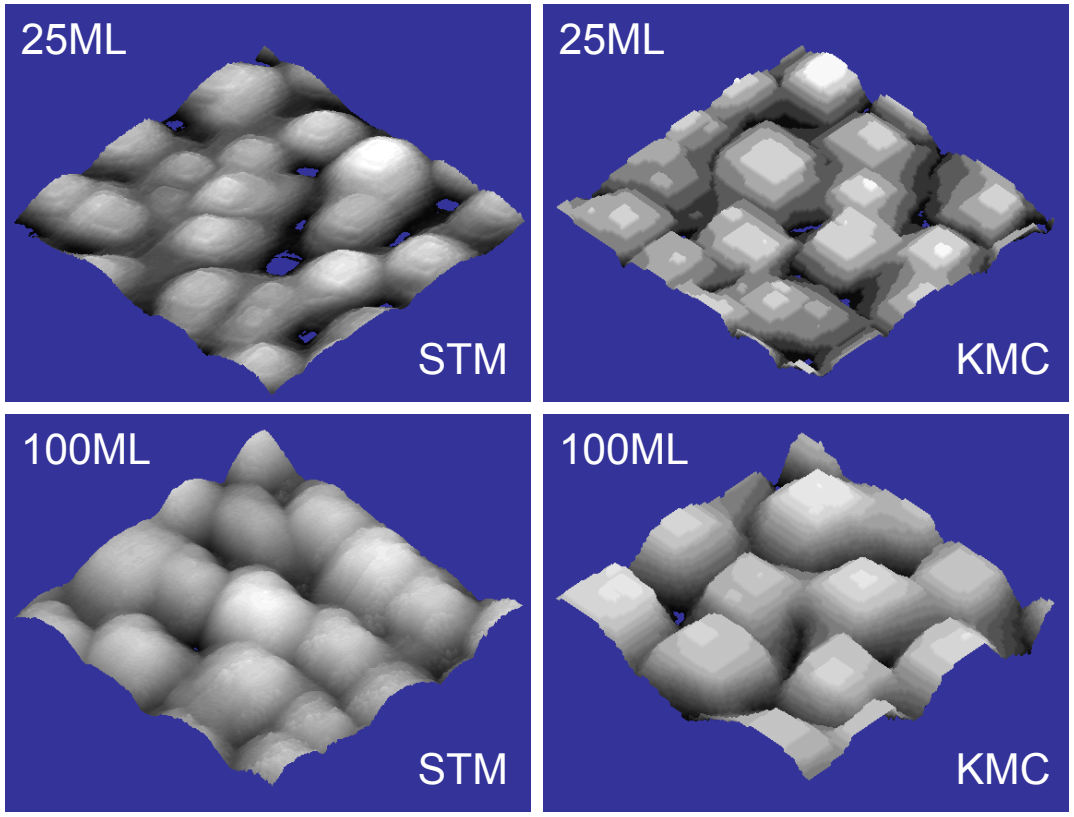
Experiment: Conrad Stoldt[3], Tony Layson[4], Vincent Fournee[5], Cynthia Jenks, Patricia Thiel

Iowa State University $$$ NSF Grants CHE-0078956 and EEC-0085604



Mound Formation during Ag/Ag(100) Multilayer Growth

@ 230K ~0.02ML/s

STM vs. Atomistic Modeling (KMC)
50×50 nm^2

PRL **85** (2000) 800
PRB **63** (2001) 085401
*PRB **65** (2002) 193407

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In Memoriam: Maria Bartelt d. June 23, 2003

Born: Angola (with identical twin sister Fatima, a Mathematician) 1962
B.Sc. & Diploma (Physics), Universidade do Porto Portugal, 1979-82, 1982-84
Assistant Professor, Universidade de Aveiro Portugal, 1982-84
Ph.D. (Statistical Physics – V. Privman), Clarkson University, 1987-91
Postdoctoral Fellow, Iowa State University, 1991-96
Physicist, Sandia National Laboratory – Livermore, 1996-1999
Physicist, Lawrence Livermore National Laboratory, 2000-2003
Group Leader (interim), Biophysical & Interfacial Science, CMS-LLNL, 2001
Group Leader, Computational Materials Science, CMS-LLNL, 2002-03

Diploma Graduation 1984
Universidade do Porto

from LLNL CMS News 7/03

GOAL: DEVELOP MODELS with QUANTITATIVE PREDICTIVE CAPABILITY for COMPLEX FAR-FROM-EQUILIBRIUM GROWTH MORPHOLOGIES of specific EPITAXIAL METAL FILMS SYSTEMS for a range of T (& F)

- Extract parameters (activation barriers, rates) describing key atomistic processes
- Elucidate observed morphologies; predict growth under other (less accessible) conditions

SUCCESS STORY: Tailored atomistic model for mound formation during multilayer growth of Ag on Ag(100) up to 1000's ML for 200K < T < 300K

- Parameters: E_d=0.40eV (terrace diff.); $E_{ES[110]}$=0.07eV, $E_{ES[100]} \approx$ 0eV [100] (step edge barrier)
  E_{KES}=0.16eV (extra kink rounding barrier); $E_{PD[110]}$=low (precise value not relevant)
- Key Prediction: Ag/Ag(100) at 300K regarded as PROTOTYPE for smooth growth, but in fact growth of thicker films from 100's-1000's ML is very rough !!
- Other predictions: Mound coarsening dynamics (stochastic) is distinct from predictions of 3D continuum theories (deterministic, "roof-top" defect-mediated)

OUTLINE:

SUBMONOLAYER GROWTH

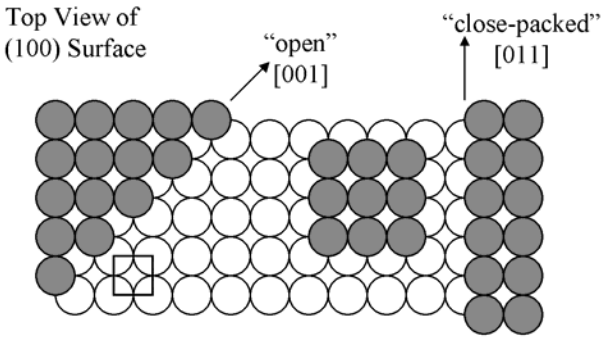
- *Tailored* atomistic LG model for island formation in metal(100) systems
- Application to Ag/Ag(100) homoepitaxy for 130K<T<300K
- Failure of classic mean-field rate equation theory for island size distributions
  Analytic beyond-mean-field theories (JPD equations, *spatial aspects* of nucleation)
- Continuum PDE-based Simulation of island formation: challenges for description of non-equilibrium island growth (and growth coalescence) shapes
- Geometry-Based Simulation (GBS): new approach via a geometric description of island nucleation (along CZ boundaries) and growth (rates from CZ areas)

