Fluctuations and Nanoscale Structures*

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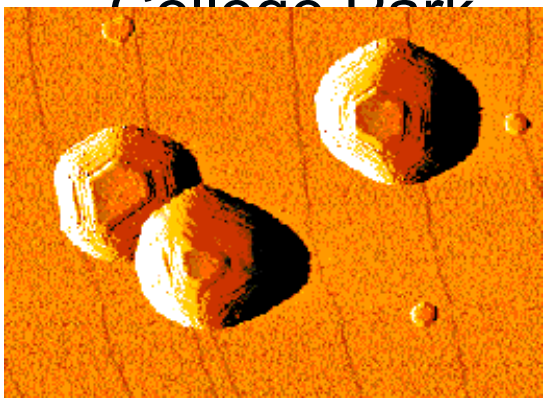

Crystalline Nanostructures

- Not molecules, not macroscopic solids
- A large fraction of the material is on the surface
- Edge boundary fluctuations determine structural evolution
- Deterministic vs. Stochastic behavior

*Supported by the NSF-MRSEC and the Laboratory for Physical Science

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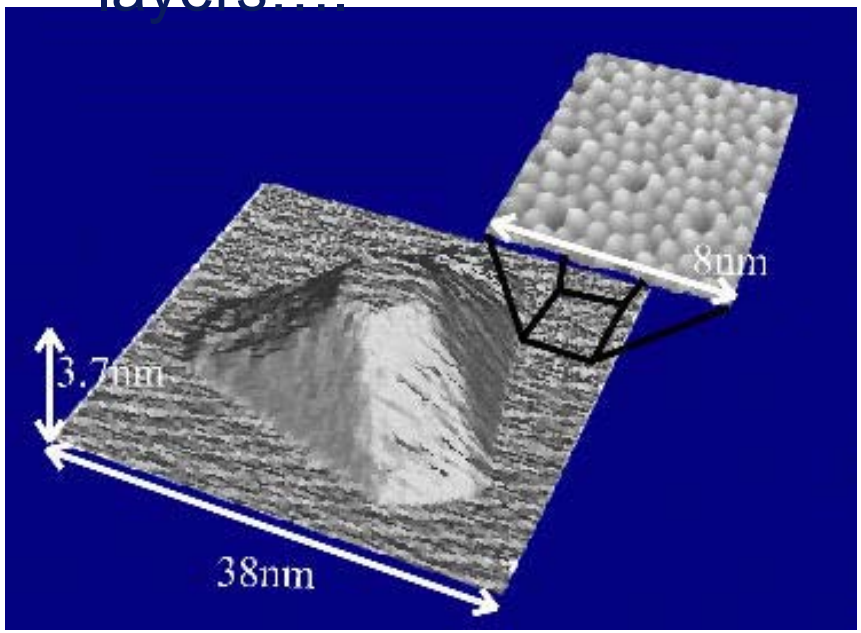
Mass Transport Kinetics

- In crystalline structures, mass transport is most commonly dominated by atomic motion at step edges. Structure modeling then explicitly includes the edges of atomic layers….



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A. Ichimiya, et al.

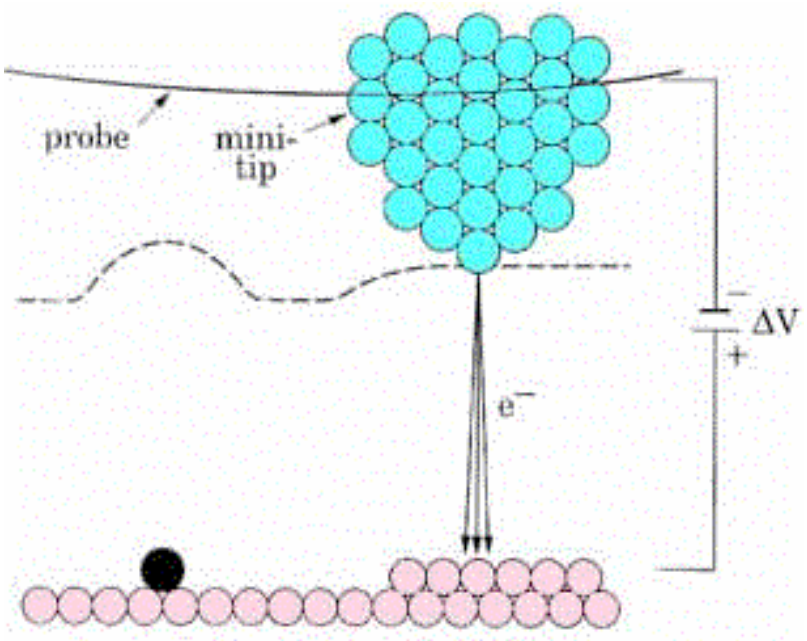
Phys. Rev. Lett. 84, 3662 (2000)

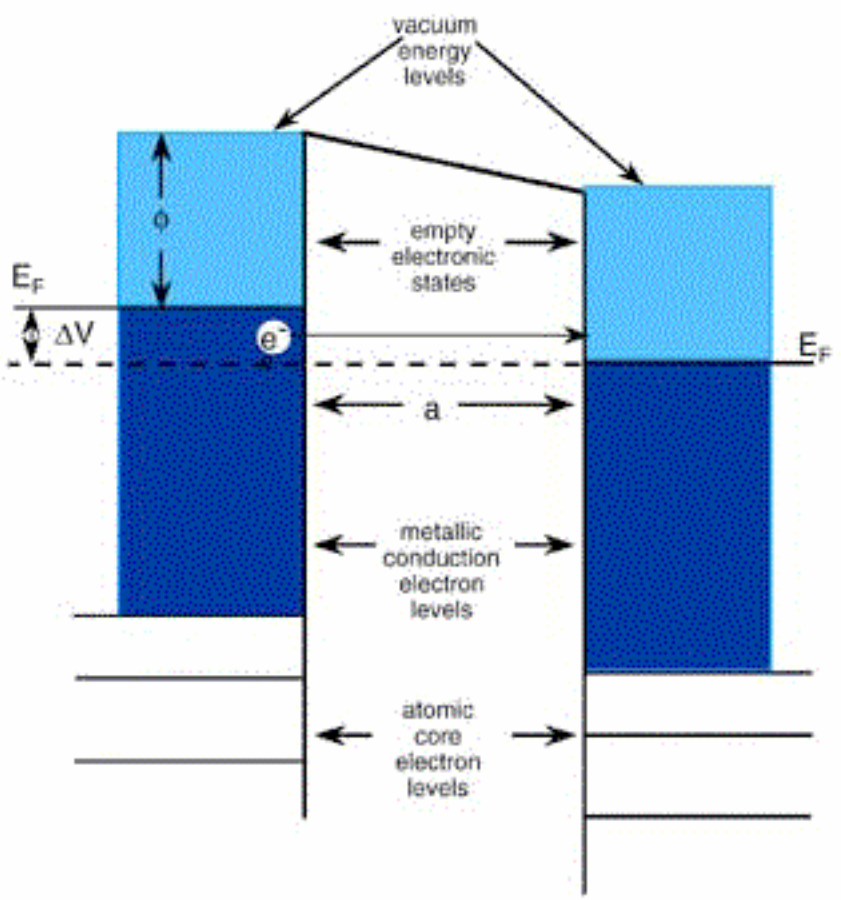
Decay of metastable nanostructure - elapsed time 30 minutes -

Outline
Questions, Questions….

- Statistical mechanics of line boundaries
  - Lattice models work for predicting temperature dependence
  - How to predict effective energies?
- Chemical potential gradients and kinetic coefficients
  - Evolution of nanoscale structures
  - Boundary conditions and the final state?
- Stochastic vs. Deterministic
  - Persistence and Survival
  - Sampling time, step correlation length
  - Is it good for anything?

Scanning Tunneling Microscopy





Continuum Step Model

- Langevin Equations

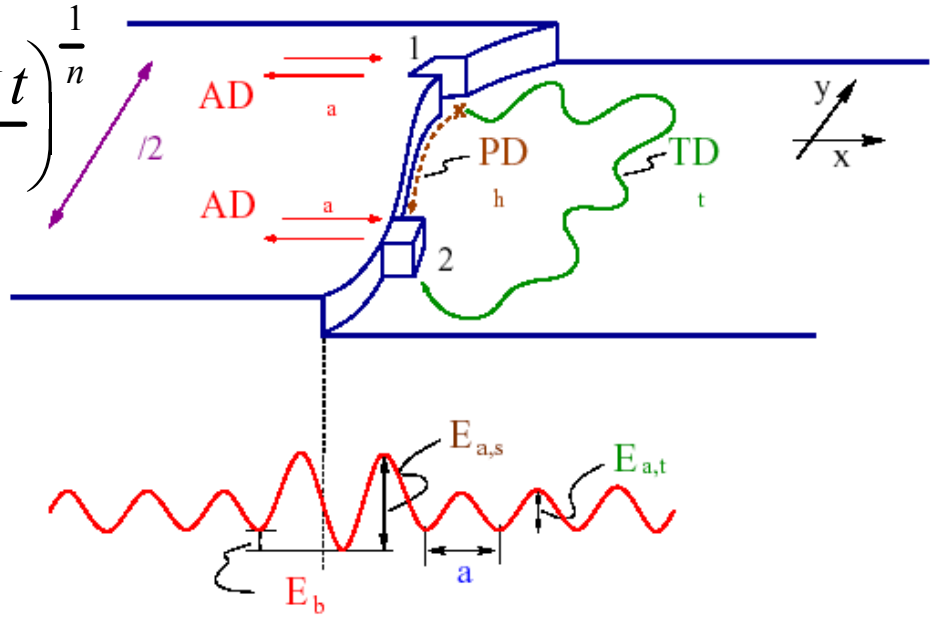
step edge attachment $$\frac{\partial x}{\partial t} = \frac{\Gamma_A \tilde{\beta}}{kT}\frac{\partial^2 x}{\partial y^2} + \eta_{non-conserved} \qquad \Gamma_A = \frac{a^3}{\tau_a}$$

step edge diffusion $$\frac{\partial x}{\partial t} = \frac{\Gamma_P \tilde{\beta}}{kT}\frac{\partial^4 x}{\partial y^4} + \eta_{conserved} \qquad \Gamma_P = \frac{a^5}{\tau_h}$$

- Correlation Functions

$$G(t) = \left\langle \left(x(t) - x(0)\right)^2 \right\rangle = \left(\frac{kT}{\tilde{\beta}}\right)^{\frac{n-1}{n}} \left(\frac{a^{n+1} t}{\tau}\right)^{\frac{1}{n}}$$

$$G(y) = \left\langle \left(x(y) - x(0)\right)^2 \right\rangle = \frac{kT}{\tilde{\beta}} y$$

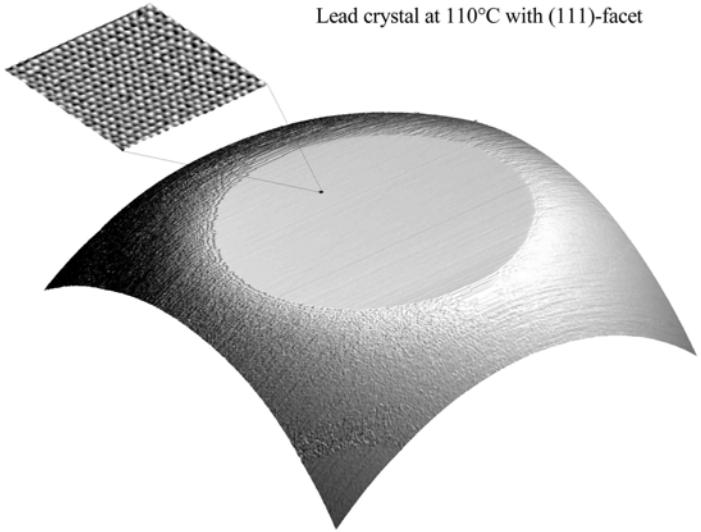


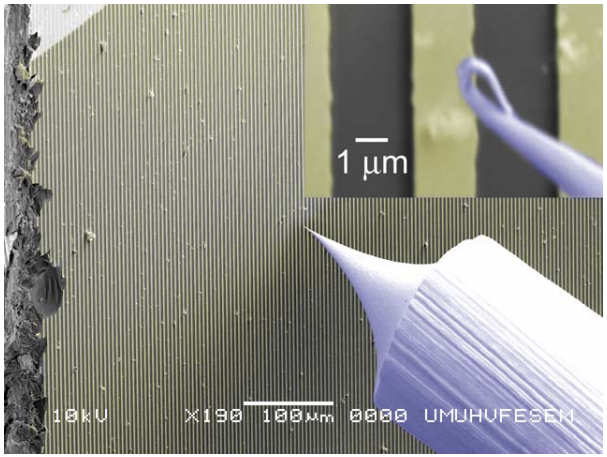
Determining the Continuum Step Parameters

- The complexity of the atomic scale behavior is encapsulated in a small number of parameters that describe the rate limiting characteristics of the system
- Example: Al/Si(111) Step Fluctuations
  - Igor Lyubinetsky and Dan Daugherty
    - UMD - MRSEC
  - Variable temperature STM measurements performed in the UMD-MRSEC shared experimental scanned probe facility

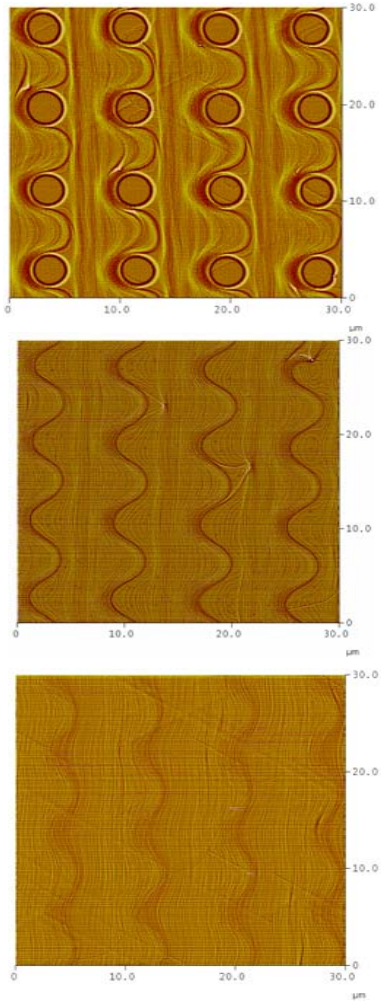
Experimental Statistical Mechanics at the Nanoscale

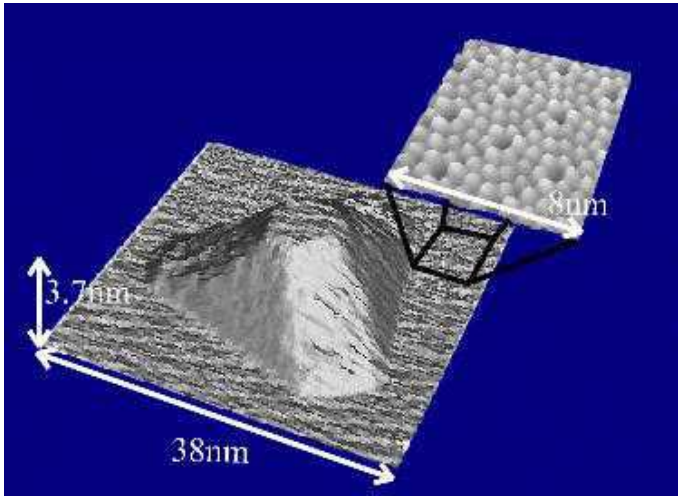
Nanoscale structures: fabrication, stability and evolution

