Kinetic Monte Carlo Study of Pt on Au(111) with applications to catalysis

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Overview

- Metropolis Monte Carlo
- Kinetic Monte Carlo (KMC)
- Why Pt on Au(111)
- KMC applied to Pt Nanostructure growth on Au(111) surface
- Altering Pt Nanostructure morphology
  - Total width
  - Average width
  - Nanostructure growth Pattern
  - Roughness
- Some Observations
- Applications to Catalysis

Metropolis Monte Carlo

- Try random configuration change
- Apply Metropolis Acceptance criteria min(1,exp($-\beta\Delta E$))
  - Need Potential Energy function
- Make the configuration change if accepted
- And repeat
- Large proportion of rejected attempts

Kinetic Monte Carlo

- Rejection Free
- Need catalog of events and their rates
- Each step pick one of the valid moves
- Provides a KMC time
- Typically use lattice approximation
  - Atoms Hop between Lattice Sites
  - Don't model atomic vibrations
- Handle larger size scales and longer time scales than Molecular Dynamics
- Widely used e.g.
  - Epitaxial Crystal growth (long time scale)
  - Vacancy diffusion   - Studies of Catalysis

Kinetic Monte Carlo – Details

- Arrhenius form for rate of configuration change (thermally activated event)
- $Rate_i = A \exp(- E_i /kT)$
  - Attempt frequency   A   ~ 10^13 1/s
  - Energy Barriers E_i ~ 0.1 – 1 eV
  - Probability of success $\exp(- E_i /kT)$

- Produce a rate catalog (possible events and corresponding rates)
  Incomplete !!

- Need to determine Energy Barriers
  - atomic species, local atomic configuration
  - Use Nudged Elastic Band method and Johnson EAM potential
    - Find maximum energy along minimum energy path

Kinetic Monte Carlo – Algorithm

- At each Monte Carlo step
  - Determine possible events based on current configuration
  - Get the corresponding rates from the catalog
  - Pick event at random (but in proportion to its rate of occurrence)
  - KMC time for the step is proportional to 1/(sum of rates)
  - Carry out chosen event by updating the configuration

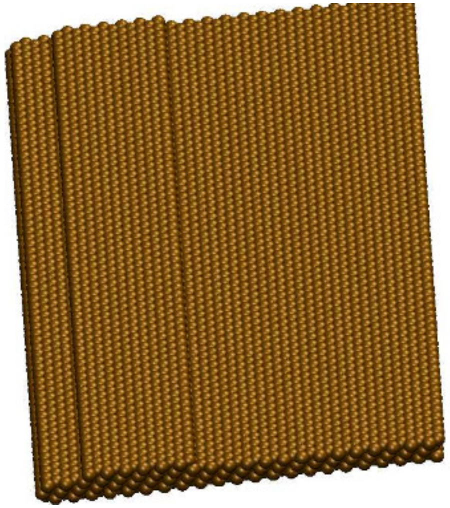
Why Pt on Au(111)

- Catalysis
  - Bimetallic catalysts
    - Can be more reactive
    - Potentially more cost effective
  - PtAu Nanostructures, Formic Acid Oxidation Oxygen Reduction

- Interested in forming Linear Nanostructures
  - Novel Bimetallic Nanocatalysts more surface less Pt required
  - Patterned Surfaces as Templates
  - 1D Nanowires quantum confinement effects

- Au(111) close packed surface
- Pt on Au(111) not well studied by modelling/simulation

KMC applied to Pt Nanostructure growth on Au(111) surface



- Use Au island edge as a trapping site /template to nucleate a Pt Nanostructure in an Molecular Beam Epitaxy (MBE) growth process
- Pt deposited at random on Au surface
  - Low deposition rate to avoid islands forming on the terrace
- Pt diffuses and trapped at Au island edge
  - Pt adatom and dimer diffusion over Au surface and along Au island edge
- Pt Nanostructure grows at island edge
  - Pt adatom and dimer diffusion along Pt Nanostructure edge
- Pt hopping up not modelled - high Energy Barrier
- Pt monolayer growth is experimentally observed
- Pt embedding into Au island edge via exchange