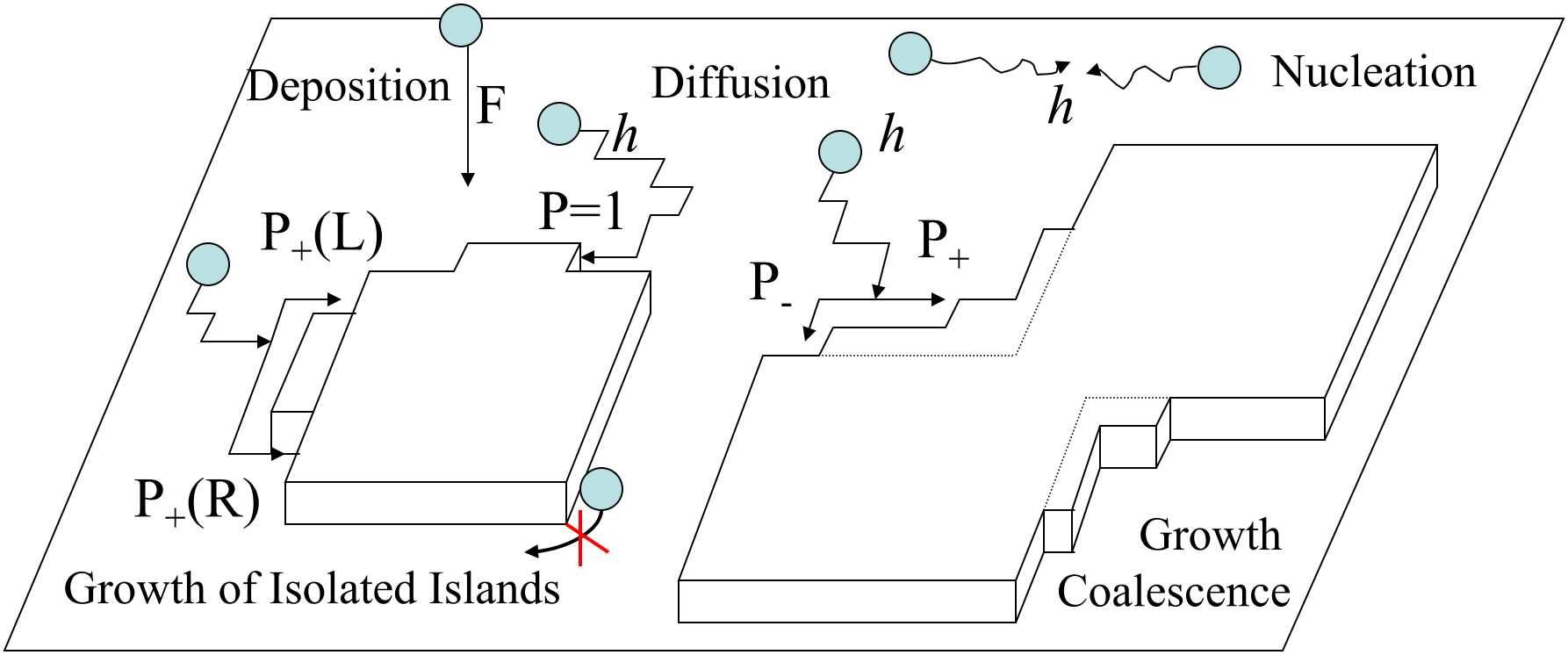
MULTILAYER GROWTH

- *Tailored* atomistic LG model for mound formation in metal(100) systems
- Application to kinetic roughening during Ag/Ag(100) homoepitaxy for 200K<T<300K, and predictions of growth for thick films (100's -1000's ML)
- Predictions of long-time mound dynamics (fluctuation dominated) and comparison with 3D continuum theories (deterministic "defect"- mediated)

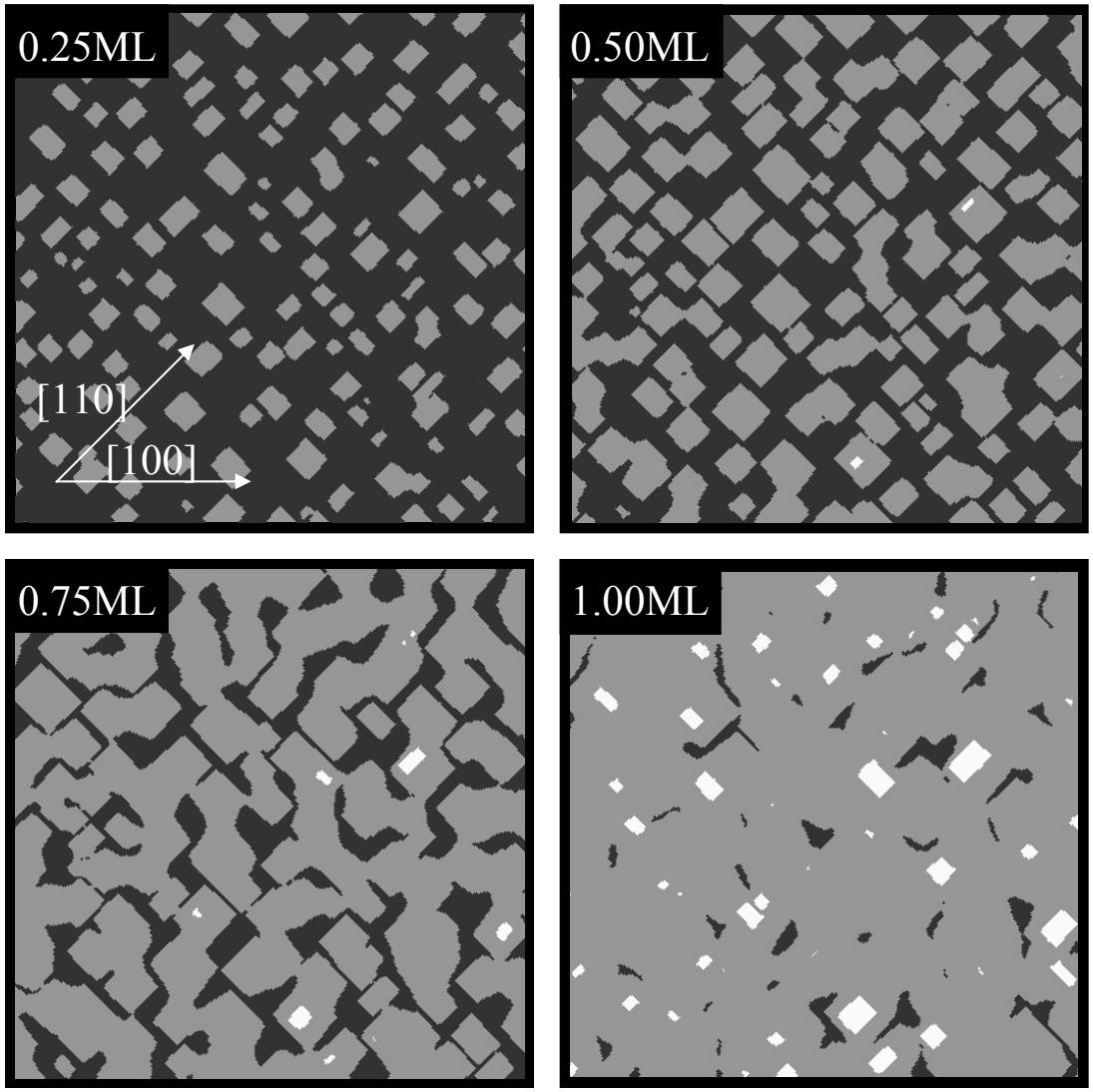
SUBMONOLAYER METAL(100) HOMOEPITAXY: Models for 2D Island Nucleation and Growth with EFFICIENT EDGE DIFF.N & KINK ROUNDING

Caspersen et al. PRB **63** (2001) 085401; Li & Evans, PRB **69** (2004)





Extra Kink Rounding Barrier = 0: $P_{\pm}$ or $P_{-}(L,R) \propto$ distance to kink (1D RW theory)
Extra Kink Rounding Barrier = small: $P_{+}=1$, $P_{-}=0$ (biased attachment without rounding)