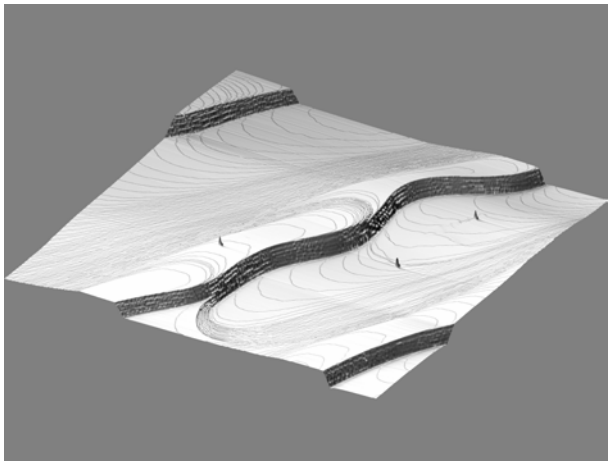




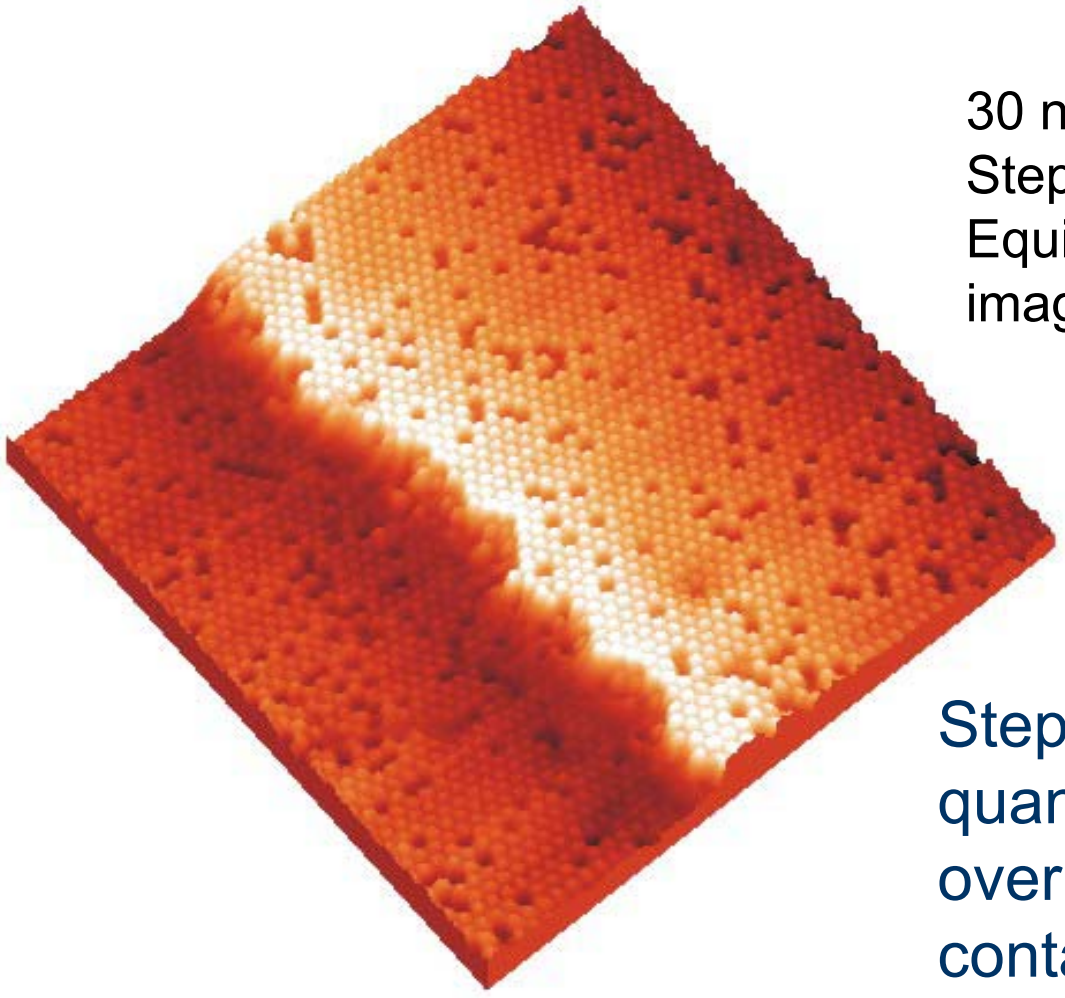
4 μ dia







Al/Si(111): $(\sqrt{3}x\sqrt{3})R30^o$ *phase*



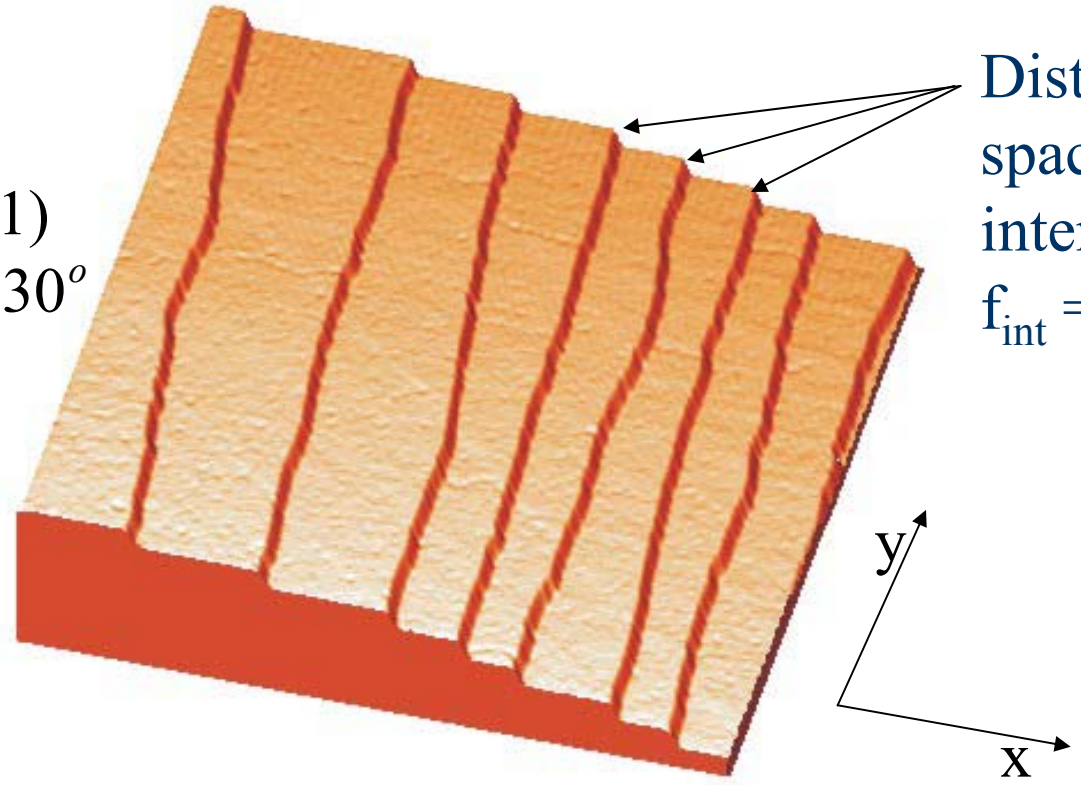
30 nm x 30 nm
Step height 0.31 nm
Equilibrated at high temperature, and imaged at room temperature

Step edge wandering is quantized in units of the overlayer unit cell, which contains 6 Si atoms and one Al atom.

I. Lyubinetsky
MRSEC

Continuum Step Model
Step Wandering Reveals Step Free Energy

Al/Si(111)
$(\sqrt{3}x\sqrt{3})R30^o$



Distribution of step-step spacings reveals step-interaction free energy, $f_{int} = g tan^3\phi$

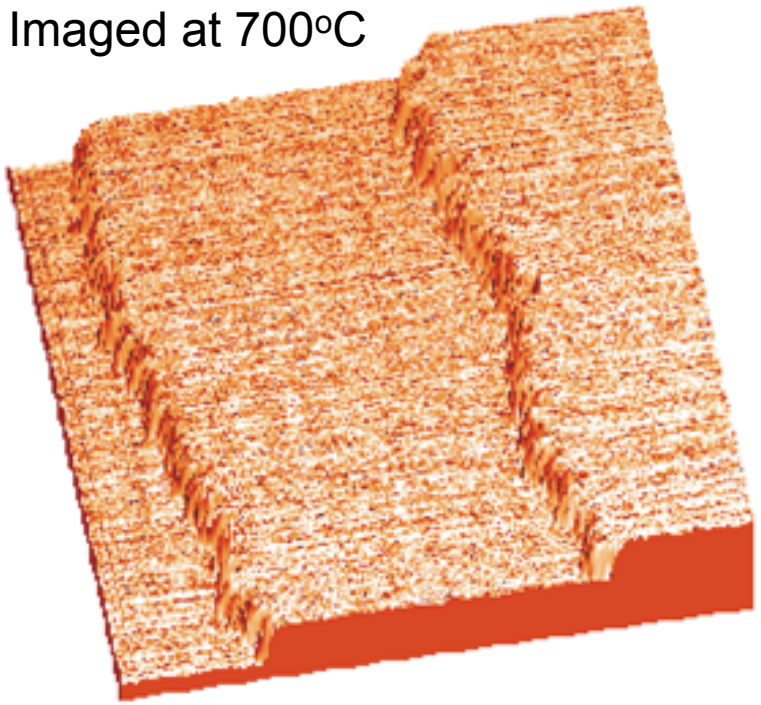
500 nm x 500 nm area, step height 0.31 nm

Spatial Step Correlation Function:

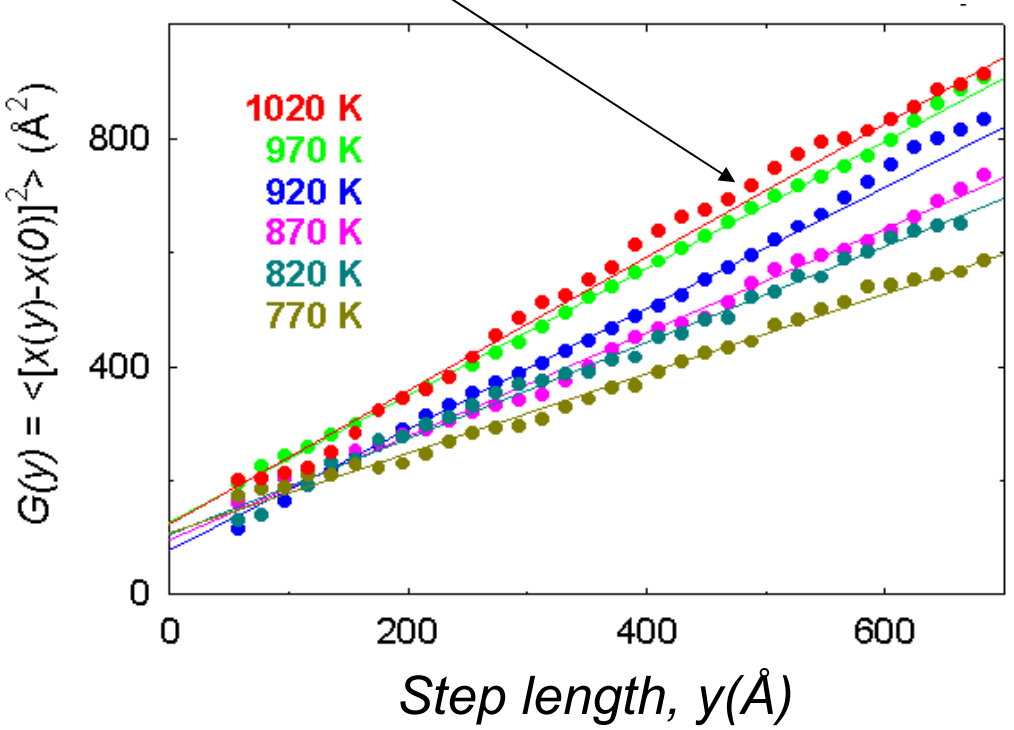
$$G(y) = \left\langle \left(x(y) - x(0)\right)^2 \right\rangle = \left(\frac{kT}{\tilde{\beta}}\right) y$$

Spatial Correlation Function

Al/Si(111) $(\sqrt{3}x\sqrt{3})R30^{\circ}$ phase
75 x 75 nm
step height 0.31 nm
Imaged at 700°C



$$slope = kT / \tilde{\beta}$$

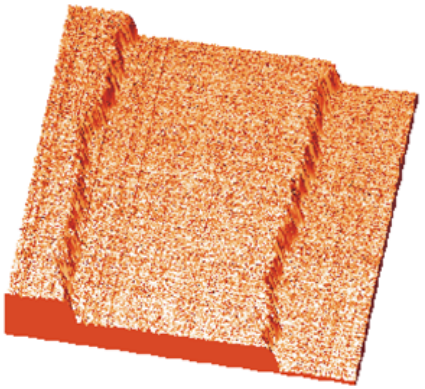


Lyubinetsky, et al. Surf. Sci 492 L671 2001

Continuum Step Model

temporal variation reveals kinetic parameters

- Al $(\sqrt{3}x\sqrt{3})R30^o$ on Si(111)
- Image size 75 nm x 75 nm
- Imaging Temperature 700^{o}C
- Repeated scans perpendicular to one location on step edge
- Animation is real time
- Care in imaging and analysis to avoid tip interaction effects



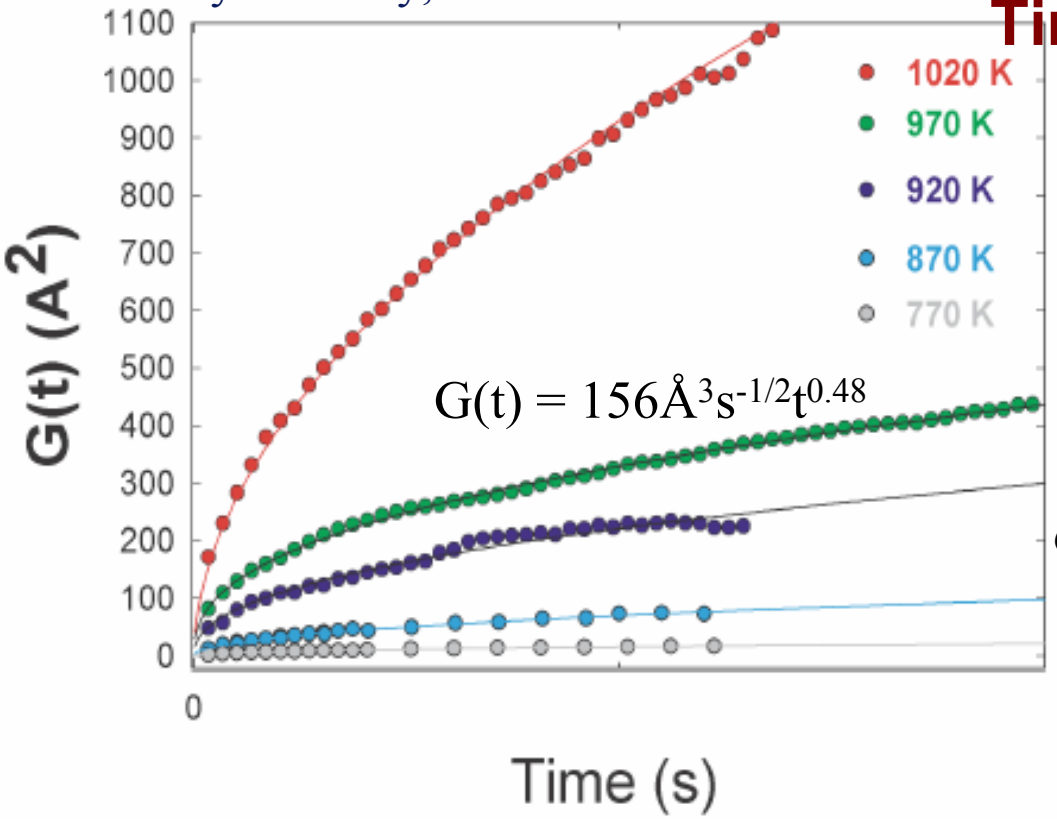
QuickTime™ and a
decompressor
are needed to see this picture.