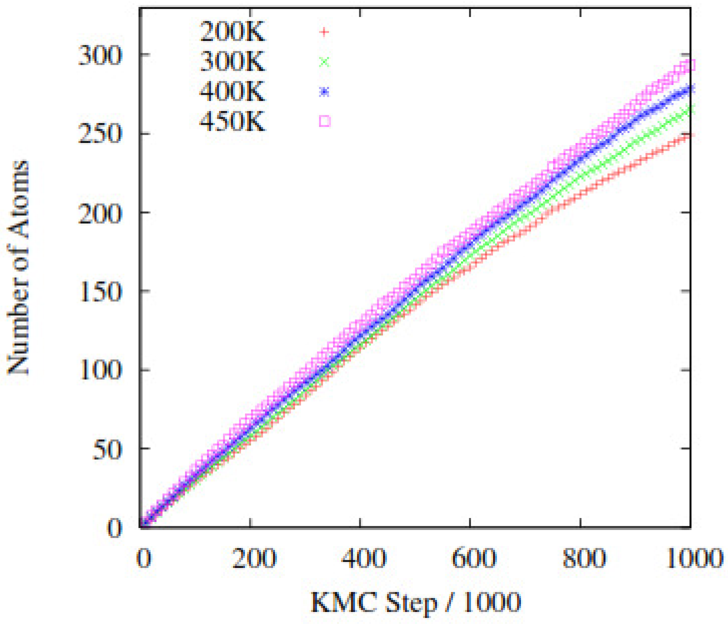
Altering Nanostructure Morphology

- Key controllable parameters in MBE are Temperature and Deposition rate
  - Higher Temperatures
    - faster adatom diffusion
    - increased chances of atomic rearrangements
  - Lower deposition rates
    - More opportunities for atomic rearrangements

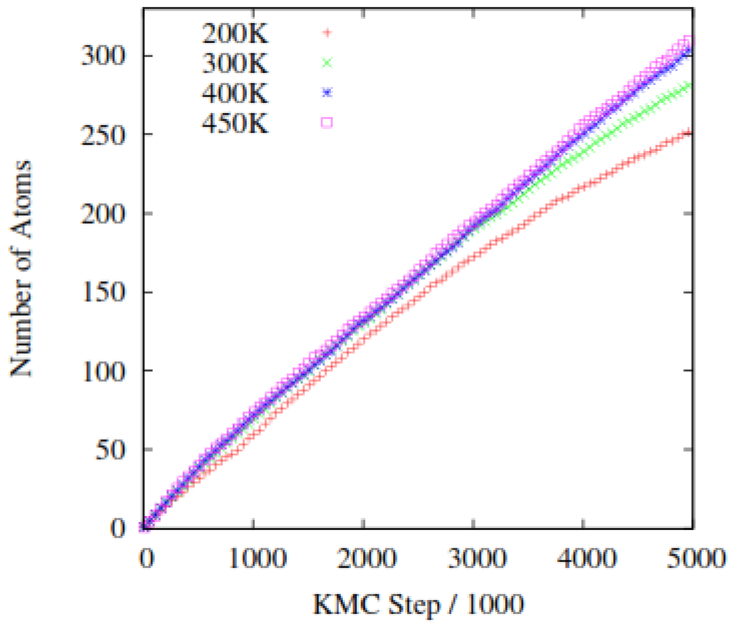
- Such atomic rearrangements typically result in more compact less branched Nanostructures

Total Width of Nanostructure

- Measured directly outward from island edge at each site – ignores branches
- Steady growth with Pt deposition
- Greater at higher temperature and lower deposition rate