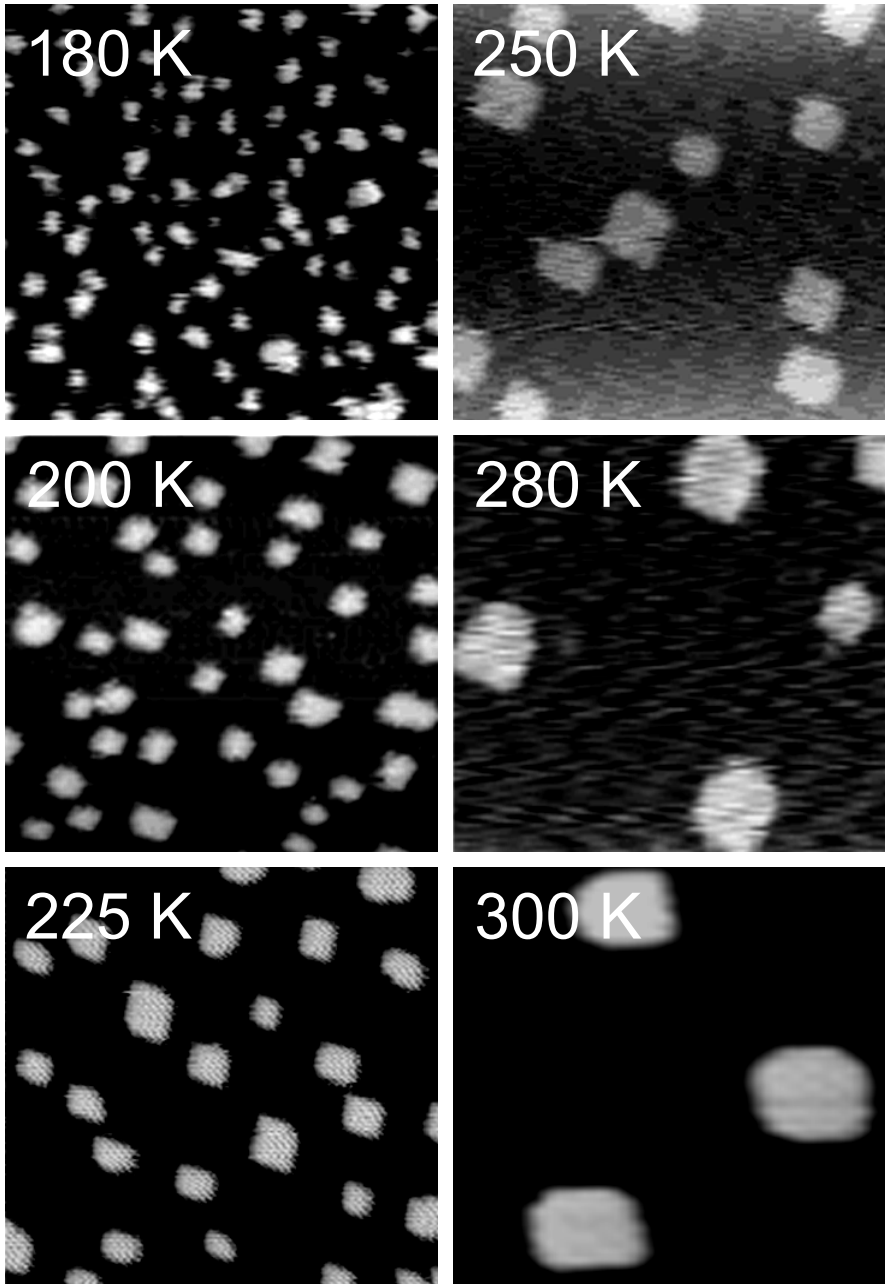


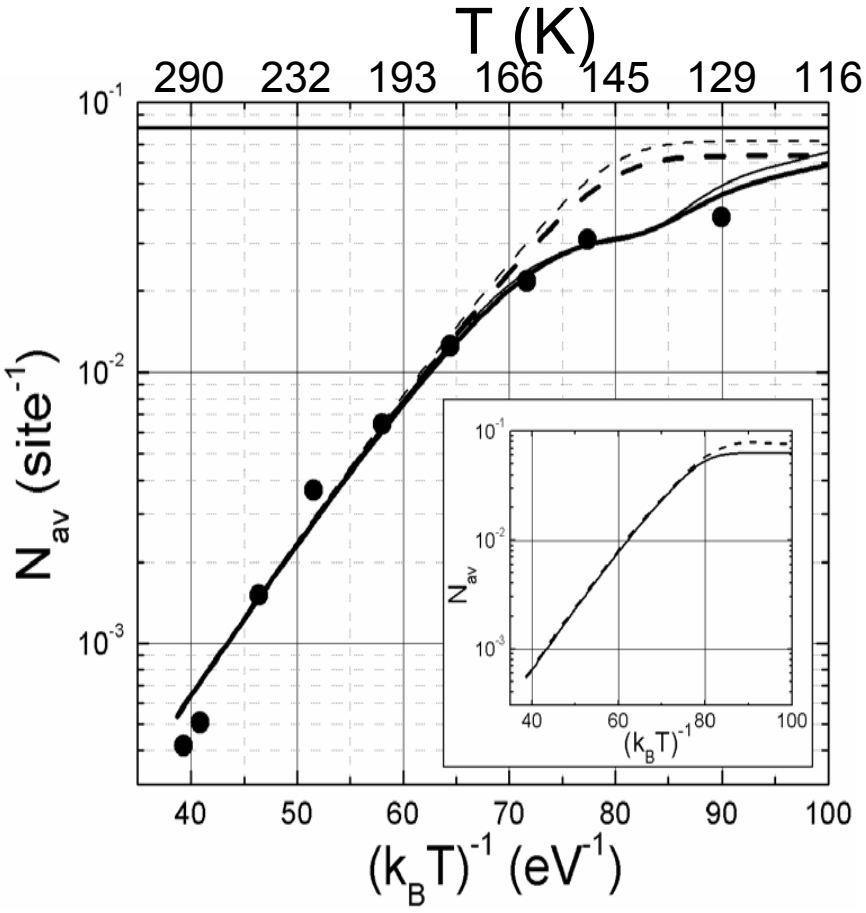
KMC SIMULATIONS
of island distributions
in the initial stages of
Ag/Ag(100) growth
at 300K with F=0.055ML/s
(102×102 nm^2 images)

EFFICIENT KINK ROUNDING (EKR) MODEL with E_d=0.04eV
(terrace diffusion barrier)

Also $E_{ES[110]}$=0.07eV, $E_{ES[100]}$=0eV

Caspersen, Stoldt, Layson
Bartelt, Thiel & Evans
PRB **63** (2001) 085401
Appendix Fig.20





Frank, Wedler, Behm (U. Ulm)
Rottler, Maass (U. Konstanz)
Caspersen, Stoldt, Thiel, Evans,
Phys. Rev. B **66** (2002) 155435

RATE EQUNS FOR ISLAND SIZE DISTRIBUTIONS: FAILURE OF MF THEORY

Rate Equns: N_S = density of islands of size S; $R_{agg}(S) = \sigma_S\, h\, N_1 N_S$ = aggregation rate

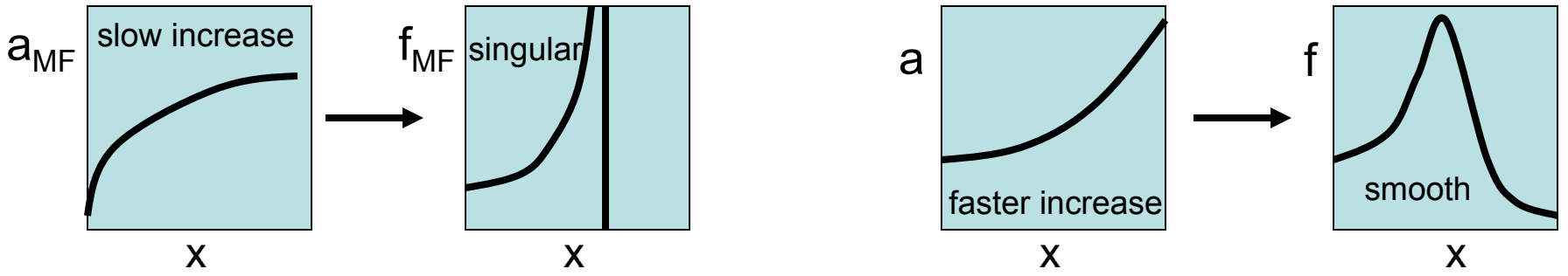
$d/dt\ N_S \approx R_{agg}(S-1) - R_{agg}(S)$ --- analysis: Bartelt & Evans PRB **54** (96) --->

Scaling form of $N_S \approx N_{av}/S_{av}\ f(x=S/S_{av})$ determined by that of "capture numbers"

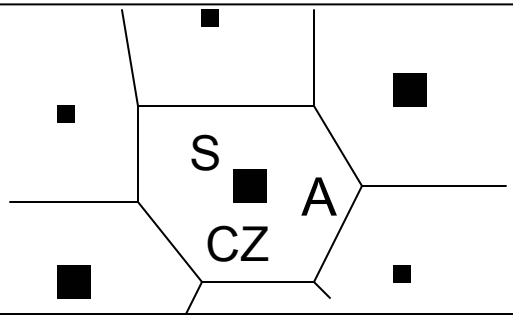
$\sigma_S \approx \sigma_{av}\ a(x=S/S_{av})$ via the EXACT formula $f(x) = \int_0^x dy\ [(2z-1)-a'(y)]/[a(y)-zy]$

MF TREATMENT of CAPTURE **vs.** **PRECISE KMC ANALYSIS of CAPTURE**

Venables (70's), Bales & Chrzan PRB (94) Bartelt & Evans, PRB (96)



Geometric picture of adatom capture:
Capture number ∝ *Capture Zone Area*
$\sigma_S \propto A_S$



Failure of MF theory:
Larger islands have "much larger" CZ's ⇒ correlations between island size & separation

BEYOND-MEAN-FIELD TREATMENTS OF ISLAND NUCLEATION & GROWTH

HEURISTIC RATE EQUATIONS FOR (MEAN) CZ AREAS A_S:

$d/dt\ (A_S N_S) = \ldots$ Evans & Bartelt, in *Morphological Organization…* (World Sci. 98), PRB **63** (01)

…yields non-MF behavior sensitive to prescription of nucleation

RATE EQUATIONS FOR THE JPD FOR ISLAND SIZES AND CZ AREAS $N_{S,A}$:

$d/dt\ N_{S,A} = \ldots.$ Mulheran & Robbie, EPL **49** (2000) 617

…populations change due to island growth and due to island nucleation (shown below)

EXISTING TREATMENTS:

Amar et al. PRL (01)
Don't treat spatial aspects of nucleation

Mulheran & Robbie EPL (00)
Treat spatial aspects of nucleation by assuming nucleation fragments existing CZ

Evans & Bartelt PRB (02), MRS (03)
Treat realistically spatial aspects of nucleation: just nucleated CZ overlaps ~5.5 existing CZ's