Thermal Fluctuations of Step Edges

Temporal Correlation Function

$$G(t) = \left\langle \left(x(t) - x(0) \right)^2 \right\rangle$$

Lyubinetsky, et al. PRB **66** 85327 2002



Time Constant for Step-Terrac Atom Exchange, τ

$$G(t) = \left[4\Omega_v kTt / \pi\tilde{\beta}\tau \right]^{1/2}$$

Diffusion Constant $D_s c_o$ for Step-to-Step Terrace Diffusion

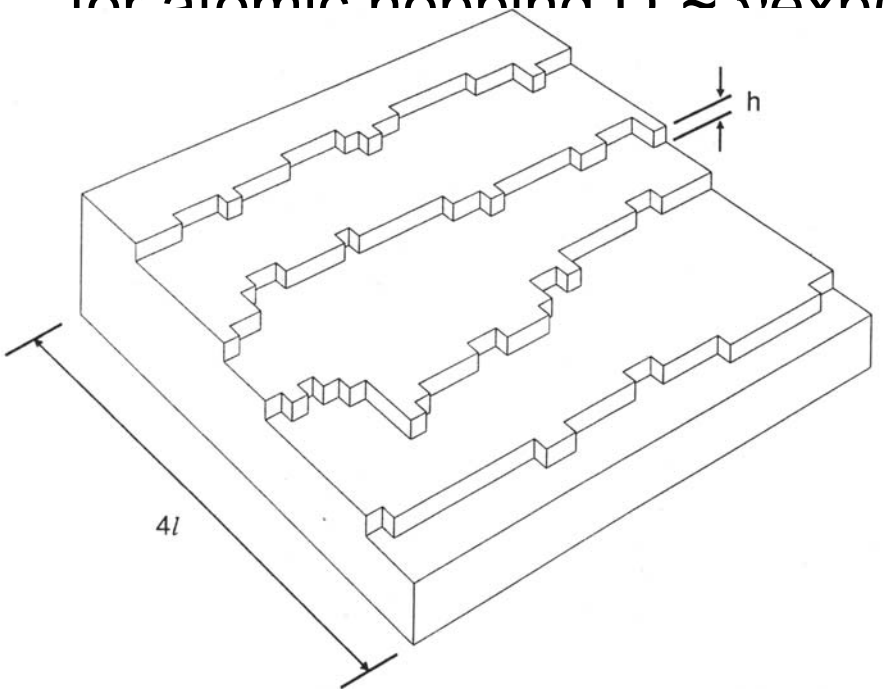
$$G(t) \cong \frac{2b^2 L}{\pi a_p} \left[\sqrt{\frac{tA_3}{L^3}} Erf\left(\sqrt{\frac{tA_3}{L^3}} \right) + \left(\frac{tA_3}{L^3} \right)^{\frac{1}{3}} \Gamma\left(\frac{2}{3}, \frac{tA_3}{L^3} \right) \right]$$

$$A_3 = \frac{2\Omega^2 a_p D_s c_o}{b^2},$$

Red Herring: Step-Terrace Exchange vs. Terrace Diffusion

Structural Fluctuations
atomistic interpretation

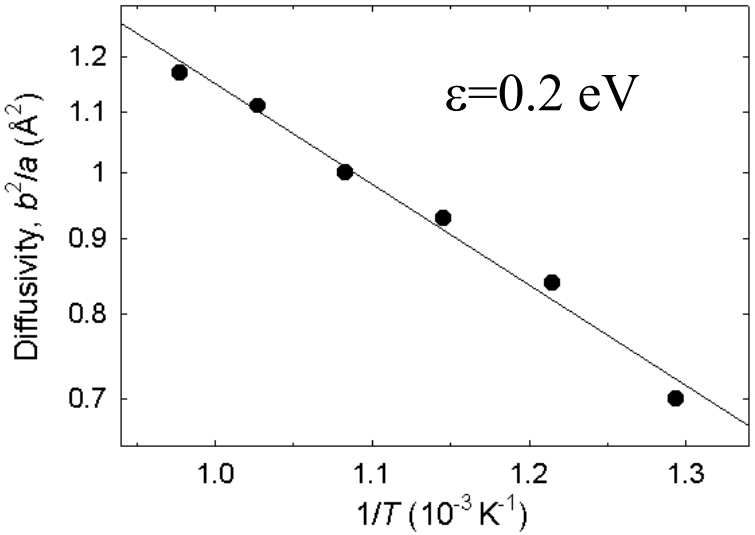
- Thermal excitation at step edges - requires bond breaking, P_k, ~ exp(-ε/kT) - causes steps to wander structurally, gaining entropy. "Stiff" steps have larger excitation cost.
- Rates of wandering determined by activation energies for atomic hopping D ~ νexp(-E_a/kT)



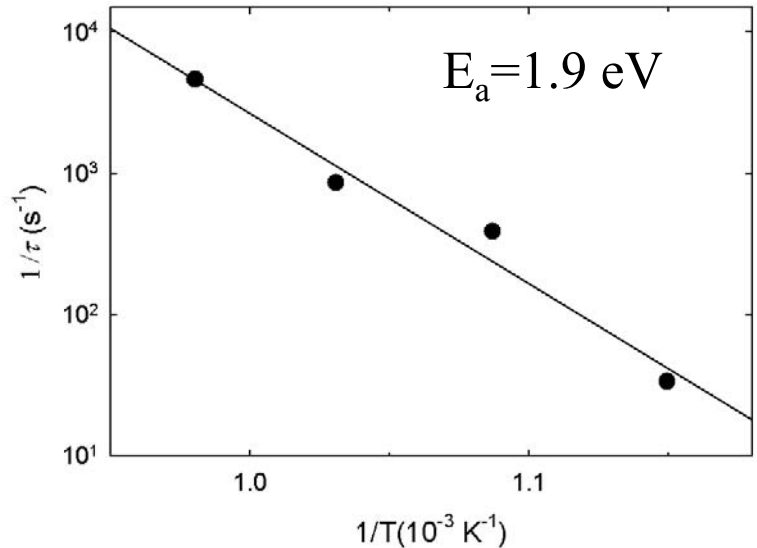
Lattice models, in which nearest neighbor atomic units interact with a binding energy e, and activation energies are associated with making and breaking near-neighbor bonds provide a predictive understanding of temperature variation

Effective Energies

Boltzmann - Step Free Energy



Arrhenius - Step Fluctuation Rate



Using lattice models of spatial and temporal step wandering yields effective energy scales

Step stiffness decreases from 95 to 75 meV/Å as temperature increases from 770K to 1020K. Apparent kink formation energy is ε = 0.14 eV.

$$\frac{kT}{\tilde{\beta}} = \frac{b^2(T)}{a} = a\exp(-\varepsilon/kT)$$

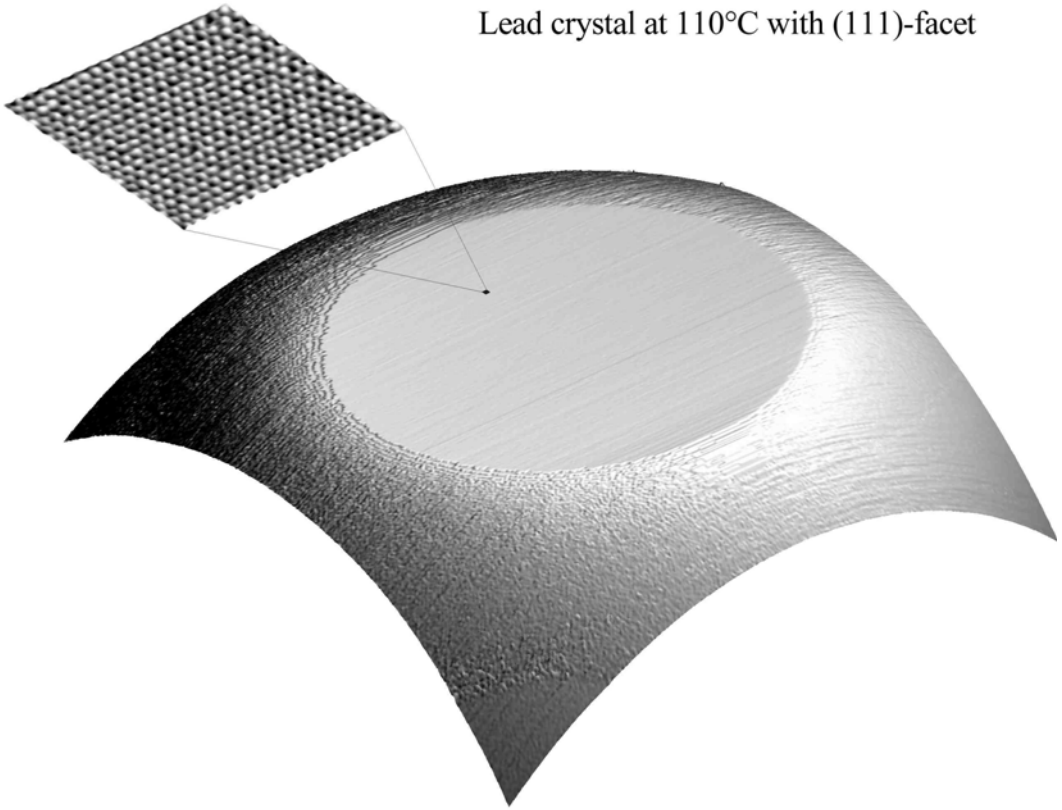
Time constant decreases from 260 ms at 770K to 0.3 ms at 1020K. Apparent activation energy is E_a = 2.4 eV.

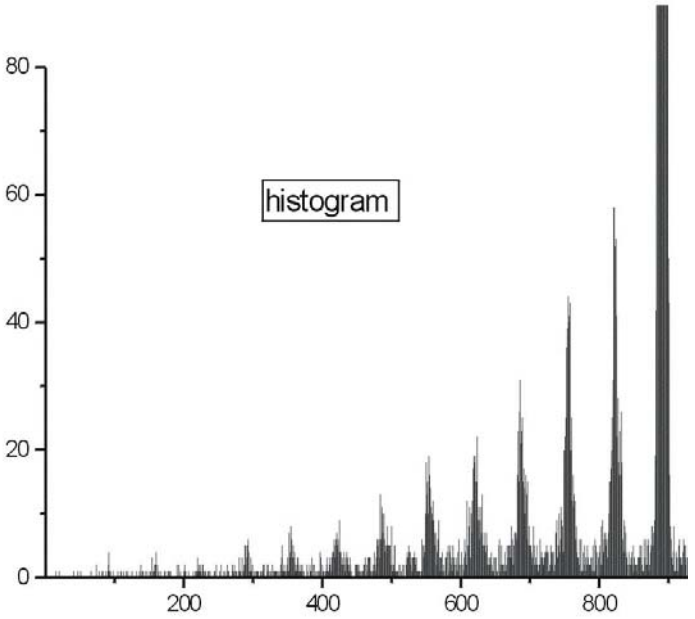
Structure Evolution: The Deterministic Envelope

$$J = \lambda \nabla \mu$$

- Continuum step parameters yield chemical potential gradients and time constants appropriate to mass transport:
- Evaluating the Driving Force; Pb Crystallites
  - K. Thürmer, J. Reutt-Robey, D. Dougherty, M. Degawa, W. Cullen, E.D. Williams - U. of Maryland
  - M. Uwaha - Nagoya University

In-Situ Imaging: Pb Crystallite at 110°C





- Rounded edges of crystallite formed by a staircase of steps of decreasing width

K. Thürmer, UMD-MRSEC

Step Chemical Potential

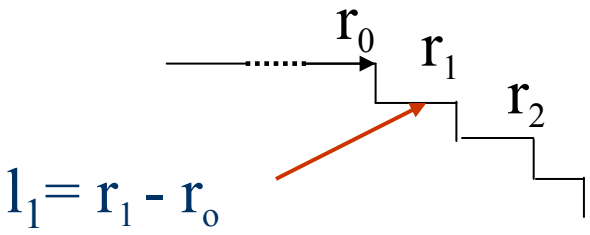
- Surface free energy:

$$f(\phi) = \gamma_0 + \frac{\beta(\theta,T)}{h}\tan\varphi + g(\theta,T)\tan^3\varphi$$

(1-d staircase of step density $\rho = \tan\phi = h/l$, azimuthal angle θ)

- Surface Chemical Potential:

$$\mu_s = \frac{\partial(f/\rho)}{\partial(1/\rho)}$$



- Step Chemical Potential:

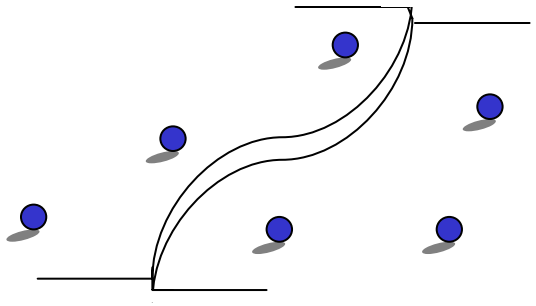
$$\mu_i = \Omega\left(\frac{\beta}{r_i} + \frac{gh^3}{2r_i}\left(\frac{1}{l_i^2} + \frac{1}{l_{i+1}^2}\right) - \frac{gh^3}{r_i}\left(\frac{r_{i-1}+r_i}{l_i^3} - \frac{r_i+r_{i+1}}{l_{i+1}^3}\right)\right)$$

(circularly symmetric step array)

Step Chemical Potential

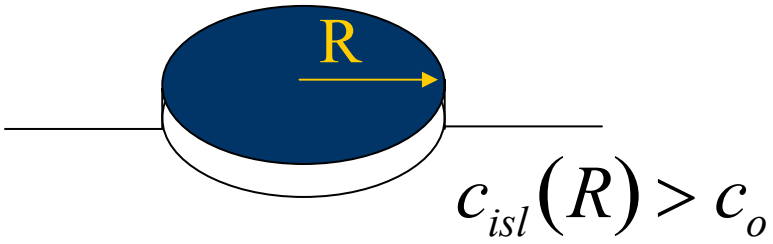
- Isolated Straight Step:

$$\mu_s = 0 = kT \ln\left(c_{loc} / c_o\right)$$



- Single-Layer Island:

$$\mu_s = \Omega\tilde{\beta} / R = kT \ln\left(c_{isl}(R) / c_o\right)$$

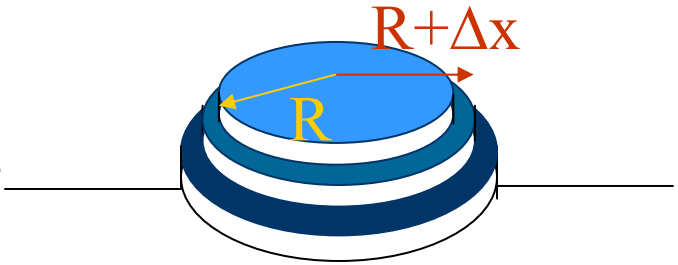


$$c_{isl}(R) > c_o$$

- Stack of Circular Layers:

$$\mu_s = \frac{\Omega\beta}{r_N} + \text{ step interaction terms}$$

$$= kT \ln\left(c_{stack}(R) / c_o\right)$$



$$c_{stack}(R) > c_{isl}(R)$$

Equilibrium Crystal Shape

- Crystal shape determined by requirement that all steps have the same chemical potential:

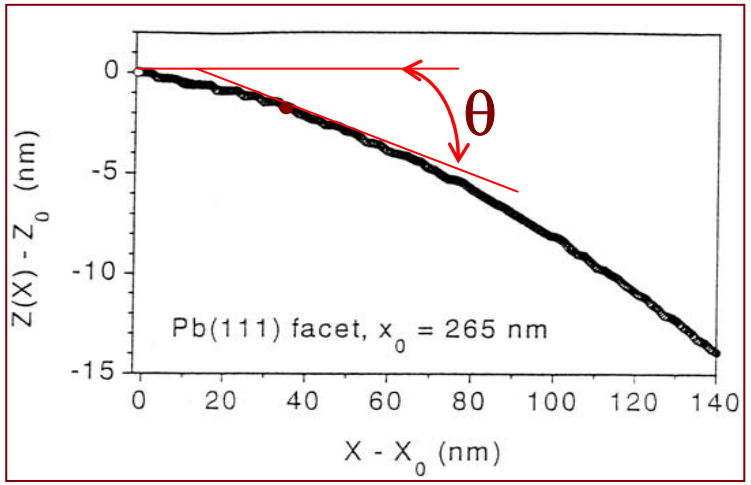
$$\mu_s = \frac{2\Omega\beta}{r_N}$$

- Yields Pokrovsky-Talapov prediction for shape of the rounded edge

$$z_o - z(x) = \frac{2}{3}\left(\frac{\beta / h}{3g}\right)^{1/2}(x - x_o)^{3/2}$$

- Fit to measured profile yields

$$z_o - z(x) = 0.0032\,\text{Å}^{-1/2}(x - x_o)^{1.49\pm0.006}$$



A. Emundts, et al.,
Surface Science **481** 13-24, 2001

Preparation of Lead Crystallites

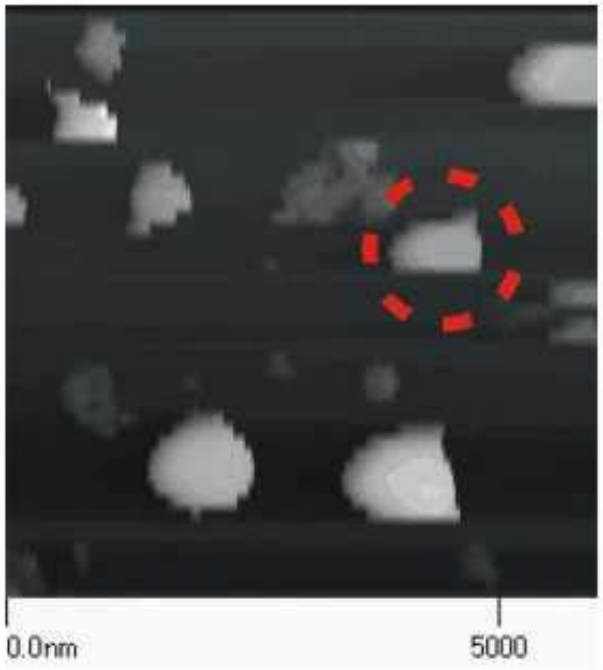
Deposition of ~300Å of Pb onto
Ru(001) at RT in UHV

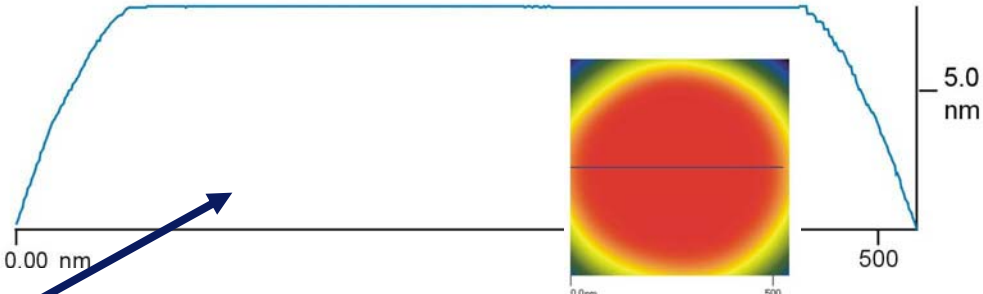
Heating T>Tm
Dewetting of Pb Film

Slow Solidification by Cooling
~20K/min

Identifying Crystallites for Imaging

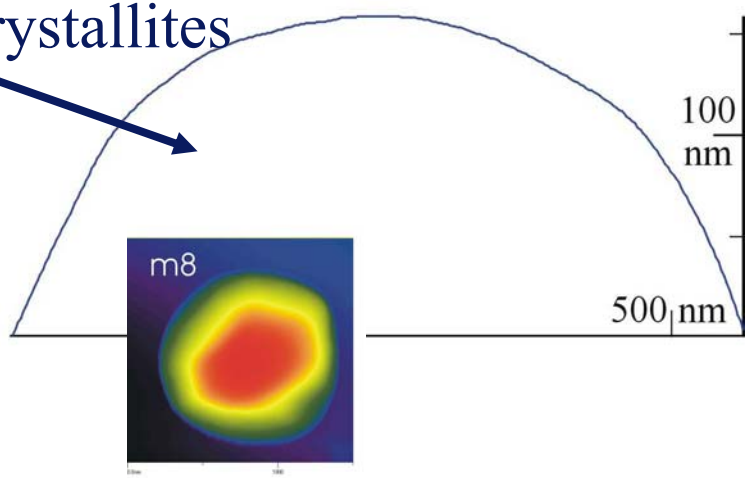
Large area scan (>5μm) to locate crystallites - zoom in for high resolution





Usually - flat topped crystallites

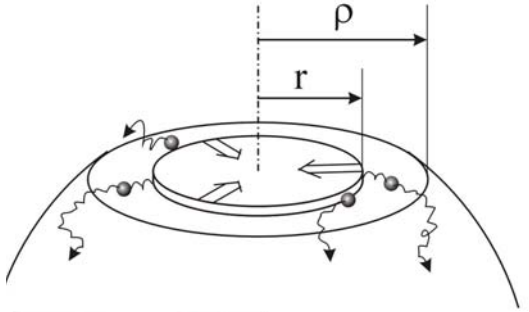
Occasionally - round topped crystallites

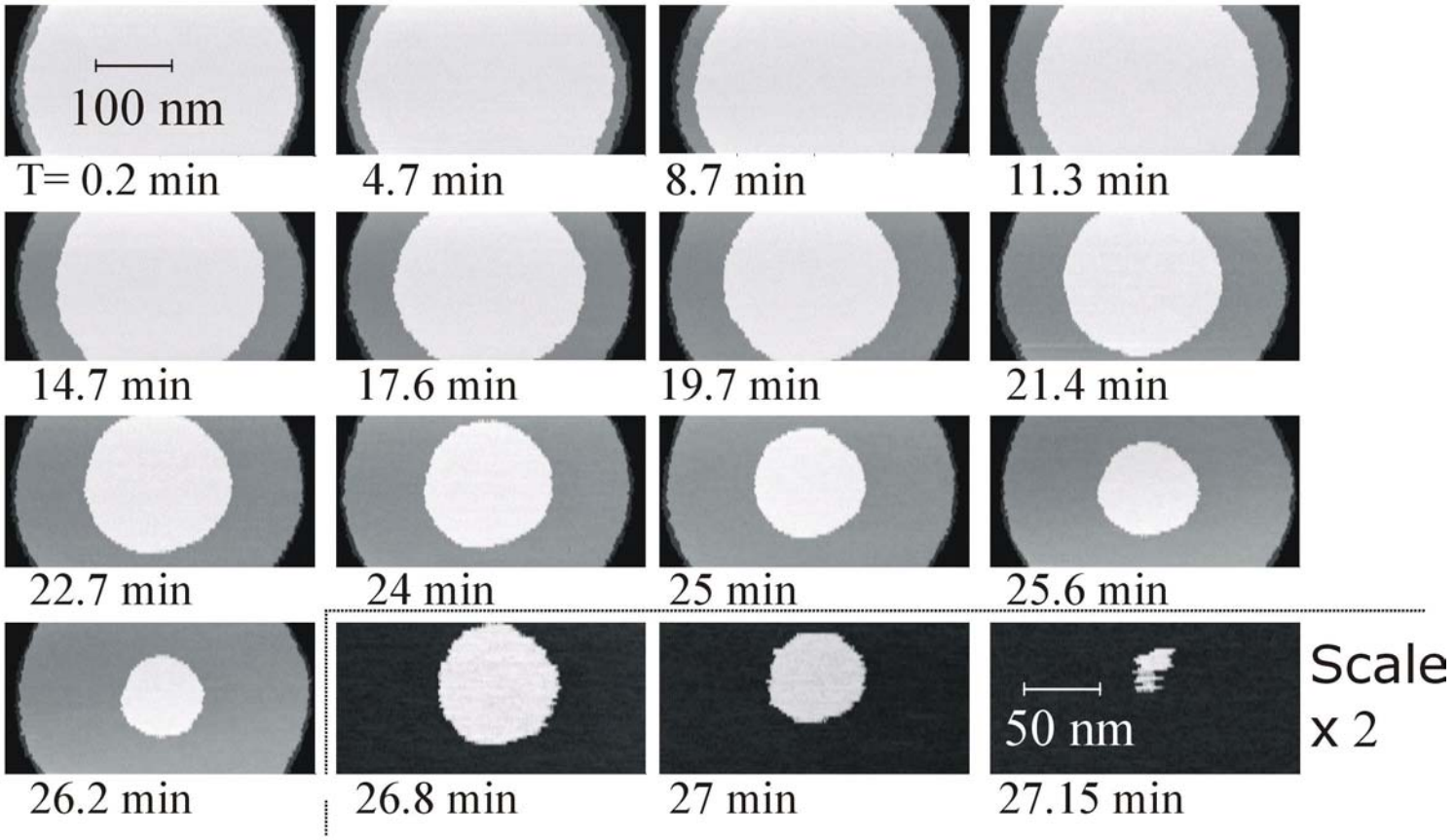


At room temperature, crystallite shapes are frozen

Temporal Evolution

Flat-topped Crystallite



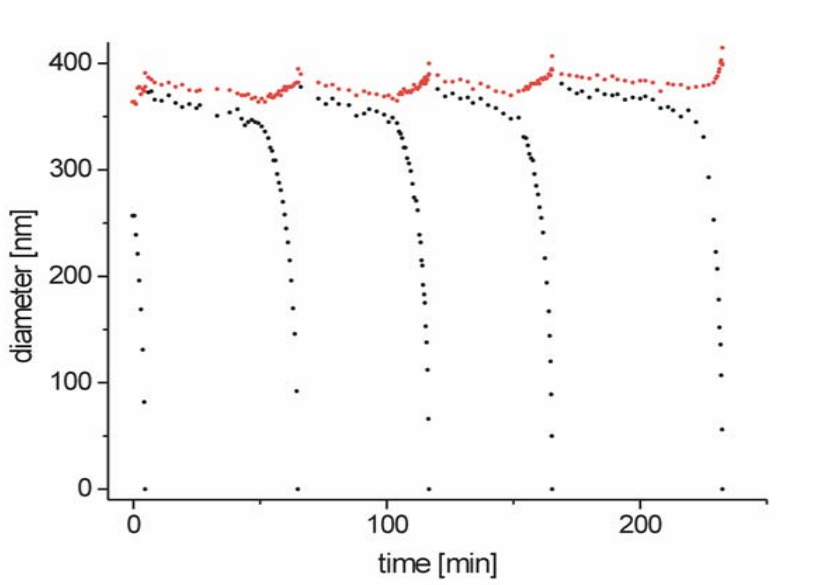


Following rapid Temperature Change
from ~280°C to 80°C

Pb Crystallite Relaxation

- Imaging Temperature 80°C
- Field of View 350 nm
- Quench from 300°C occurred ~60 minutes before first image

QuickTime™ and a
decompressor
are needed to see this picture.

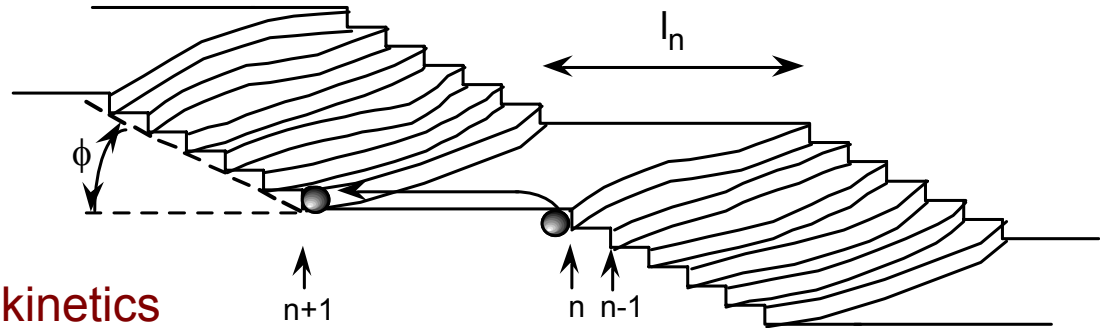


Early stage of each layer decay involves:

- Influence of layer radius
- step-step repulsions
- redistribution of mass down the step staircase

Linear Kinetics - The Rate Constant

- Linear Kinetics: The rate of motion of a step edge is proportional to a difference in chemical potential



- Attachment limited kinetics

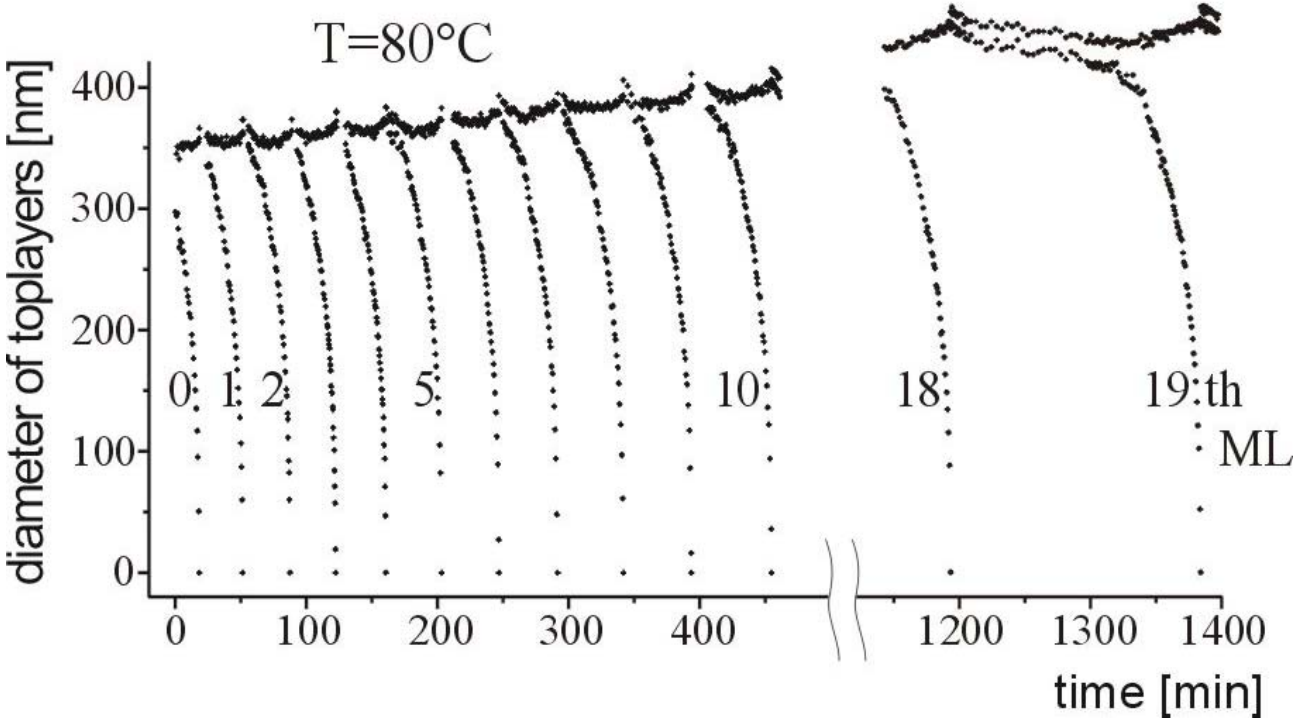
$$dx_n/dt = \frac{a}{2\tau_a kT}(2\mu_n - \mu_{n+1} - \mu_{n-1})$$