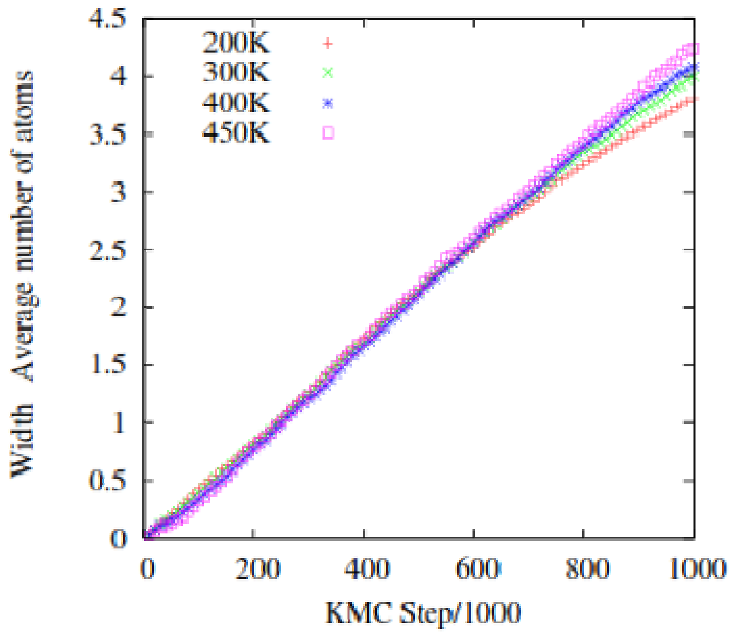
(a) High Deposition Rate



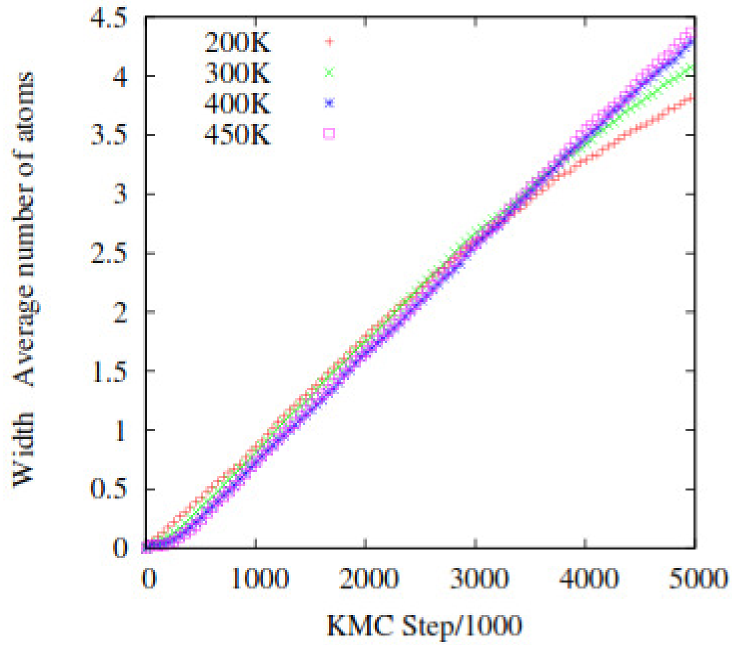
(b) Low Deposition Rate

Average Width of Nanostructure

- Initial slow growth in average width due to Pt embedding
  - more so at low deposition and higher temperatures
- Subsequent linear growth which then slows (with temperature) as include less filled rows
- More variability with temperature at low deposition
- Choose average width by stopping deposition