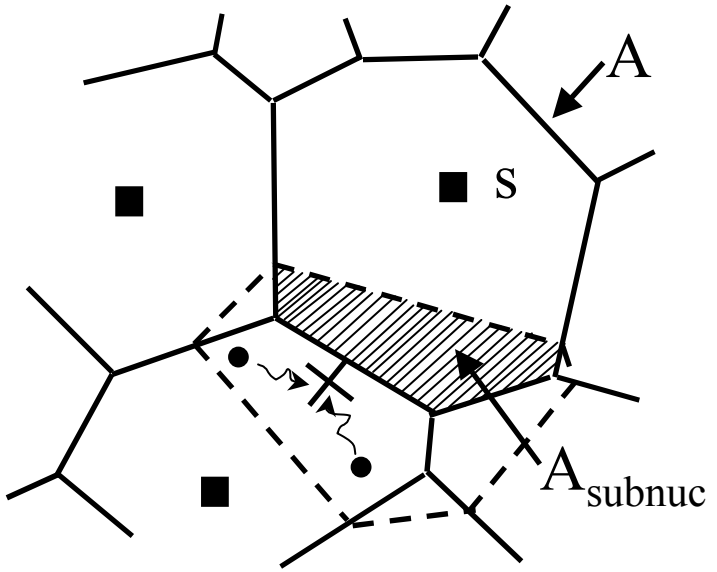
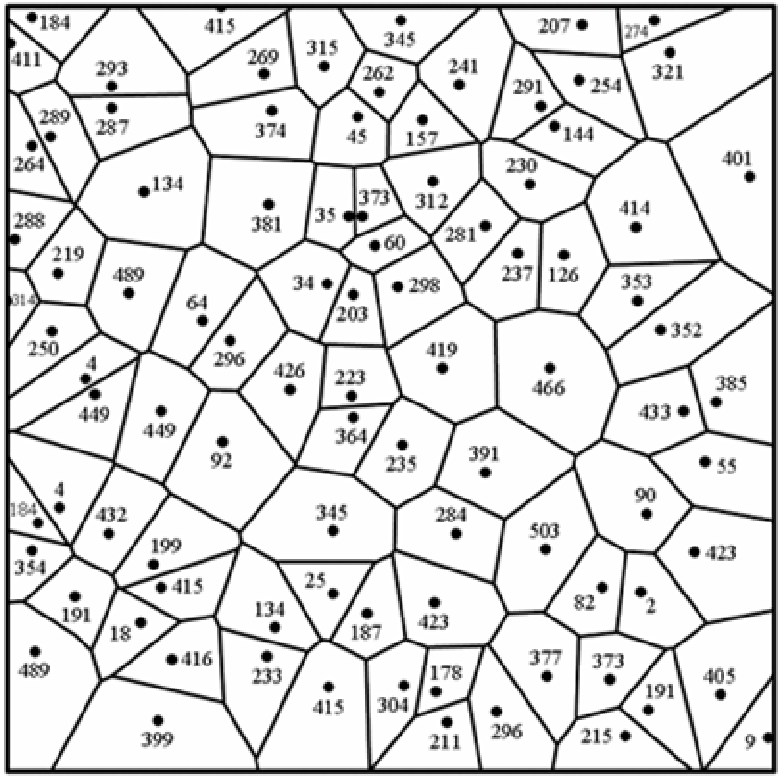


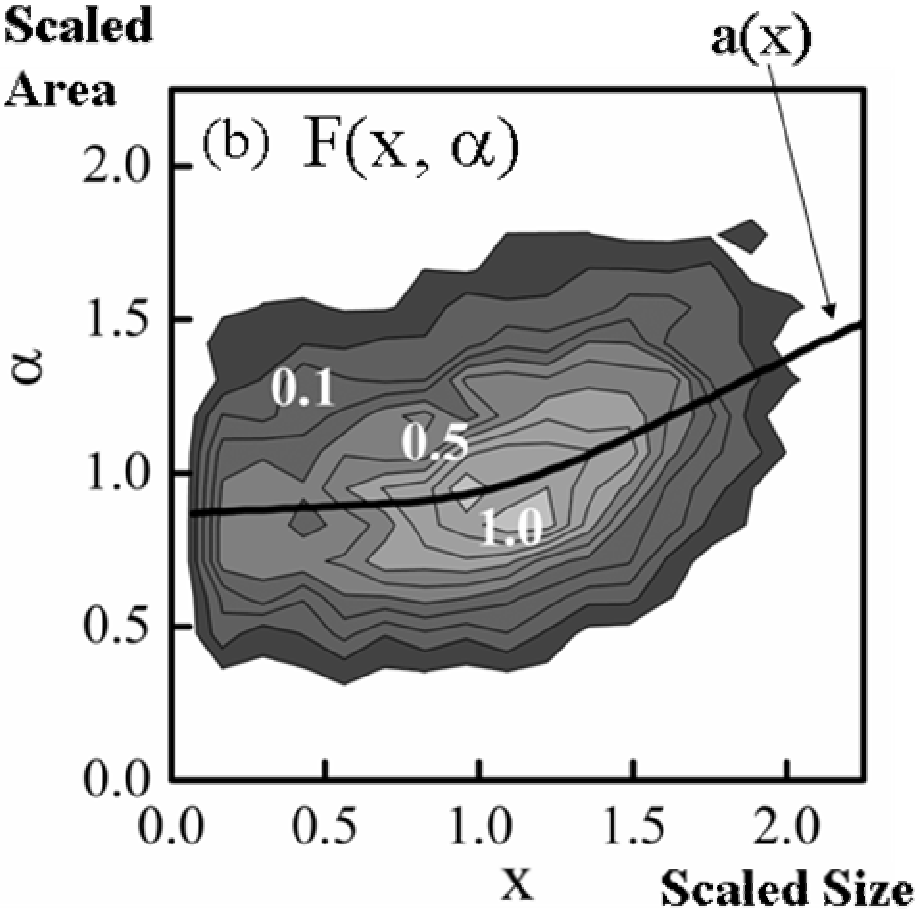
Fig.8: Evans & Bartelt PRB **66** (2002) 235410

SIMULATION RESULTS FOR THE JPD (POINT ISLANDS)

$N_{S,A}$ (islands size s & CZ area A) $\approx N_{isl}/(A_{av}S_{av})\ F(x=S/S_{av}, \alpha=A/A_{av})$

with the *factorization property* that $F(x,\alpha) \approx f(x)G(\alpha - a(x))$ where CZ area distr. G is size independent (skewed Gaussian, width $w_A \approx 0.25$)





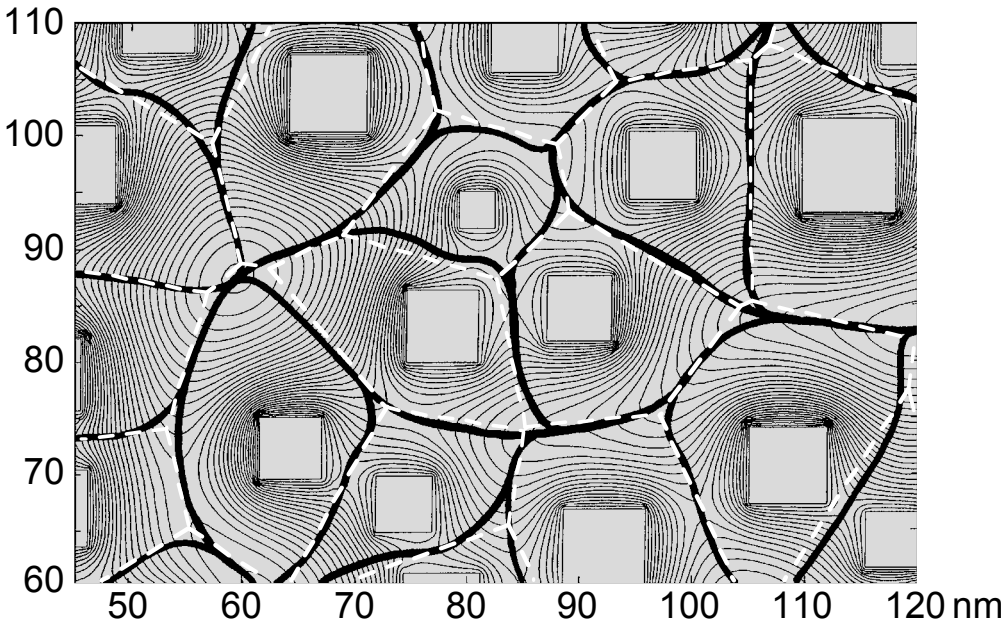
CONTINUUM PDE-BASED SIMULATION OF ISLAND NUCLEATION & GROWTH

KEY INGREDIENTS:

(I) Replace atomistic simulation of deposition, diffusion, and capture with continuum PDE analysis of BVP

- ♦ Confirm recovery of atomistic behavior
- ♦ Construct EXACT CZ's as "diffusion cells"
- ♦ Compare exact CZ's with simpler geometric constructions (VC's, EC's)

Bartelt et al., PRL **81** (98) 1901; PRB **59** (99) 3125



*2D Ag islands on Ag(100) @ 300K: PRB **59** (99)*

Analysis of BVP for deposition-diffusion equation

(II) Nucleation as in classic theories:

- ♦ Nucleation rate $\propto$ (local adatom density)$^{i+1}$

Ratsch et al. (UCLA group) PRB, PRE, MRS

(III) Continuum treatment for evolution of <u>non-equilibrium</u> growth shapes ???