- Diffusion limited kinetics

$$dx_n/dt = \frac{D_s c_o \Omega}{kT}\left\{\frac{\mu_n - \mu_{n-1}}{x_n - x_{n-1}} + \frac{\mu_n - \mu_{n+1}}{x_{n+1} - x_n}\right\}$$

Step chemical potentials determined by step stiffness and step-step-interactions

Cooperative Mass Redistribution

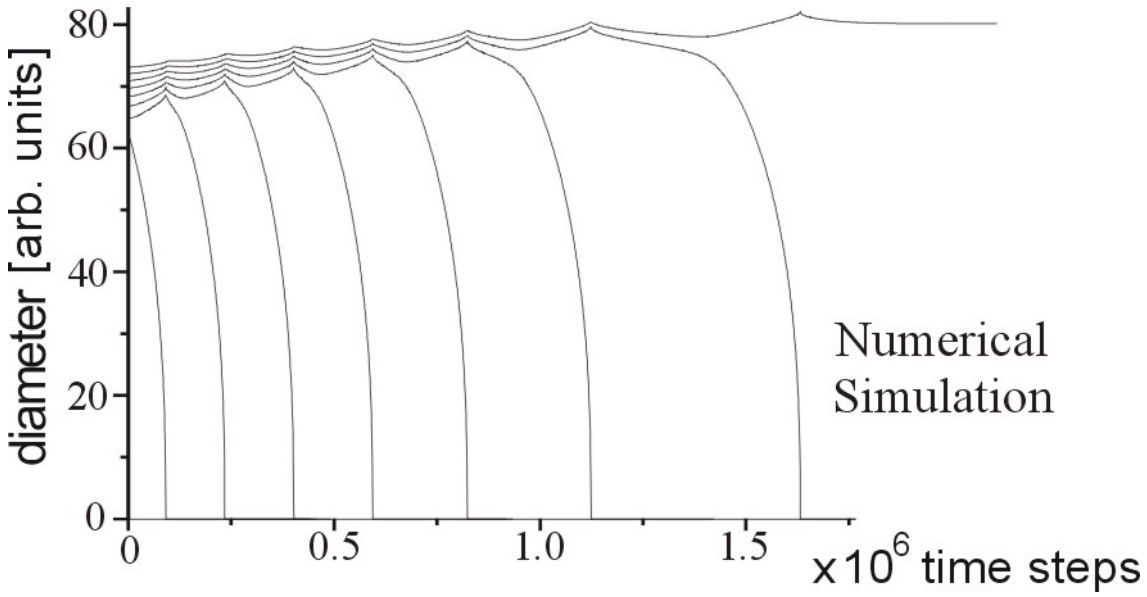


Flux across terrace i:

$$J_i = \frac{2\pi}{kT} \frac{\mu_s^{i+1} - \mu_s^i}{\ln\left(R_i/R_{i+1}\right)/D_s c_o + \left(a\tau_a\right)\left(R_i^{-1} + R_{i+1}^{-1}\right)}$$

Given initial step configuration (values of R_i) numerically solve for step motion based on flux between steps:

Step Thermodynamic Parameters - Preliminary



Numerical simulation - initial configuration is high-T equilibrium shape. Change of step parameters to low-T values creates chemical potential gradients driving mass transport

Time Constant

Fits to rate of decay indicate diffusion limited regime (slow terrace diffusion, fast edge attachment)

$$D_s c_o > 3.7x10^4 s^{-1}$$

$$\tau_a \approx 0.12ms$$

Step Stiffness

Independent measurements of island shape indicate

$$\beta \cong \tilde{\beta} \approx 25meV/\mathring{A}$$

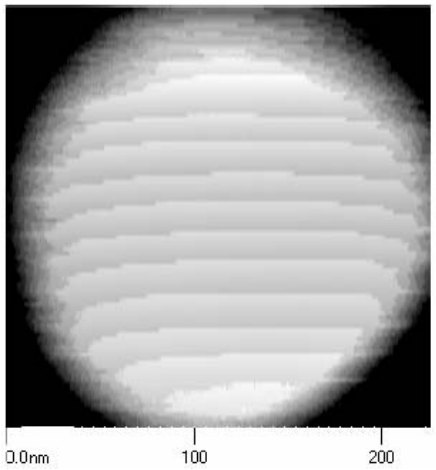
Step Interactions

Stress mediated interaction estimate based on calculated (111) surface stress

$$g(80^oC) \approx 10meV/\mathring{A}$$

Round-Topped Crystallite

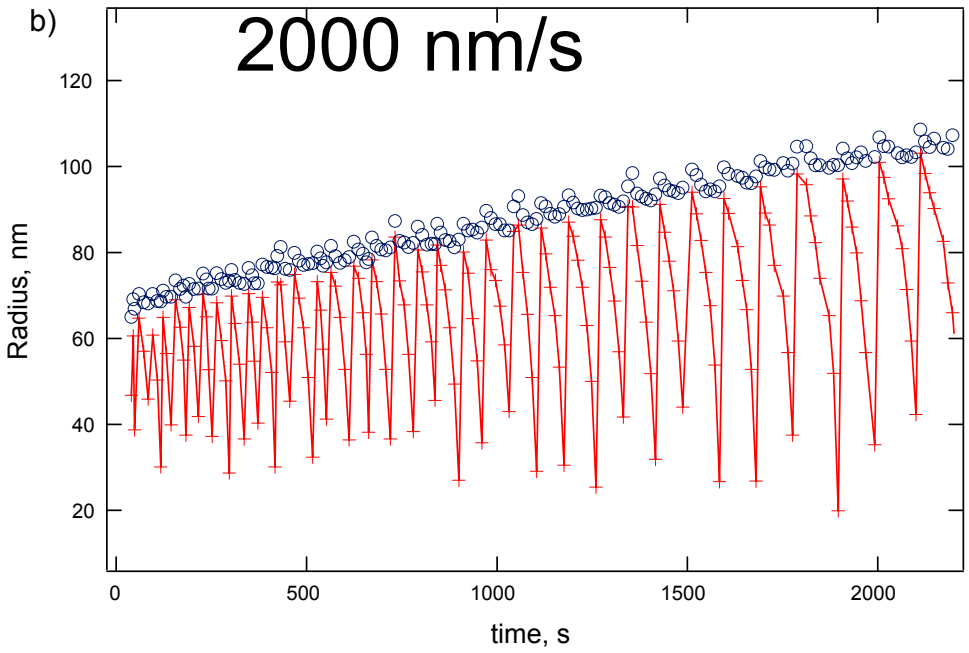
- Round topped crystallites are found even after equilibration at elevated temperature for up 48 hours
- Engagement of the STM tip for higher resolution imaging at elevated temperature results in immediate rapid changes in structure…



slow scan: 50nm/s

Rapid Decay

- Decay triggered by STM scanning
- Initial decay 18s per layer, measured with fast scan of 2000 nm/s



QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

Simplified modeling

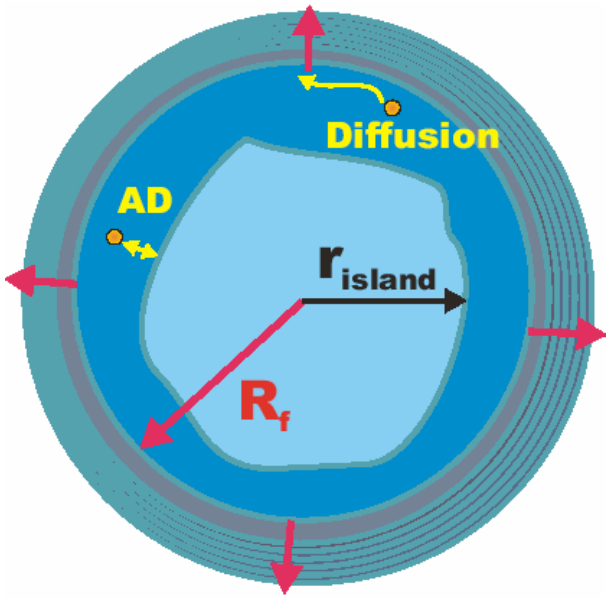
Shape Preserving Decay

$$\frac{dR_f}{dt} = -\left.\frac{dR}{dz}\right|_{zf} 2\Omega h \frac{j(R_f)}{R_f}$$

ADL: $$j(R_f) = \frac{\Omega h \tilde{\beta} \kappa c_{eq}^0}{2k_B T} \frac{\partial}{\partial z}\left(\frac{1}{R_f}\right)$$

TD: $$j(R_f) = \frac{\Omega \tilde{\beta} D_S c_{eq}^0}{k_B T}\left(\frac{1}{R_f}\right)^2$$

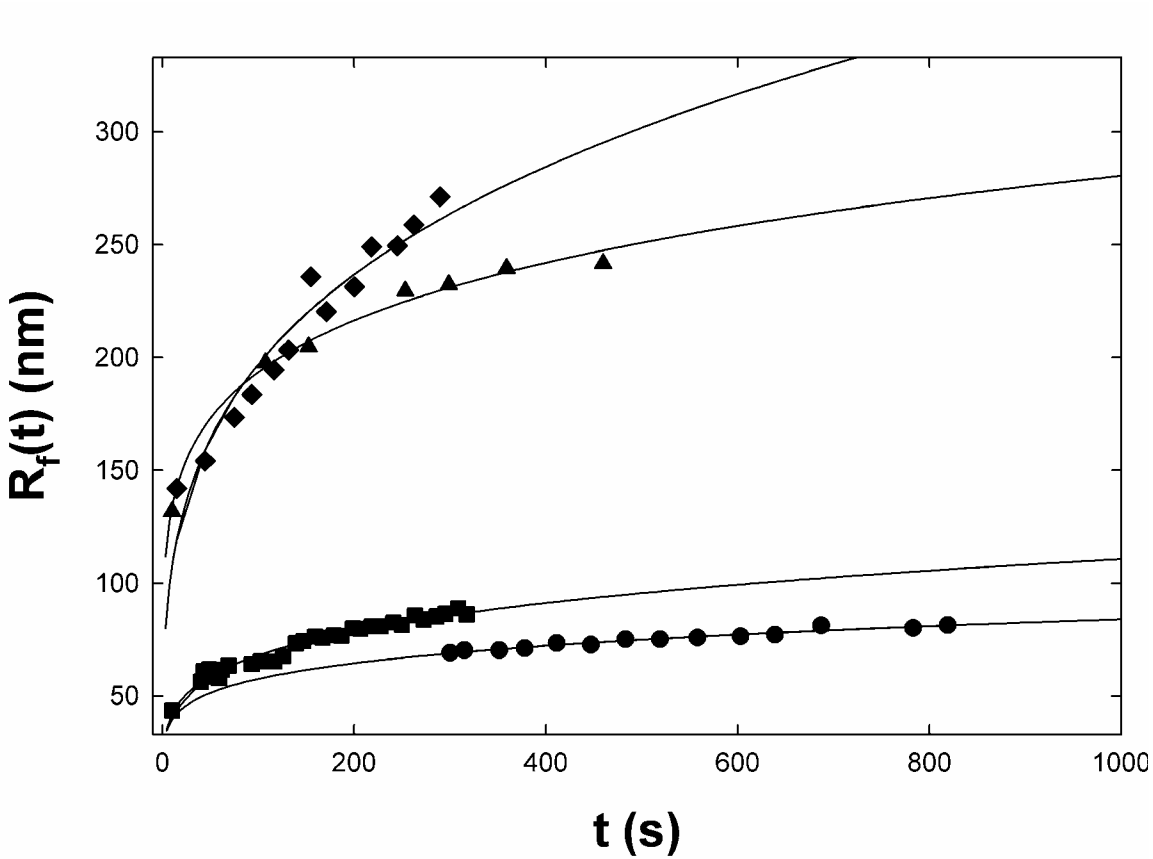
$R_f(t) \sim B(t) t^{\nu}$



For an initial P-T crystal shape and kinetic processes limited by step attachment or terrace diffusion, the exponent of the leading term *n* is 1/5 or 2/9

M. Uwaha, K. Watanabe, J. Phys. Soc. Jpn. 160, 497 (2000)

Scaling Analysis



- T=420K, ν = 0.16 T=370K, ν = 0.16
- T=390K, ν = 0.21 T=360K, ν = 0.26
- Fits are non-unique, but robust in overall range of dominant exponent.

D.Dougherty, submitted,

Fast/Slow Decay Comparison

(test shape preserving approx'n)

- Speed at which top layer shrinks and disappears primarily depends on layer radius
- Diffusion limited case:

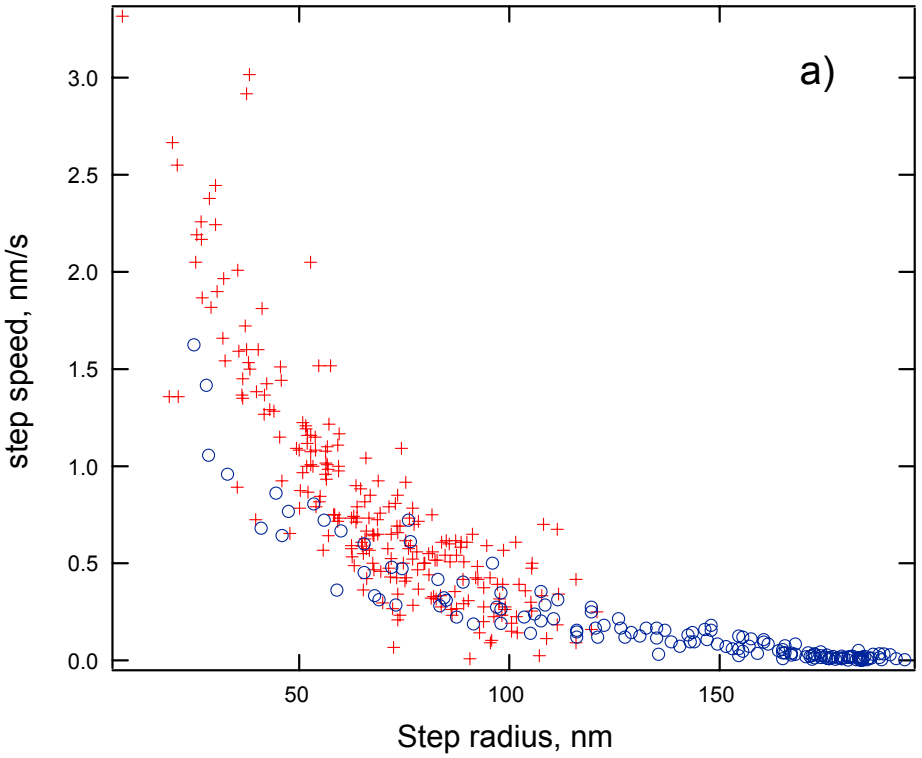
$$\frac{\mu_1 - \mu_2}{kT} = \frac{A_1 \ln(R_2/R_1)}{\Omega D_s c_{eq}^o} \frac{dR_1}{dt}$$

R_1= radius of shrinking step

R_2 = radius of second step

- Chemical potential of top step:

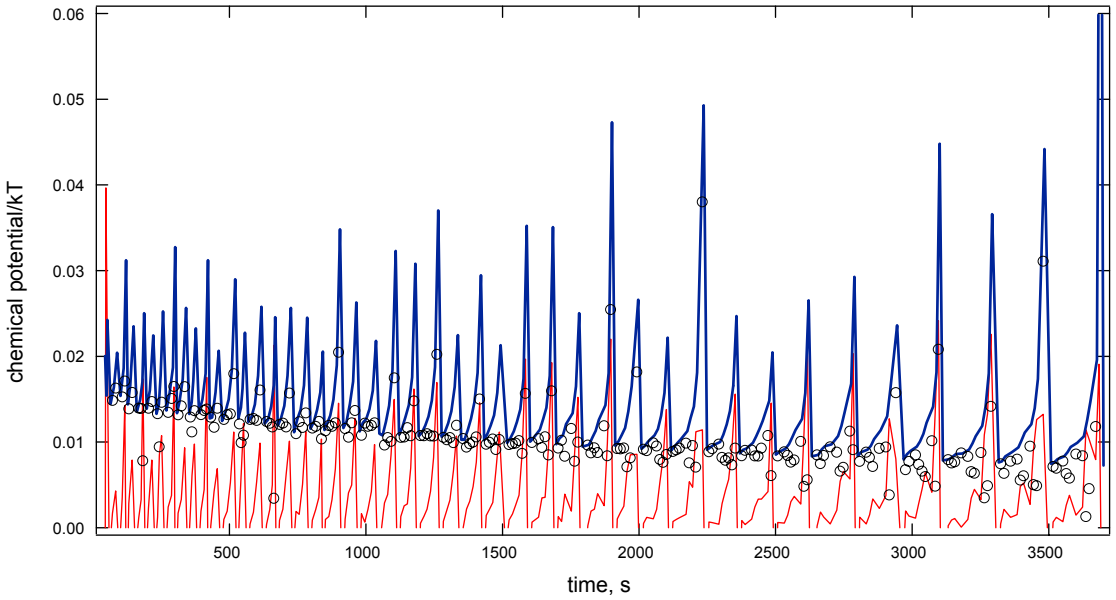
$$\mu_1 = \frac{\Omega\beta}{r_1} + \text{small step interaction terms}$$



Red: Triggered (fast) decay

Blue: Decay after quench

Evolution of Step Chemical Potential



Triggered Relaxation

- Red = $\Delta\mu/kT$, from measured r(t)
- Blue = μ_1/kT, calculated from scp formula
- Black circles - difference yields μ_2/kT
- For late stages of relaxation (measured from relaxation after quench): $\mu_2/kT \sim 0.005$

Driving Force…

- At 50 nm radius $\Delta c/c_o = \Delta\mu/kT \sim 0.01$:
- $dR_1/dt \sim 1$ nm/s

$$D_s c_o > 3.7x10^4 s^{-1}$$

$$\tau_a \approx 0.12ms$$

- About 3 in 4,000 atoms detaching from shrinking island edge fail to return…

Boundary conditions…

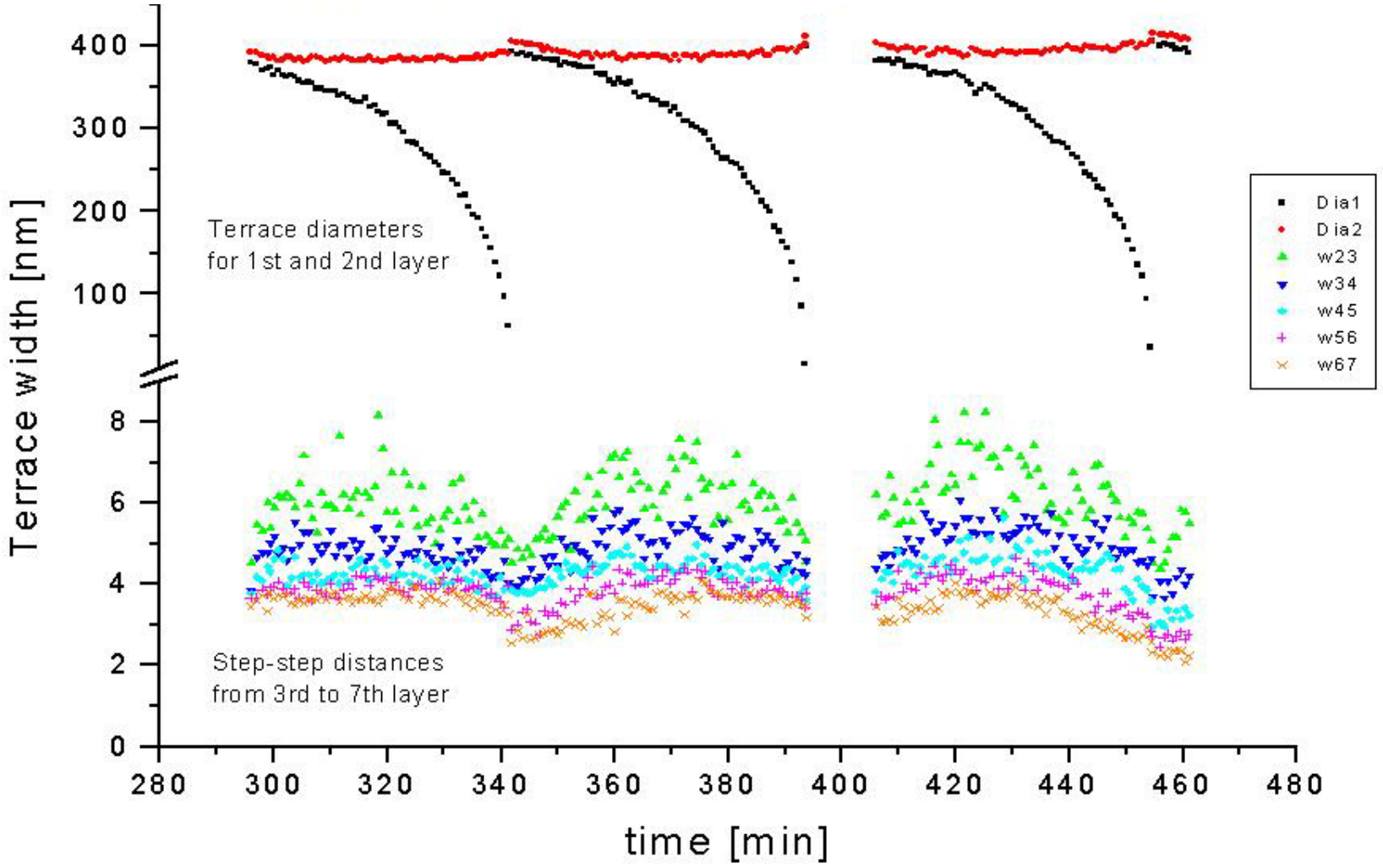
- The final state chemical potential is determined by the boundary conditions of the supported crystallite, leading to a generalized chemical potential form:

$$\mu = \frac{2\Omega(\beta r_o - 3acg)}{r_o^2}$$

- M. Degawa, in preparation 2003

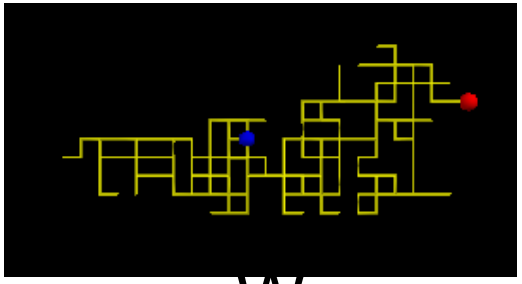
Edge Fluctuations Modulate Evolution

Pb Crystallite



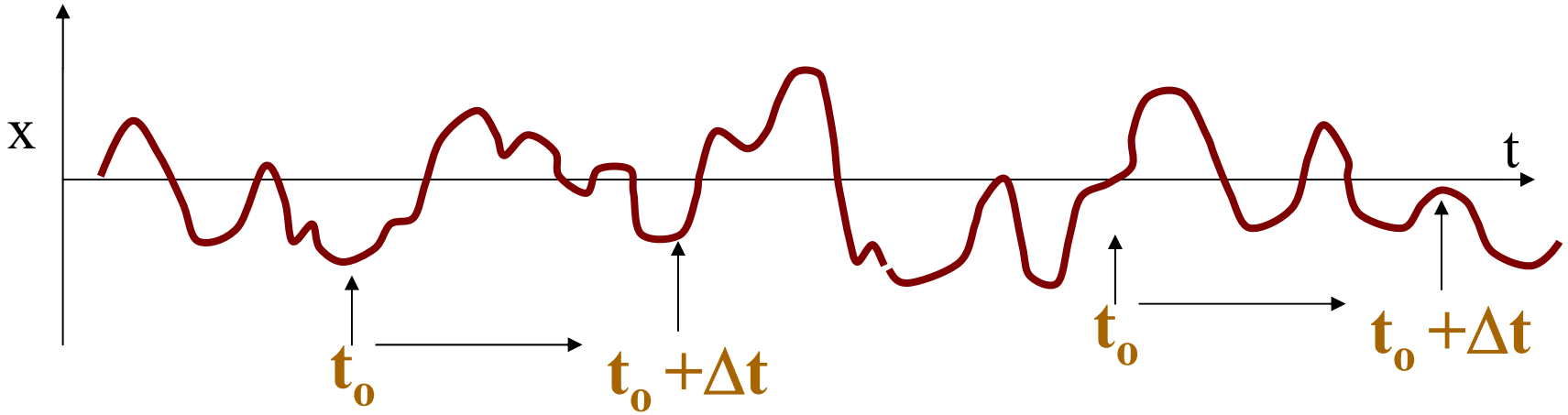
Lessons from the Random Walk

- The temporal correlation function yields thermodynamic parameters useful for predicting system average behavior.



This is similar to information about average random walk behavior, such as rms displacement

- We can ask different questions about the nature of the walk….



First Passage and Persistence

- Governing equation: $\frac{\partial x}{\partial t} = \frac{\Gamma_A \tilde{\beta}}{kT} \frac{\partial^2 x}{\partial y^2} + \eta_{non-conserved}$
- Probability distribution: $P(x,t)$
- First passage: What is the probability of first reaching position x at time t?

$$P(x,t) = \delta_{x,o}\delta_{t,o} + \sum_{t'<t} F(x,t')P(0,t-t')$$

- Persistence (survival): What is the probability of not returning to the starting position in time t?

$$p(t) = 1 - S(t) = \int_{\delta t}^{t} F(t')dt'$$

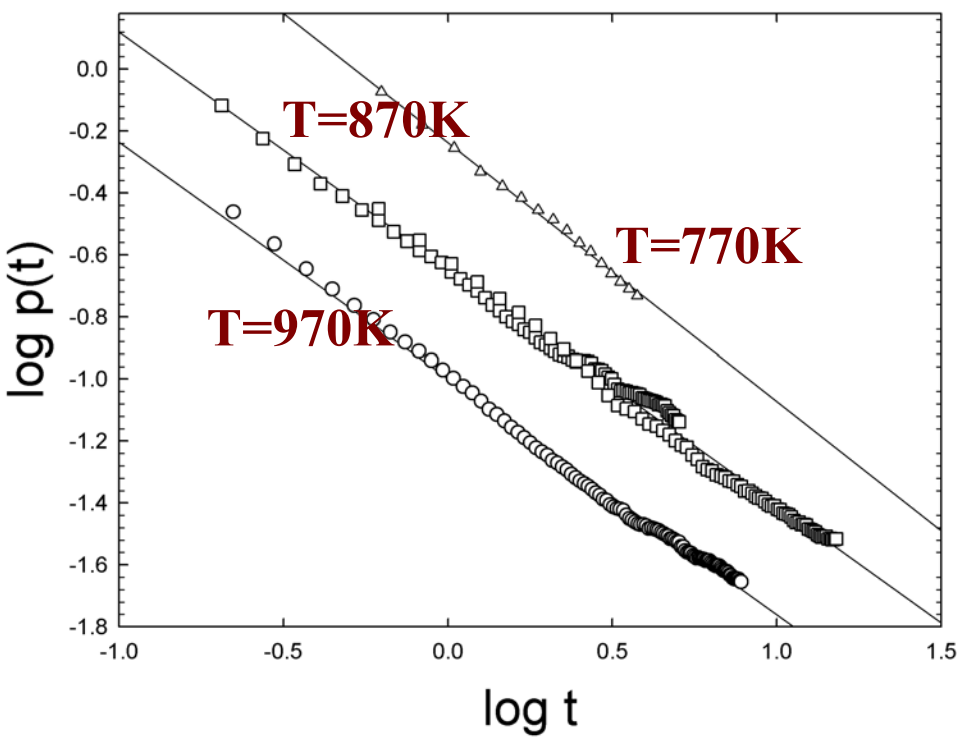
Statistical Persistence

- For measurement x(t) of fluctuating step, divide the time axis into bins of width Δt, and count the fraction in which the step does not return to the starting point of the bin.
- Theory predicts universal behavior
  $P(\Delta t) \sim \Delta t^{-\theta}$
- Experimental analysis at three temperatures yields $\theta = 0.77 \pm 0.03$.
- Theory* predicts $\theta = 3/4$ for step attachment limited kinetics (non-conserved noise)

*Krug et al. Phys Rev. E 56, 2702 1997

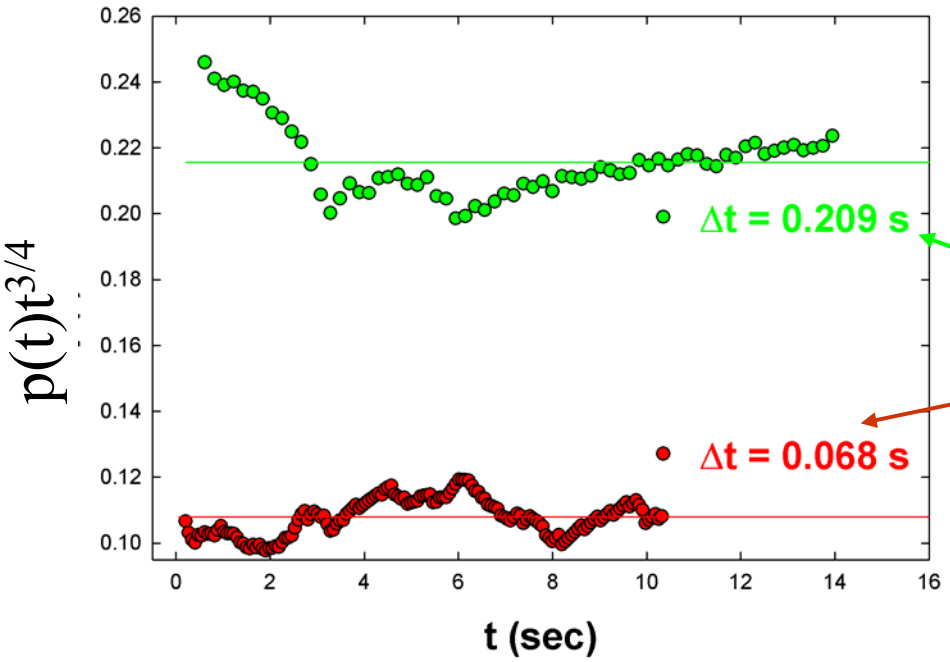
- Data measured at different temperatures collapse to the same curve when time is scaled to the minimum sampling time.