High deposition

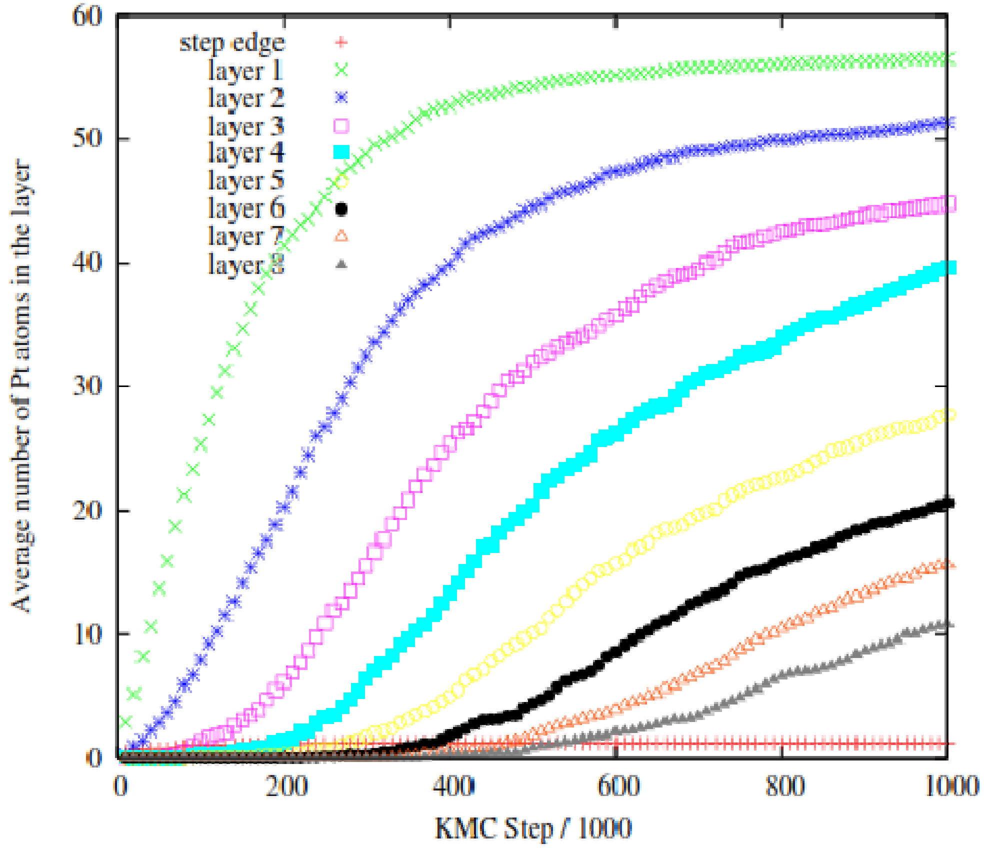


Low deposition

Nanostructure Growth Pattern (200K deposit every 1000 steps)

1000 Pt deposited

- Row 1 fills first - Fast initially then slows and saturates
- Adjacent rows fill slowly at start, speed up then slow as nearing saturation