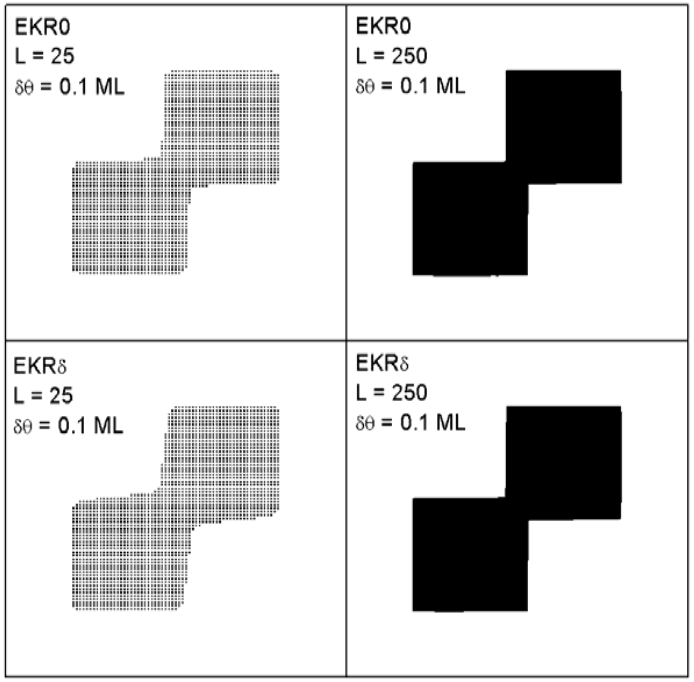
- ♦Cannot use Mullins theory for PD in describing island shape evolution
- ♦Non-equilibrium mass currents dominate equilibrating Mullins current

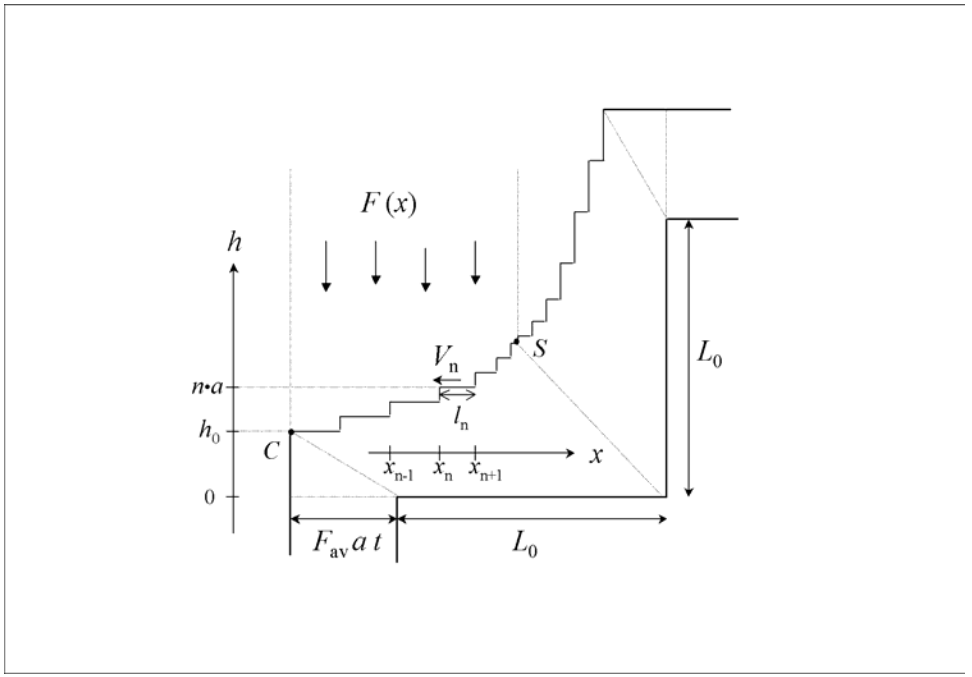
Politi & Villain, PRB (92) - surfaces; Pierre-Louis et al. PRL (99) - steps ; Li & Evans, PRB (04) - islands

GROWTH COALESCENCE SHAPES FOR EKR MODELS:

Atomistic Simulation; Deterministic Kink Dynamics (DKD) → Continuum PDE Theories

Li & Evans, PRB (04)





SIMULATION RESULTS:

- More rounding of growth shapes for biased kink attachment than for no extra kink rounding barrier
- Degree of rounding decreases with increasing island size

THEORY:

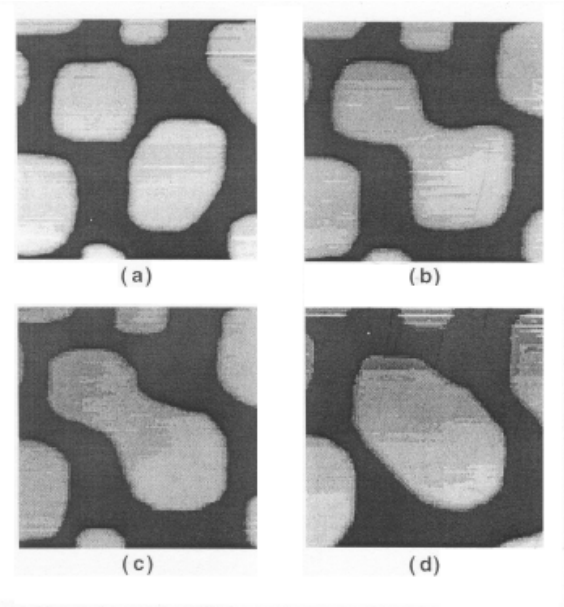
- Take continuum limit of DKD models (cf. above)
- Obtain FP-type equations for terrace width distr.
- Obtain possibly *non-conservative* PDE for step height evolution $\partial/\partial t\ h(x,t) = \ldots$
- Non-conservative ?? Role of BC's at C (& S)

POST-DEPOSITION ("DYNAMIC") vs. GROWTH ("STATIC") COALESCENCE

♦ Anisotropic continuum Mullins theory for mass transport via PD: $J_{PD} \propto \partial/\partial x\ \mu$ with $\mu \propto \beta^{\sim} \kappa$

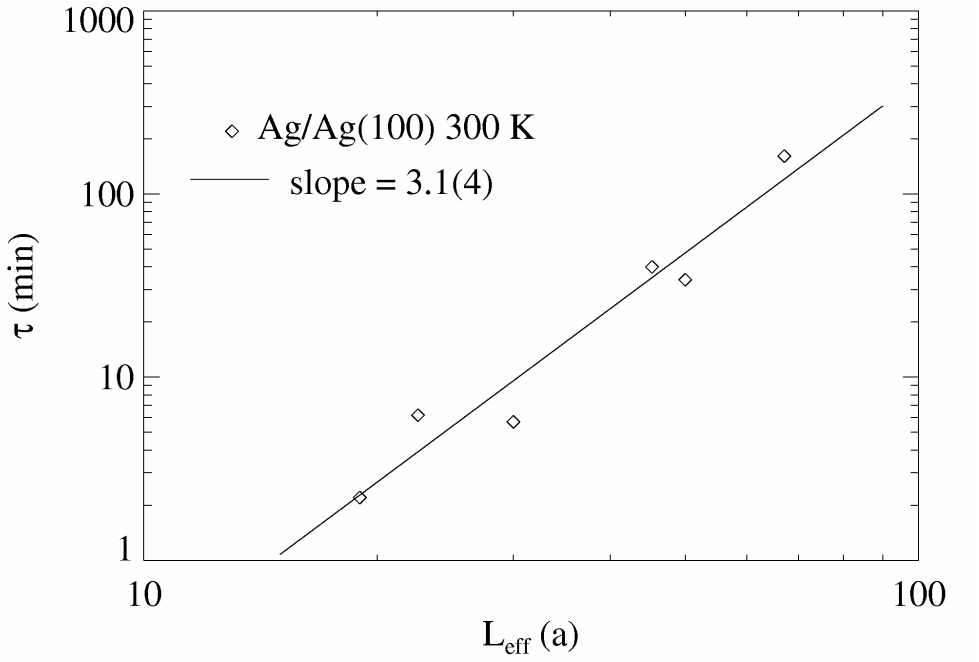
…quantitative predictive capability for large sizes: Pai, Wendelken, Stoldt, Thiel, Evans, Liu, PRL **86** (2001) 3088

♦ CAUTION: Mullins theory can fail on the nanoscale ! See below.



2D NANOSCALE SINTERING
Ag/Ag(100) @ 300K 50x50 nm^2
-36 min., 10 min., 55 min., 235 min.