Step Wandering on Al/Si(111)
$G(t) \sim t^{1/2}$



D.B. Dougherty *et al*, PRL 2002

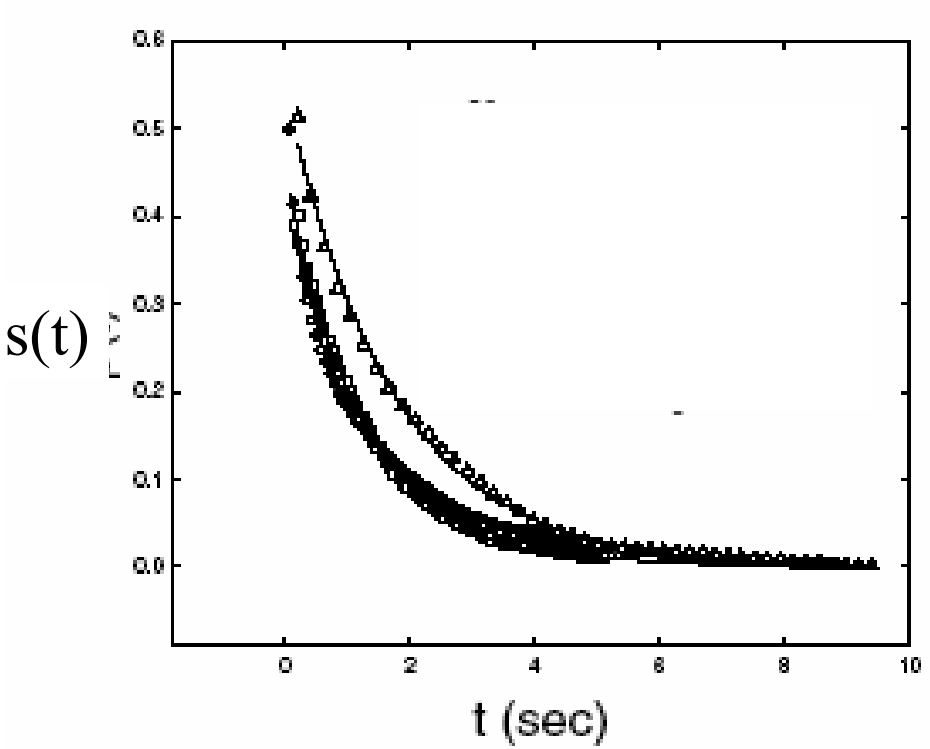
Sampling Time Effect



- Two measurements at 870K, different sampling times
- Step attachment time constant is 29 ms
- Scaling appears to follow $p(t) \sim 0.8(t/\Delta t_{samp})^{-3/4}$

Survival

D.B. Dougherty *et al*, PRL 2002

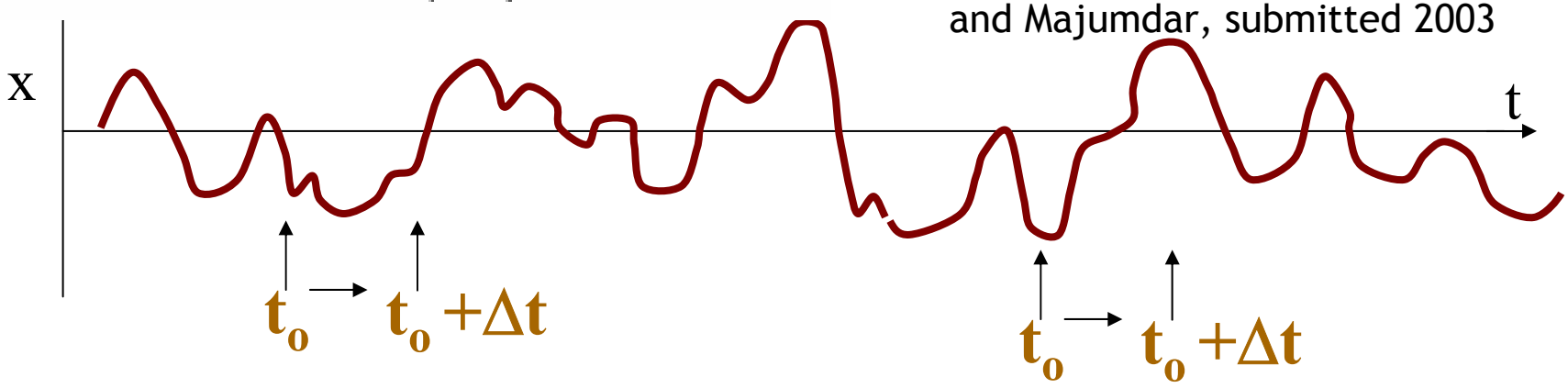


- Ask a different question: probability of returning to a fixed position (rather than position at start of time bin).
- $s(t) \sim \exp(-t/a\tau_c)$

  τ_c is the decay time of the autocorrelation function

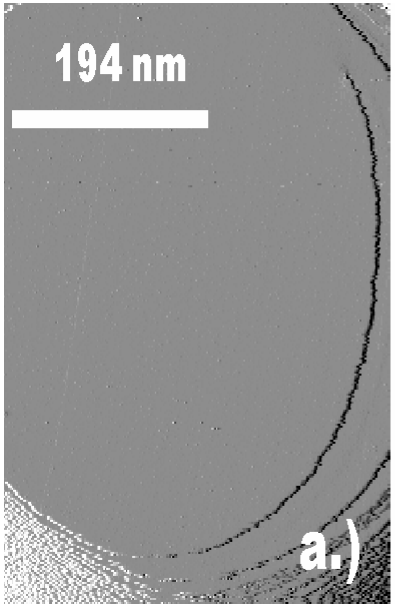
  $\tau_c = \tau_a L^2 kT/[(2\pi)^2 a^3 \beta]$

  Dasgupta, Constantin, DasSarma and Majumdar, submitted 2003

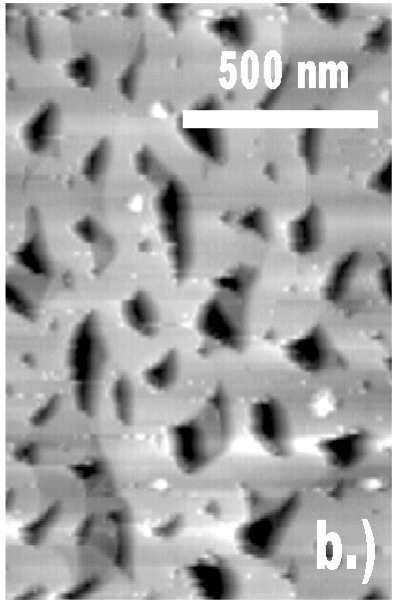


Thermal Fluctuations

- Crystalline thin films provide model cases for characterizing thermal fluctuations and correlating them with electrical properties
- Scanned probe images of crystalline structures at low magnification appear sharp but, when thermal excitations are possible, are blurred in high resolution images due to structural changes occurring on the same time scale as scanning

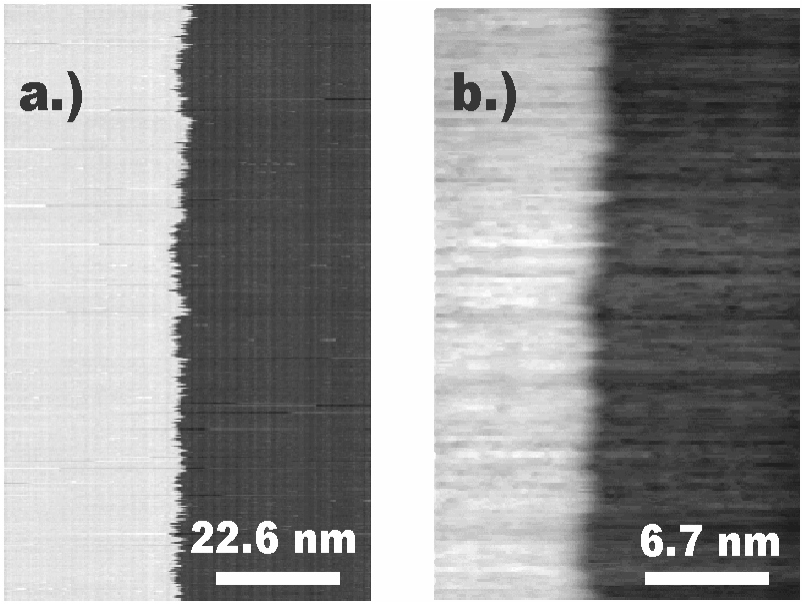


Screw dislocation on a supported Pb crystallite



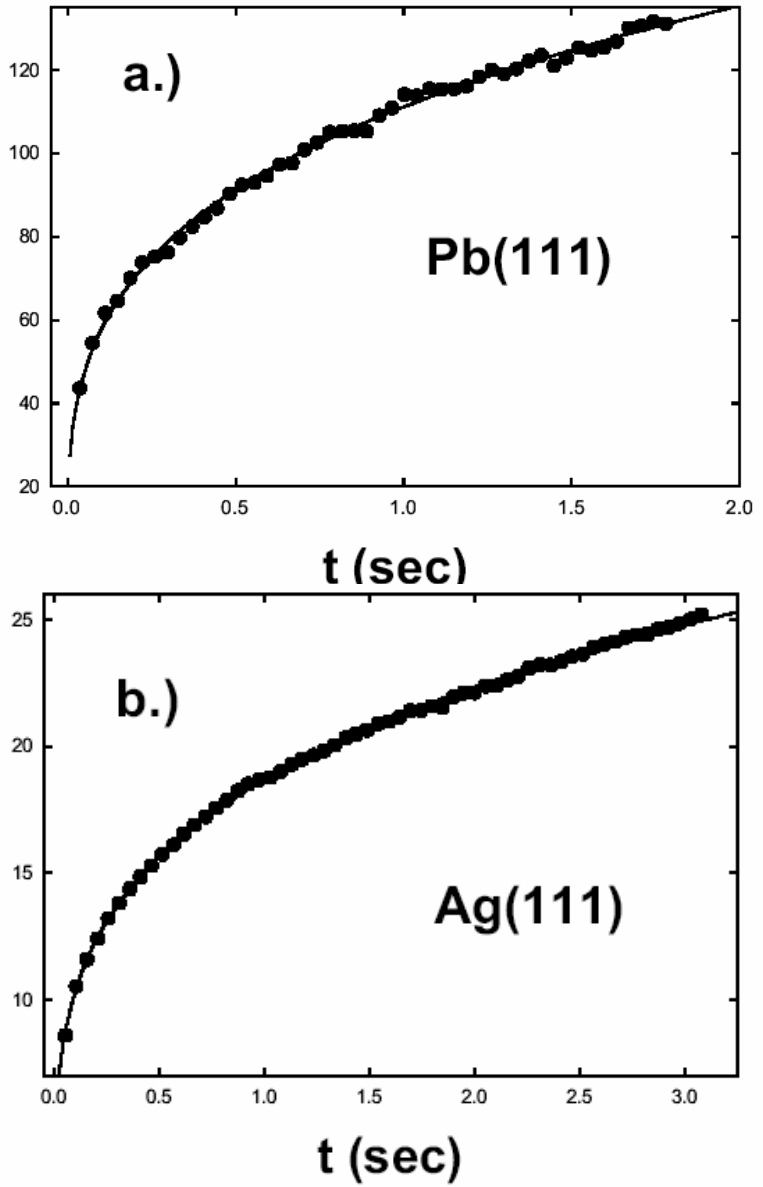
Growth pits in an epitaxial film of Ag on mica

Time Images and Correlation Functions



$$G(t) = \left\langle \left(x(t) - x(0)\right)^2 \right\rangle \sim \left(t/\tau\right)^{1/z}$$

Both Pb and Ag fit z = 4, indicating step edge-diffusion mediated fluctuations at T ~ 320K.



Statistical Persistence

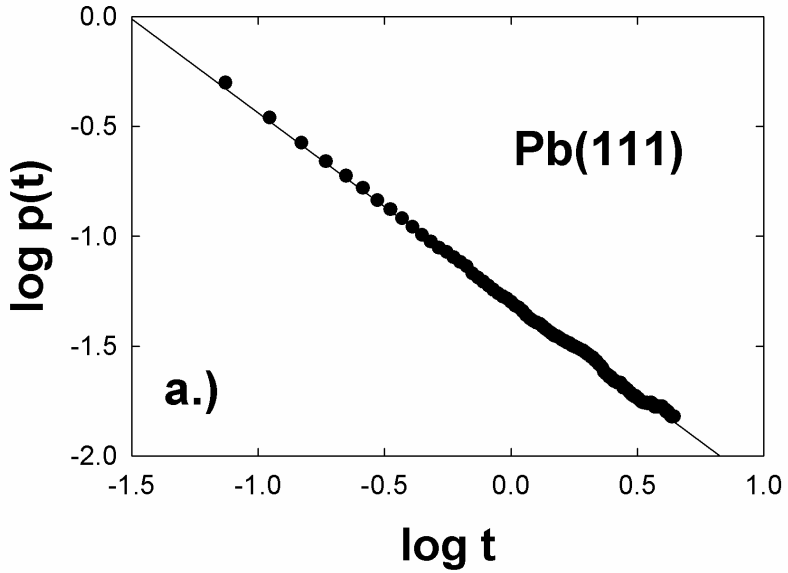
- Persistence theory predicts universal behavior
  $P(\Delta t) \sim \Delta t^{-\theta}$
  With $\theta = 7/8$ for step-diffusion limited fluctuations (conserved noise)

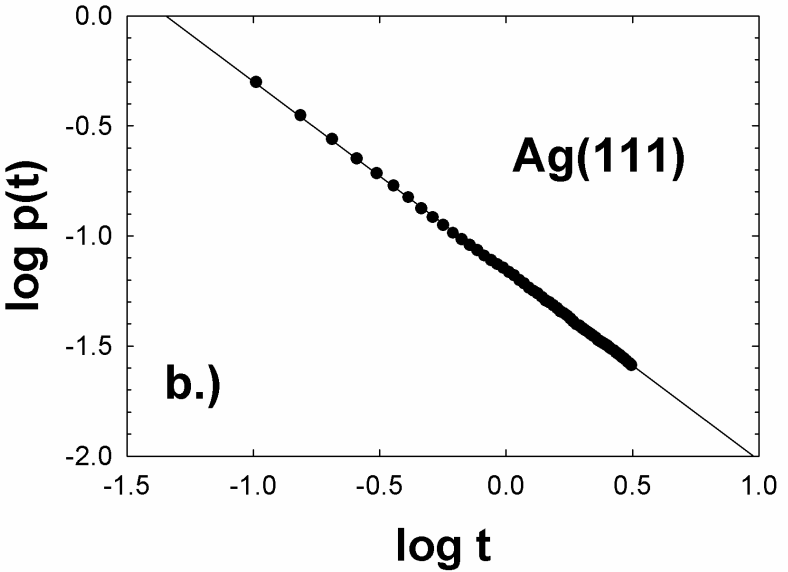
*Krug et al. Phys Rev. E 56, 2702 1997

- Experimental analysis on two different materials yields $\theta = 0.87 \pm 0.04$.