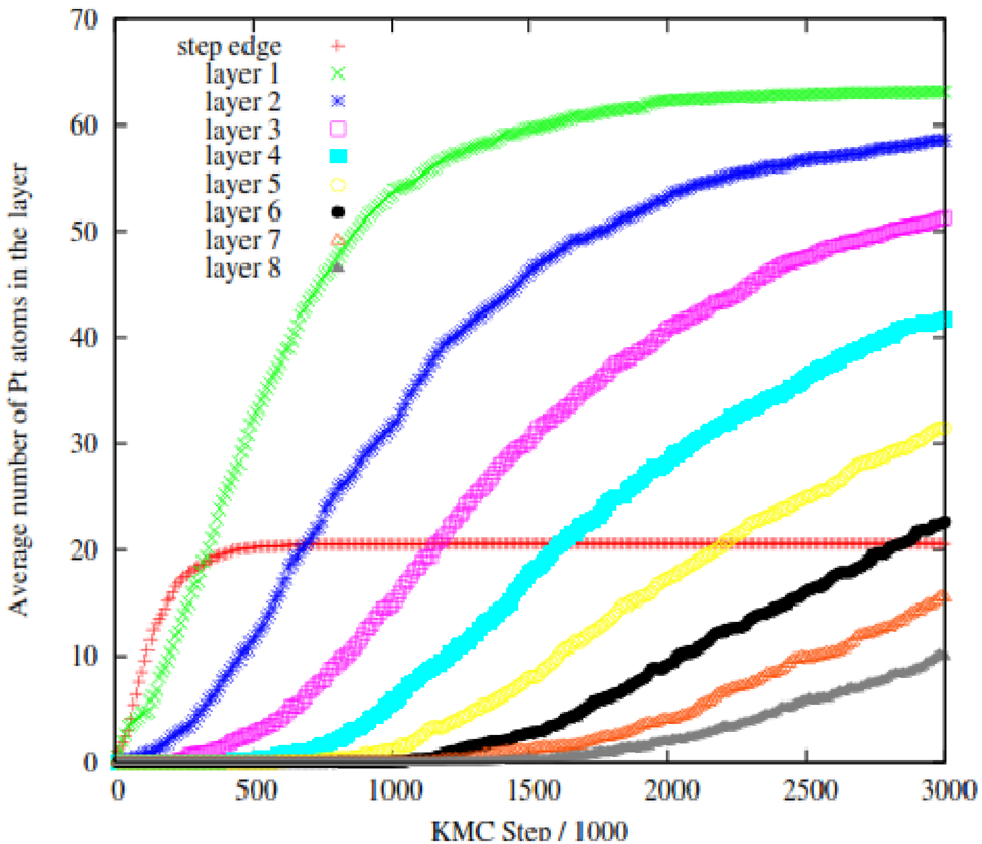
- Funnelling

1 Pt embedded

Nanostructure Growth Pattern (400K deposit every 3000 steps)

1000 Pt deposited

- Greater final coverage in rows 1-6 longer Nanostructure

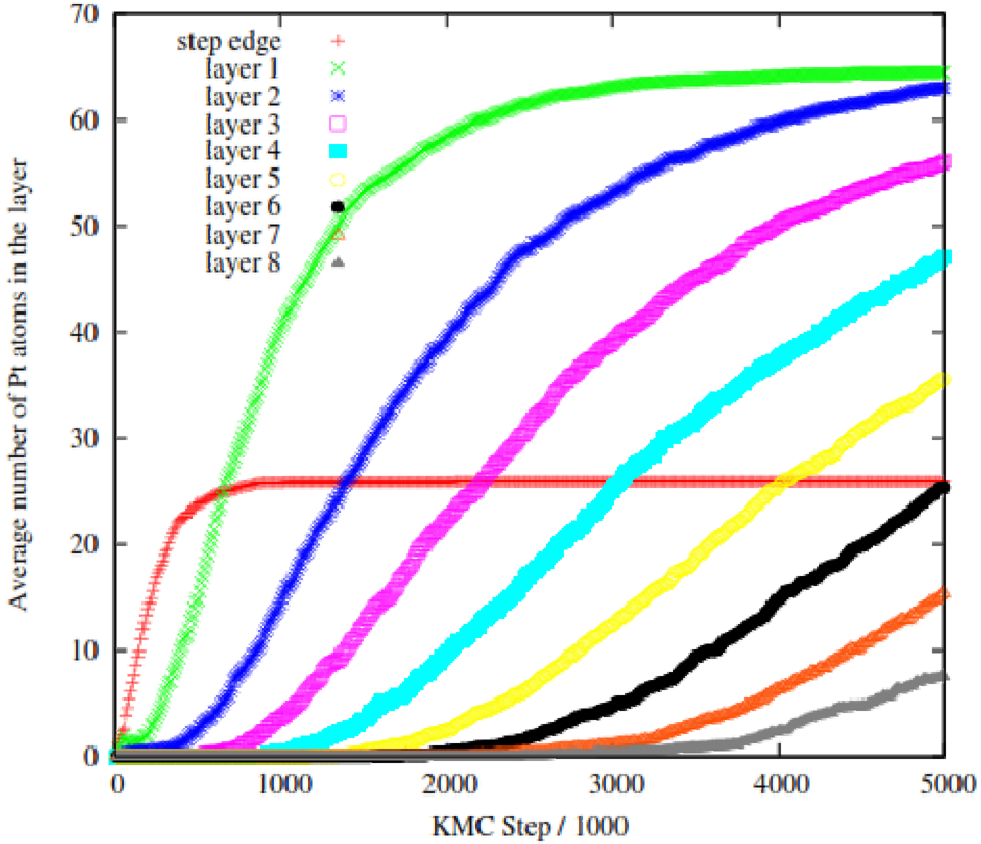


- Slightly more compact so Average Width reduced 21 Pt embedded

Nanostructure Growth Pattern (450K deposit every 5000 steps)