Liu et al. MRS Proc. **749** (2003) W2.8.1
Liu & Evans PRB **66** (2002) 165407
Stoldt et al. PRL **81** (1998) 2950



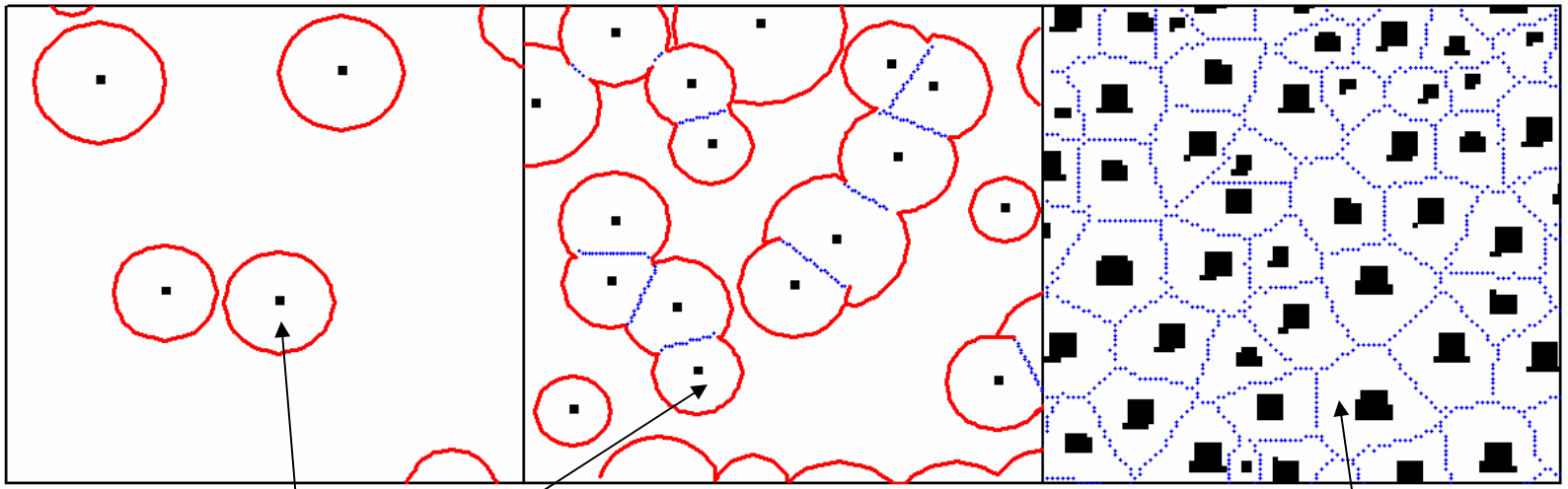
RELAXATION TIME τ vs. LINEAR SIZE L:
$\tau \sim L^4$ continuum Mullins theory
$\tau \sim L^3$ experiment (& atomistic simulation)
due to "large" kink rounding barrier

GEOMETRY-BASED SIMULATION (GBS) OF ISLAND NUCLEATION & GROWTH

…new approach which exploits physical insights into spatial aspects of nucleation and growth process & thereby side-steps need to simulate deposition-diffusion-capture or continually solve BVP for PDE

References: Li, Bartelt, Evans, PRB **68** (2003) 121401; Li & Evans, Surf. Sci., in press (2003).

Initial Regime **Crossover Regime** **Steady-State Regime**



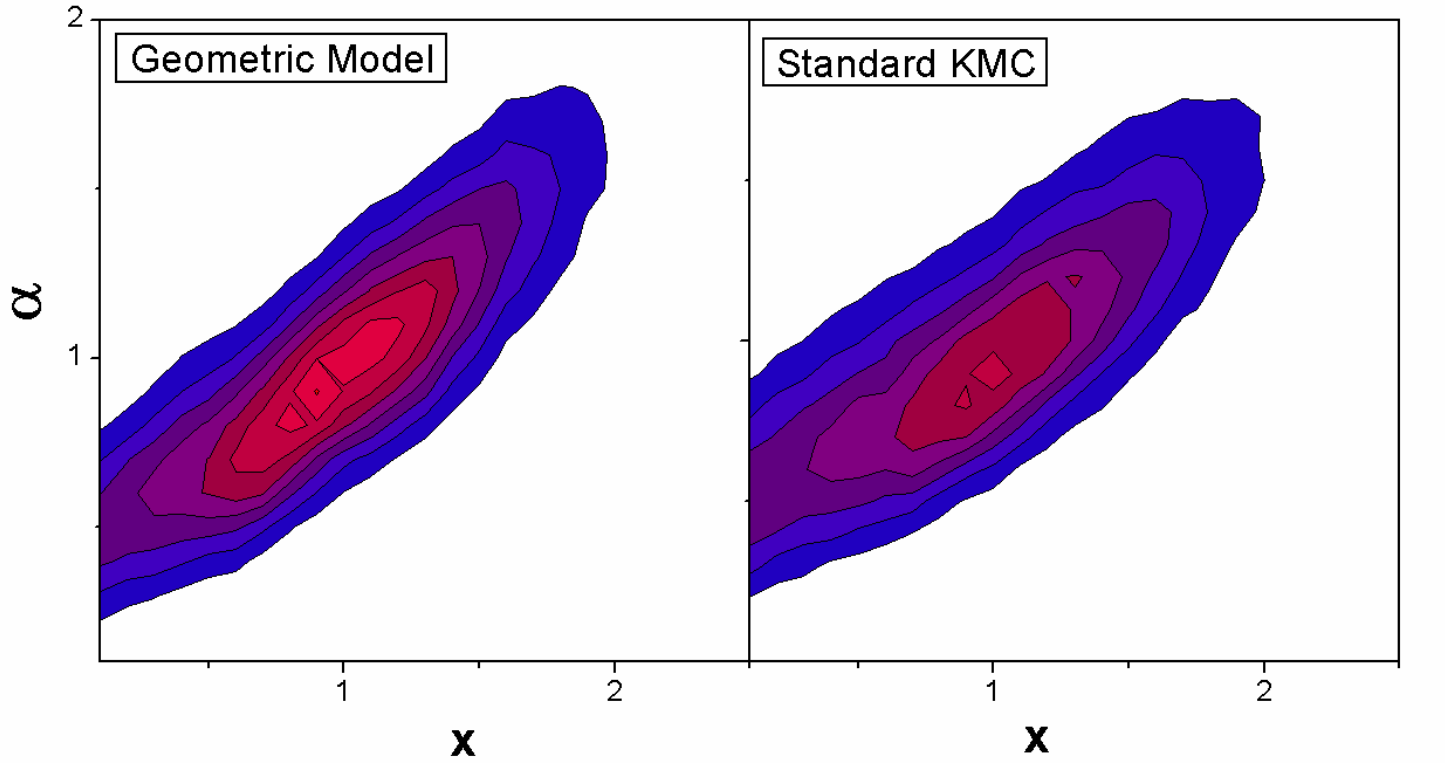
• DZ radius growth from time-dependent deposition-diffusion eq. • *Spatially Random Nucleation <u>outside</u> of DZ's* where $N_1 \approx Ft$	• Overlap of DZ's • Construct of CZ's via Voronoi-type algorithm • Continue nucleation outside DZ's.	• Islands surrounded by CZ's. • *Nucleation <u>nearby</u> CZ bndries* where steady-state density of diffusing adtoms N_1 is higher • Island growth $\propto$ CZ area.

MORE DETAILS ON ALGORITHM:

- DZ radii grow like: $R_{DZ}(\delta t) \sim (h/F)^{1/2}\, \delta t^{1/2}$ for time δt since nucleation
- Steady-state nucleation rate estimated from analytic solution for steady-state N_1 for each CZ in circular geometry approx. $\Rightarrow$ nucleation rate along CZ boundary ~ (distance to island edge)$^{2i+3}$
- Must spread nucleation positions off CZ boundaries to precisely describe island spatial correlations

TEST OF ALGORITHM:

$$\text{JPD: } N_{s,A} \approx N_{isl}\,(S_{av}\,A_{av})^{-1}\,F(x, \alpha), \quad x = s / S_{av}, \quad \alpha = A / A_{av}$$