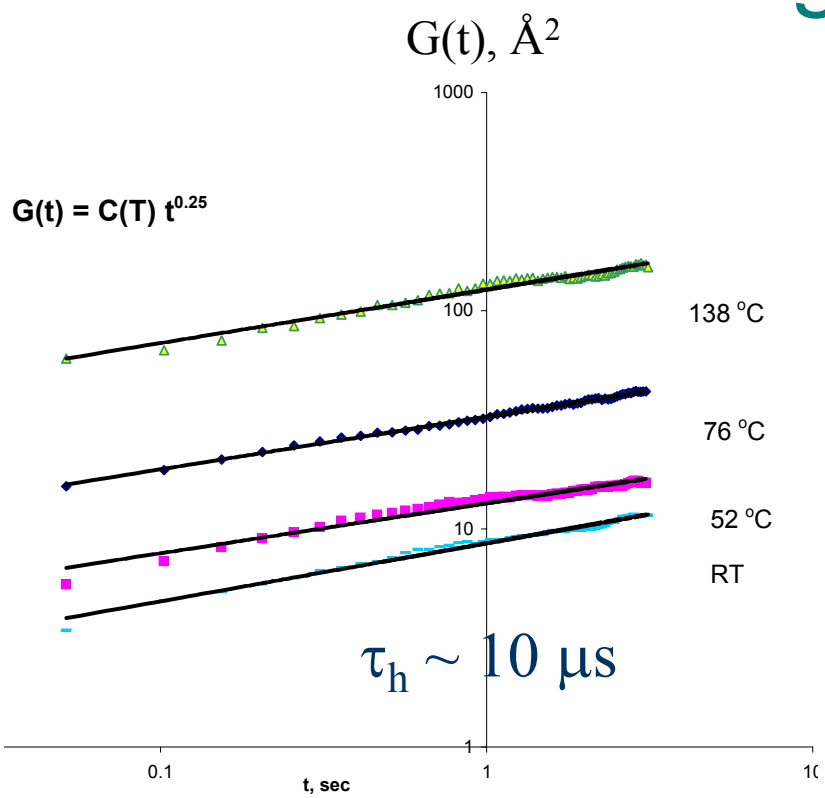
Dougherty, et al. Surface Sci. 2003

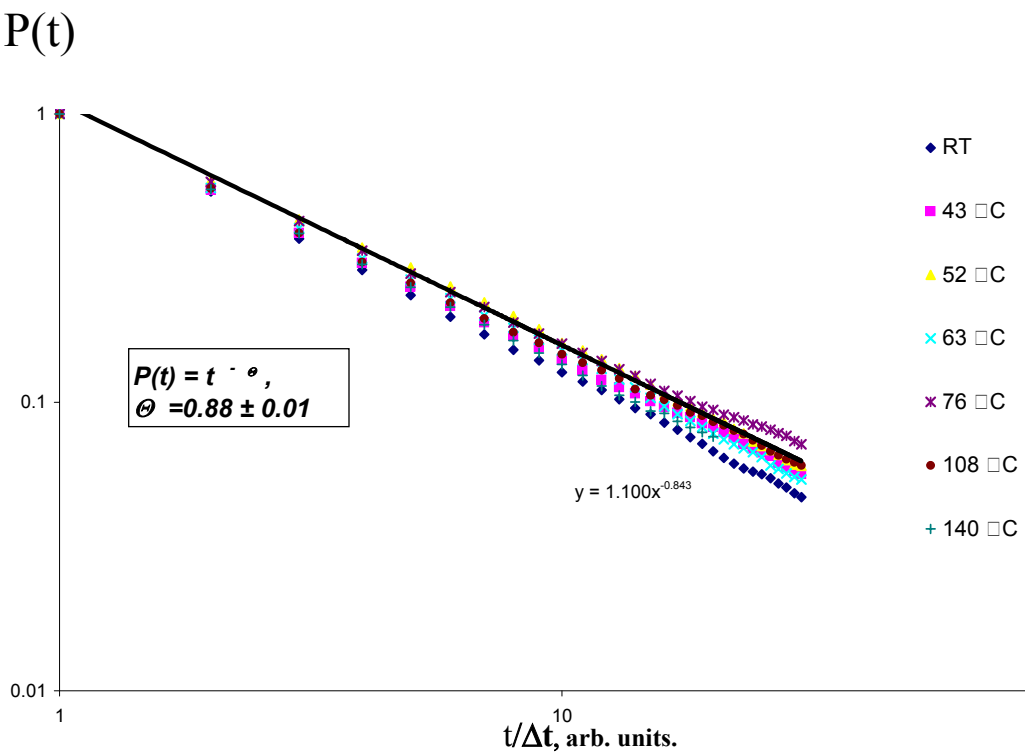
Step Wandering on Pb and Ag
$G(t) \sim t^{1/4}$





Ag(111)





- Correlation function varies as $t^{1/4}$, with ~ x10 variation over 40 -140°C, indicating x10^4 variation in physical time constant
- Persistence varies as $t^{-7/8}$, with collapse of amplitude for $t/\Delta t_{samp}$ scaling, Δt_{samp} = 57 ms

A. Bondarchuk, in preparation 2003

Questions: Persistence and Survival

- Persistence vs. survival: effects of:
  - Sampling time, choice of offset, diffusion limited process?
- Physical correlations with?
  - Onset of activated processes, switching
  - Nucleation events
  - Characterization of noise
  - Coupling of nanostructures to external fields
- Possible to extend experiment and theory to structures such as gaps, dots, wire constrictions?
  - "stochastic predictability" for nanoscale devices

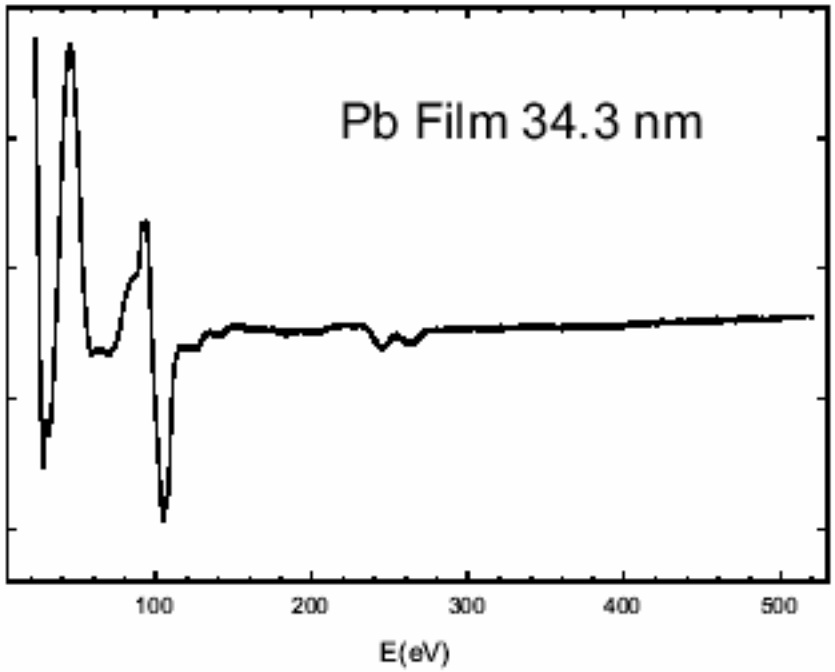
Challenges for Understanding

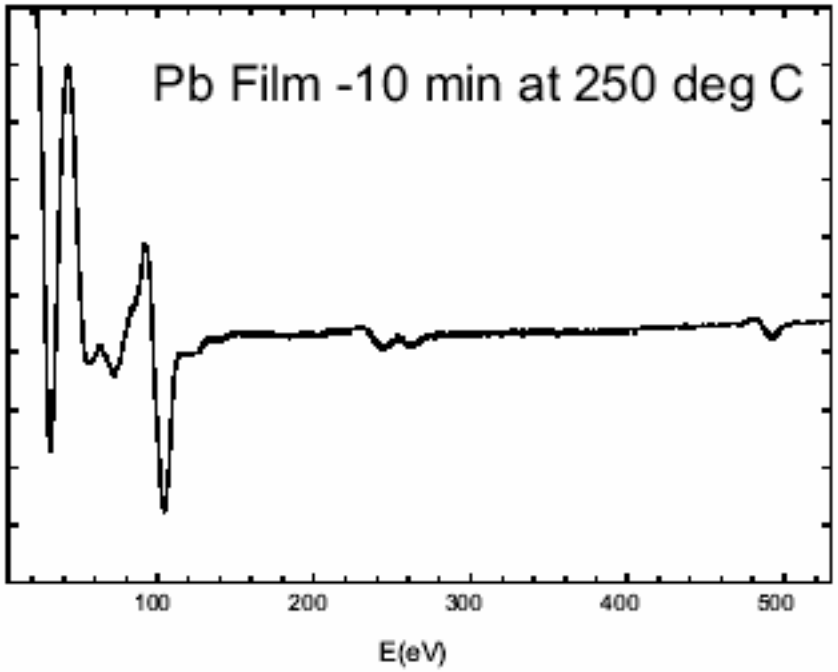
- Predict environmental sensitivity of thermodynamic step parameters from atom-scale understanding
  - Motivation: self assembly, structural stability, stochastic phenomena in nanostructures (including noise)
- Relate boundary conditions to final chemical potential for evolving structures
- Expand formalisms of stochastic predictability to more complex structural forms and physical questions
- Incorporate field dependence into modeling:
  - Motivation: surface electromigration force coupled with structural fluctuations in nanostructures may yield novel behavior

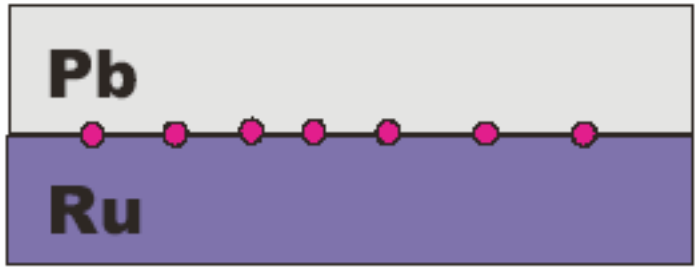
Structural Fluctuations - Impact on Nanostructure Function

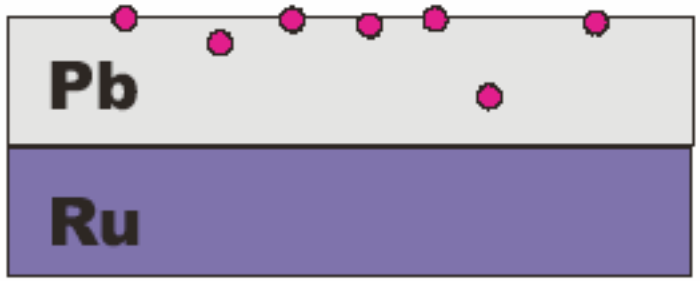
- If Activation Energy for Mass Flow ~kT
  - Allows decay of metastable structures
    - Traditionally- Bad
  - Allows structural response to environment
    - Sensors, self assembly - Good
    - Electromigration - Traditionally Bad
  - Stochastic variations of nanostructure properties dependent on shape, e.g. quantum dots, nanowires, chemical sensors…
    - Noise - Traditionally Bad
    - Work & entropy issues - Interesting
    - Stochastic Switch, Persistence Problem -

Oxygen segregation to Pb surface

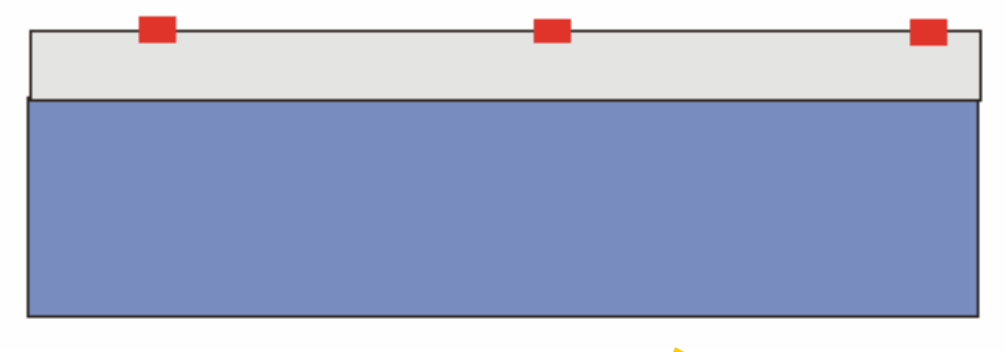






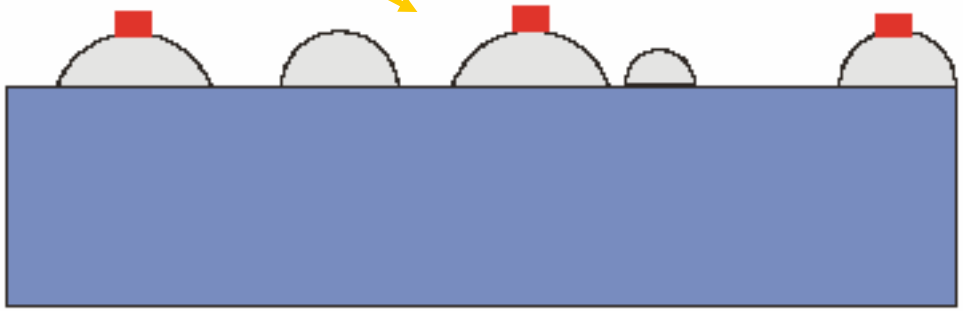


Crystallite Pinning Hypothesis

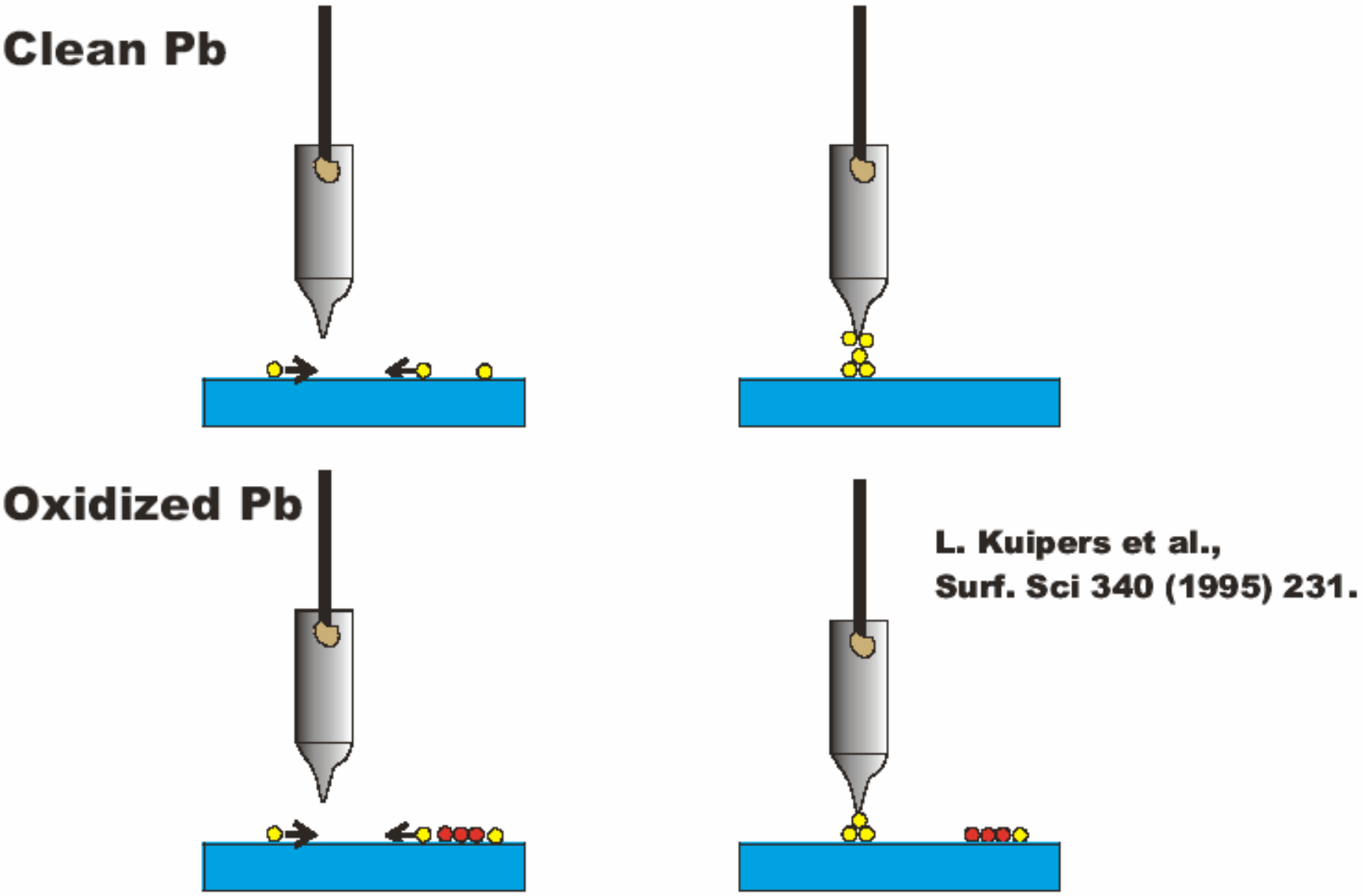


Low density of
oxygen at Pb surface

Some Pb crystallites are
immobilized by oxygen



STM-triggered crystallite decay?



T-dependence of Crystal Shape