1000 Pt deposited

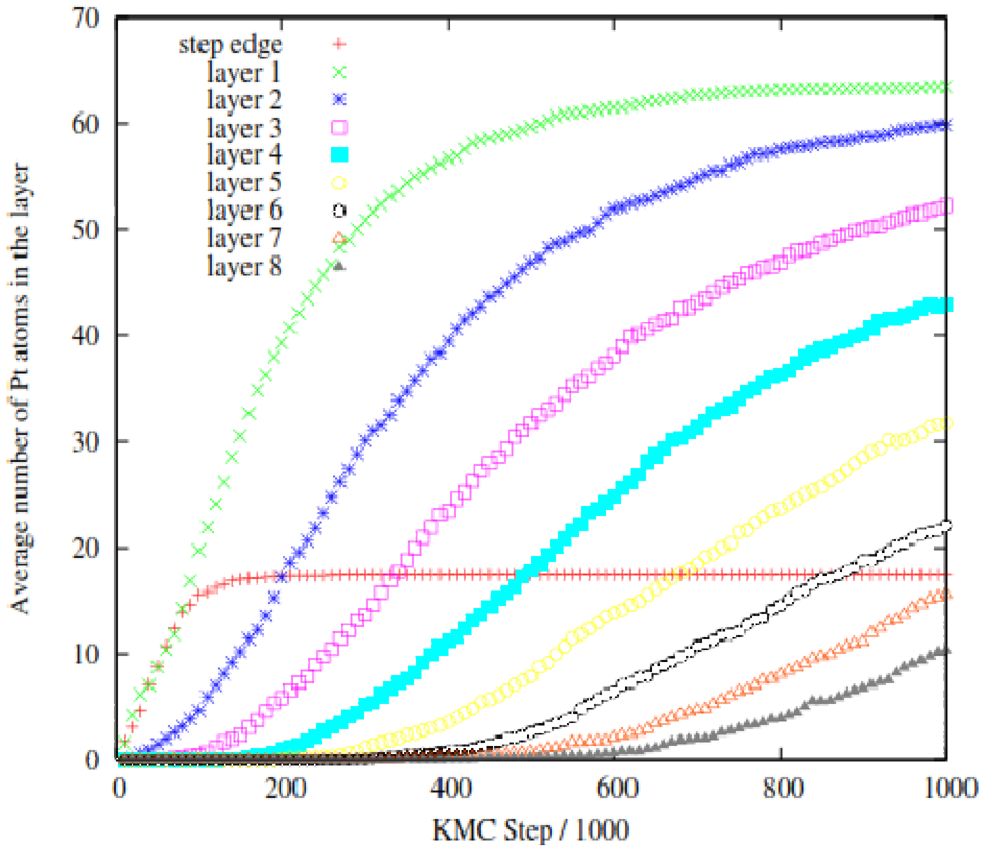
- Nearly full coverage in rows 1 and 2 - enhanced funnelling
- Increase coverage in rows 2 - 6 reduction in row 8 more compact



- Further reduction in Average Width 26 Pt embedded

Nanostructure Growth Pattern (450K deposit every 1000 steps)
1000 Pt deposited

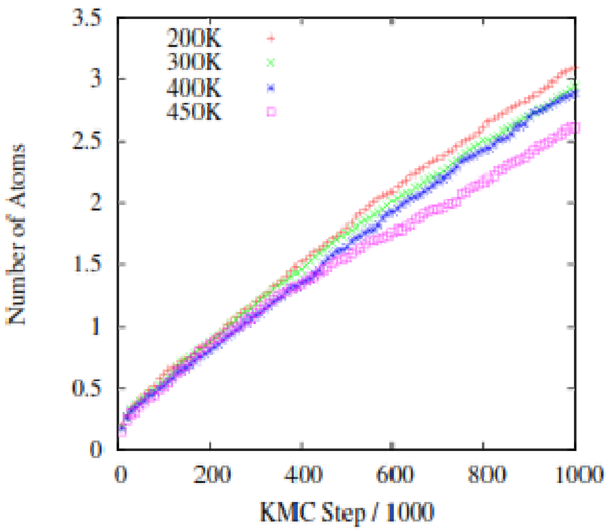
- Lower final coverage rows 1 to 6 Shorter Nanostructures