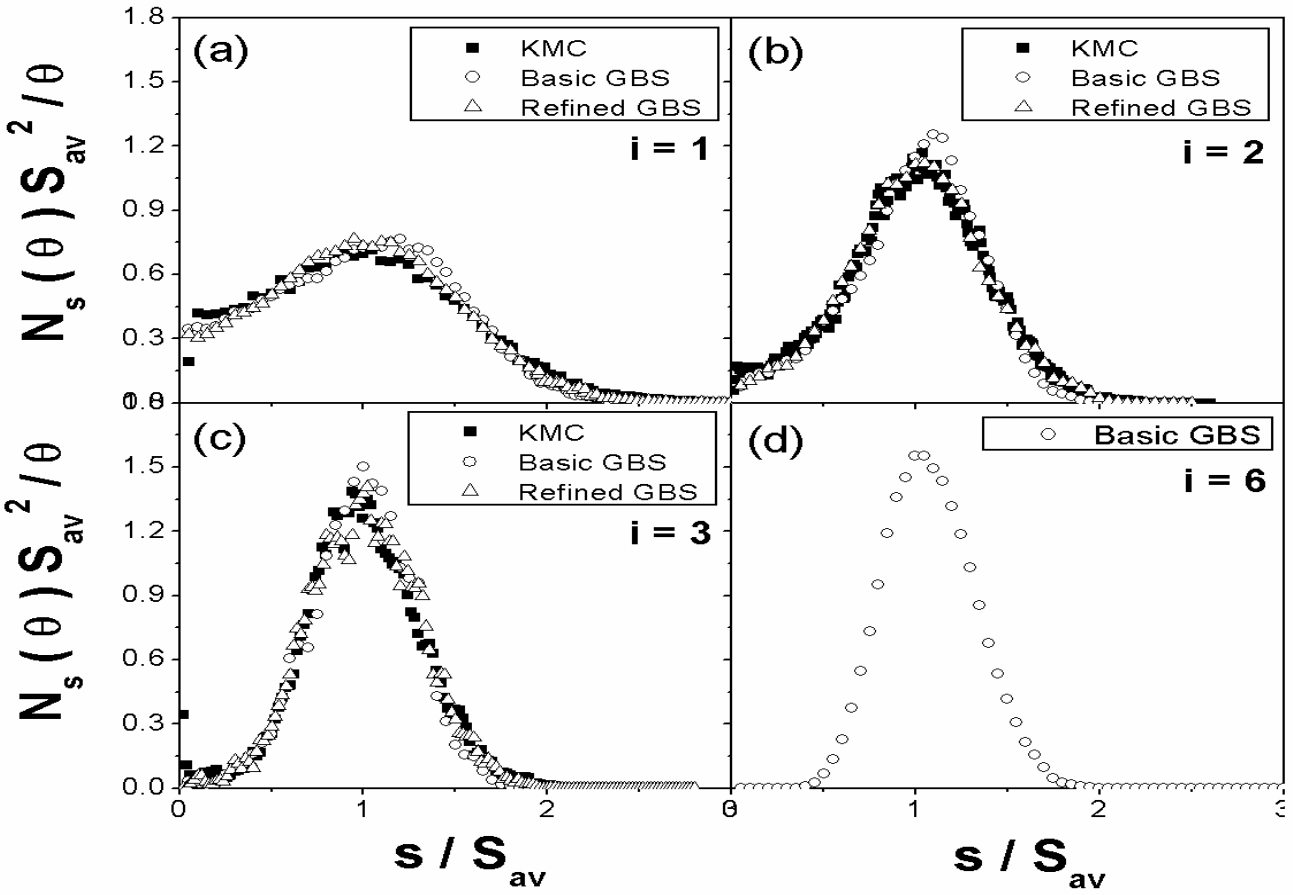


i=1 (irreversible island formation)
Square islands
$h/F = 10^6$
$\theta = 0.1$ ML

GBS SIMULATION RESULTS for ISLAND SIZE DISTRIBUTIONS when i>1

- Motivation for developing coarse-grained models is to treat strongly reversible island formation where the high density of rapidly diffusing adatoms makes conventional KMC less efficient.

- Use GBS to treat general critical size i>1 where i+1 adatoms are required to nucleate an island and clusters of i atoms or less are unstable. Note: nucleation rate $\propto (N_1)^{i+1}$



VOLUME 77, NUMBER 6 PHYSICAL REVIEW LETTERS 5 AUGUST 1996

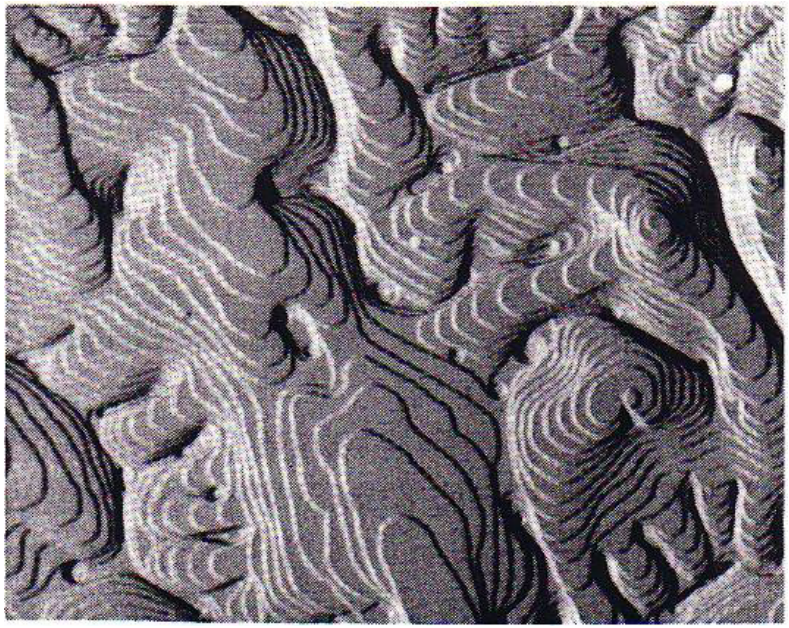
Anisotropy of Growth of the Close-Packed Surfaces of Silver

Byung Deok Yu and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany
(Received 6 March 1996)

The growth morphology of clean silver exhibits a profound anisotropy: The growing surface of Ag(111) is typically very rough while that of Ag(100) is smooth and flat. This serious and important difference is unexpected, not understood, and hitherto not observed for any other metal. Using density functional theory calculations of self-diffusion on flat and stepped Ag(100) we find, for example, that at flat regions a hopping mechanism is favored, while across step edges diffusion proceeds by an exchange process. The calculated microscopic parameters explain the experimentally reported growth properties.

Ag/Ag(111): Vrijmoeth *et al.* PRL 72 (94)
Rough "Poisson" growth: $W \sim h^{1/2}$ at 300K
Little interlayer transport; large SE barrier

Ag/Ag(100): see references below
Smooth "quasi-layer-by-layer" growth
Easy interlayer transport; low SE barrier



RHEED [Suzuki et al. JJAP **27** (88)]
...persistent oscillations ⇒ quasi-LBL

X-Ray Scattering [Miceli et al. PRB (96)]
& Atomistic KMC Simulation of Growth
[ISU group; Surface Science **406** (98)]
…slow "initial" kinetic roughening with
$W \sim h^{0.2}$ at 300K

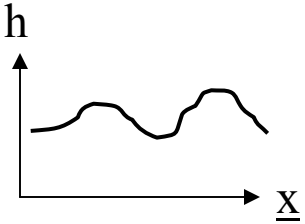
MOUND FORMATION IN MULTILAYER METAL(100) HOMOEPITAXY: TAILORED ATOMISTIC MODEL & GENERIC 3D CONTINUUM THEORY

EKR MODEL for ISLAND FORMATION + NON-UNIFORM STEP-EDGE BARRIER:

- Random deposition & terrace diffusion leads to irrev. island formation (i=1) in each layer
- EKR model for periphery diffusion determining island growth & coalescence shapes
- Downward funneling of depositing atoms at step edges to 4FH adsorption sites in lower layer
- Non-uniform step-edge barrier for downward transport: $E_{ES[100]}=0$; $E_{ES[110]}$= *key parameter*
- Determine *key parameter* $E_{ES[110]}$ by matching, e.g., 2nd layer population of 1ML film at 230K

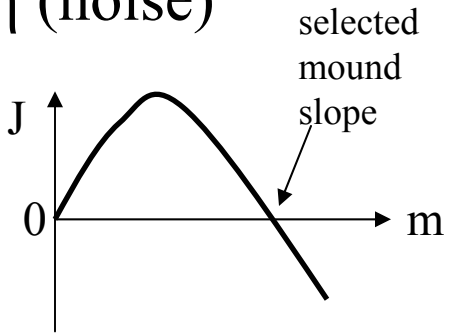
COARSE-GRAINED EVOLUTION EQUATION FOR FILM HEIGHT:

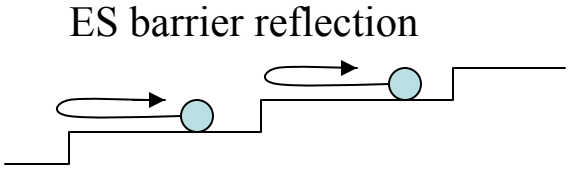
h = h(x,t) = film height at lateral position x & time t; m = ∇h = local slope



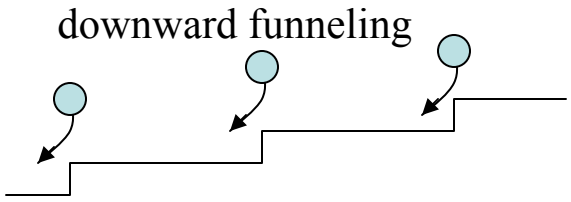
$$\partial/\partial t\, h = F \text{ (dep.n flux)} - \nabla\cdot\underline{J} \text{ (lateral mass current)} + \eta \text{ (noise)}$$

$$\underline{J} = \underline{J}_{ES}(\text{uphill-destabilizing}) + \underline{J}_{DF}(\text{downhill-stabilizing}) + \ldots =$$