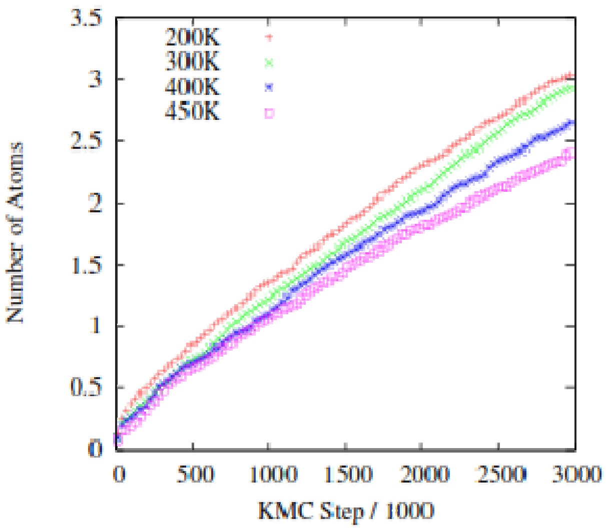
- Average Width increased 17 Pt embedded

Roughness – Standard Deviation of Width

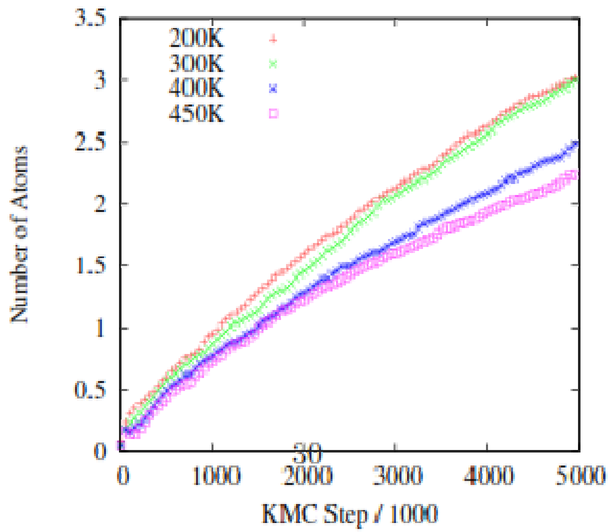
- Increases overtime   Rougher at lower temperatures
- At 400K and 450K increase slows with time   - row 1 filled   - smoothing
  - more so at low deposition



(a) High deposition rate, once every 1000 steps.



(b) Medium deposition rate, once every 3000 steps.

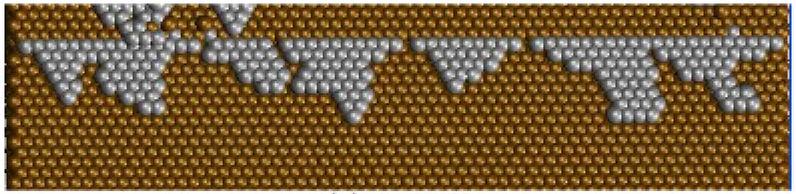


(c) Low deposition rate, once every 5000 steps.

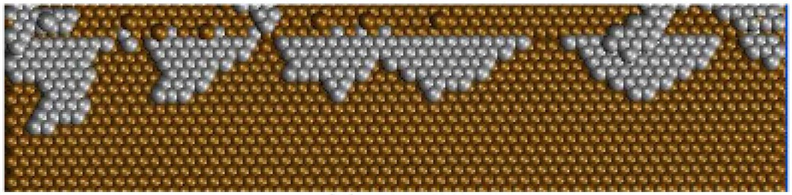
- Temperature more significant than deposition rate

Comparisons: Medium deposition rate After 2m KMC steps

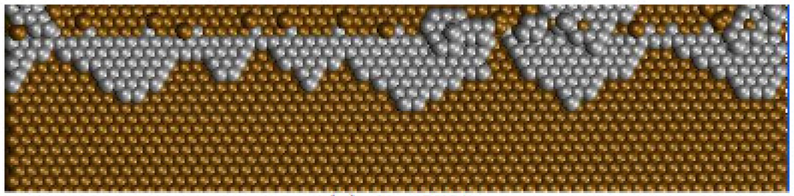
- Pt Nanostructures are smoother and more compact at higher temperature
- Almost complete island edge coverage at 450K
- Number of Pt atoms embedded in step edge increases with temperature