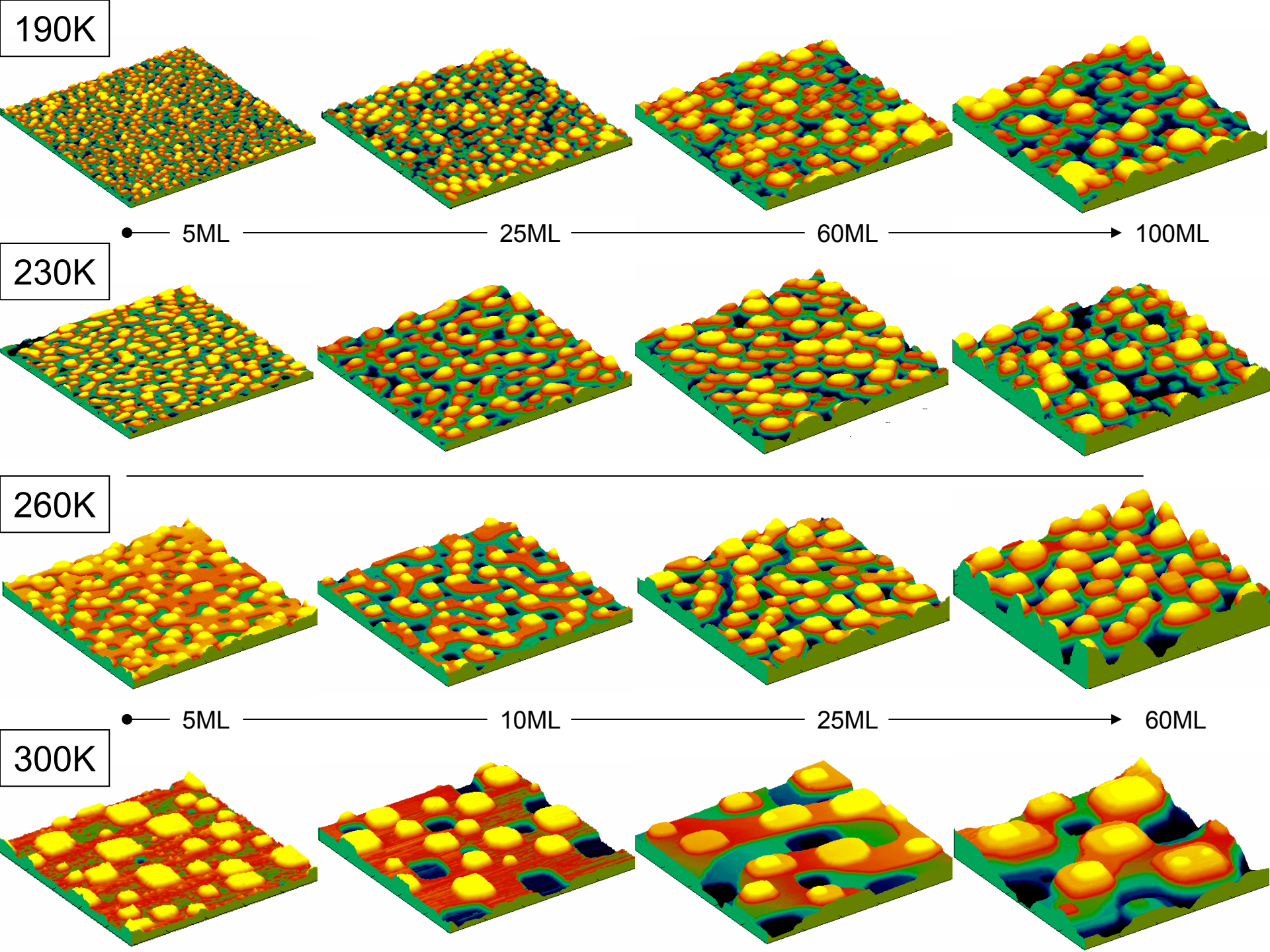


Villain J. Physique (91)

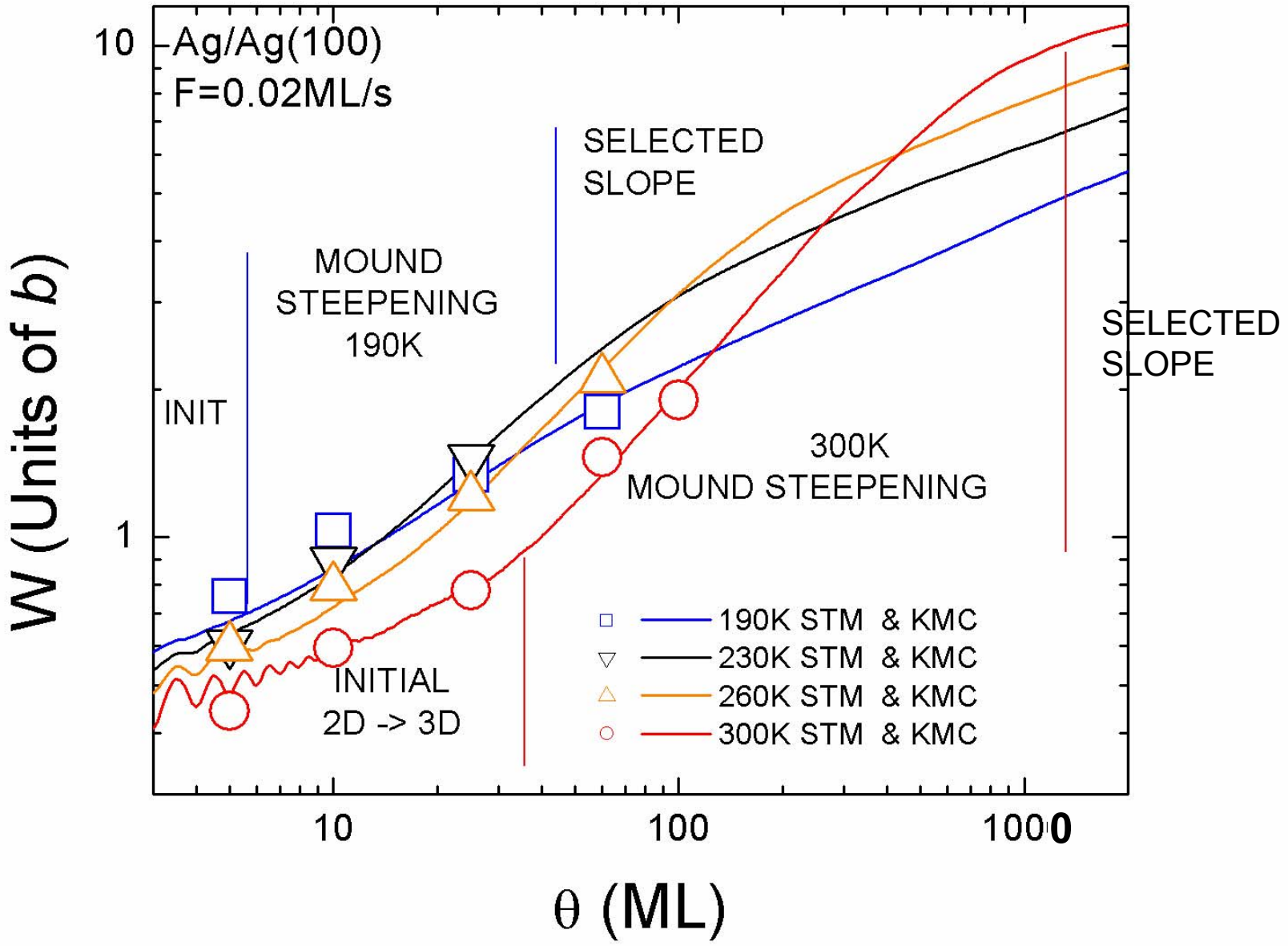


Kang & Evans SS (92)

Bartelt & Evans PRL (95)
Amar & Family PRB (96)


190K
5ML
25ML
60ML
100ML
230K
260K
5ML
10ML
25ML
60ML
300K

Caspersen, Layson, Stoldt, Fournee, Thiel & Evans, PRB 65 (02)



FLUCTUATION-MEDIATED COARSENING OF MOUNDS

PREDICTIONS from REALISTIC ATOMISTIC MODEL (i=1; EKR; DF; non-uniform ES barrier):

- Mounds order into a 1×1 pattern for long times
- Strong up-down symmetry breaking (all upward pyramidal mounds; none inverted)
- Fluctuations initiate single mound disappearance followed by concerted rearrangement