(a) At 200K



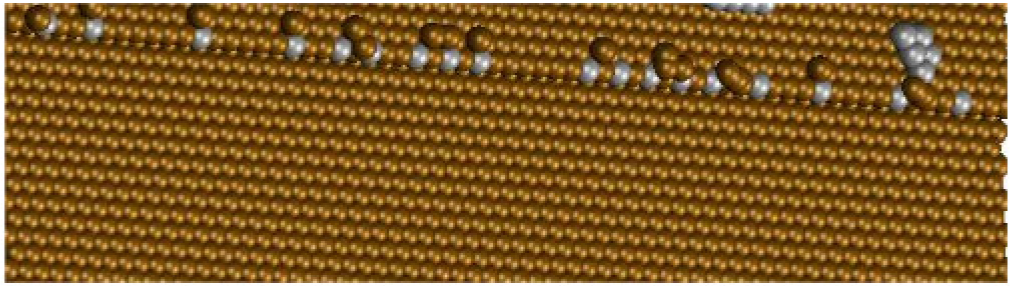
(b) At 300K



(c) At 450K

1D Pt Au Nano-alloy

- After 300k KMC steps at 450K with low deposition rate have 30% Pt in Au Alloy along the island edge



Some Observations

- Au island edge can be used to template linear (10:1 aspect ratio) monolayer Pt Nanostructures
- High temperatures and low deposition rates form smoother and more compact Pt Nanostructures
- Changes in temperature usually more significant than changes in deposition rate – but use both high temperature and low deposition rate to minimise roughness
- The number of Pt atoms embedded in the island edge can be tuned using temperature and deposition rate
- A 1D Nano-alloy of Pt in Au can be formed

Applications to Catalysis

- Pt on Au modifies the chemical reactivity
  - CO desorption on Pt monolayer stronger than with Pt alone
- 50% PtAu alloy has much higher turnover than Pt for NO decomposition
- Certain arrangements of Pt and Au atoms reduce surface poisoning by O
- On PtAu Nanoparticles preferred site for CO adsorption is Pt adjacent to Au
- A rougher Nanostructure potentially offers more sites for catalysis to occur

- Here we have an adjustable mix of Pt overlayers and a novel 1D PtAu surface alloy with a range of local environments

- Such structures are very interesting as potential bimetallic Nano catalysts

Thanks for your Attention

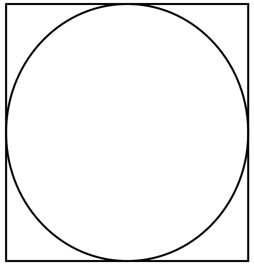
Pt Nanostructure grows row by row

- Growth by rows due to Pt adatom diffusion
  - to island edge and trapped
  - along it forming Pt dimers and longer Pt chains
  - Pt chains form Pt Nanostructure edge that traps further Pt adatoms

  PICTURES

- Pt Nanostructure grows during simulation
  - In Length and Width (measured perpendicular to island edge)
  - Can reach 10:1 aspect ratio

- Approximately 27% of Pt's deposited during simulation accumulate in monolayer Nanostructure on right hand island edge
- Observation of simulated Pt Nanostructure growth

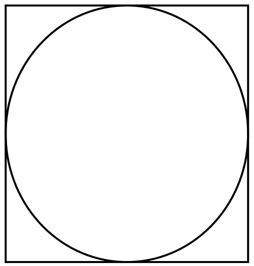


KMC movie of growth ? Observation of simulated Pt nanostructure growth

The Monte Carlo idea

- Find/create a random variable X such that the answer you seek = f(E(X))

- Examples
  - Neutron Los alamos
  - Area of circle Pi



  - Buffon needle
  - Monte Carlo integration
    - Importance sampling