OFF-LATTICE KINETIC MONTE CARLO SIMULATION OF HETEROEPITAXY WITHOUT SADDLE POINTS

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Joint work with

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Figure 1: Some Applications of Thin Films. Images from Google Images

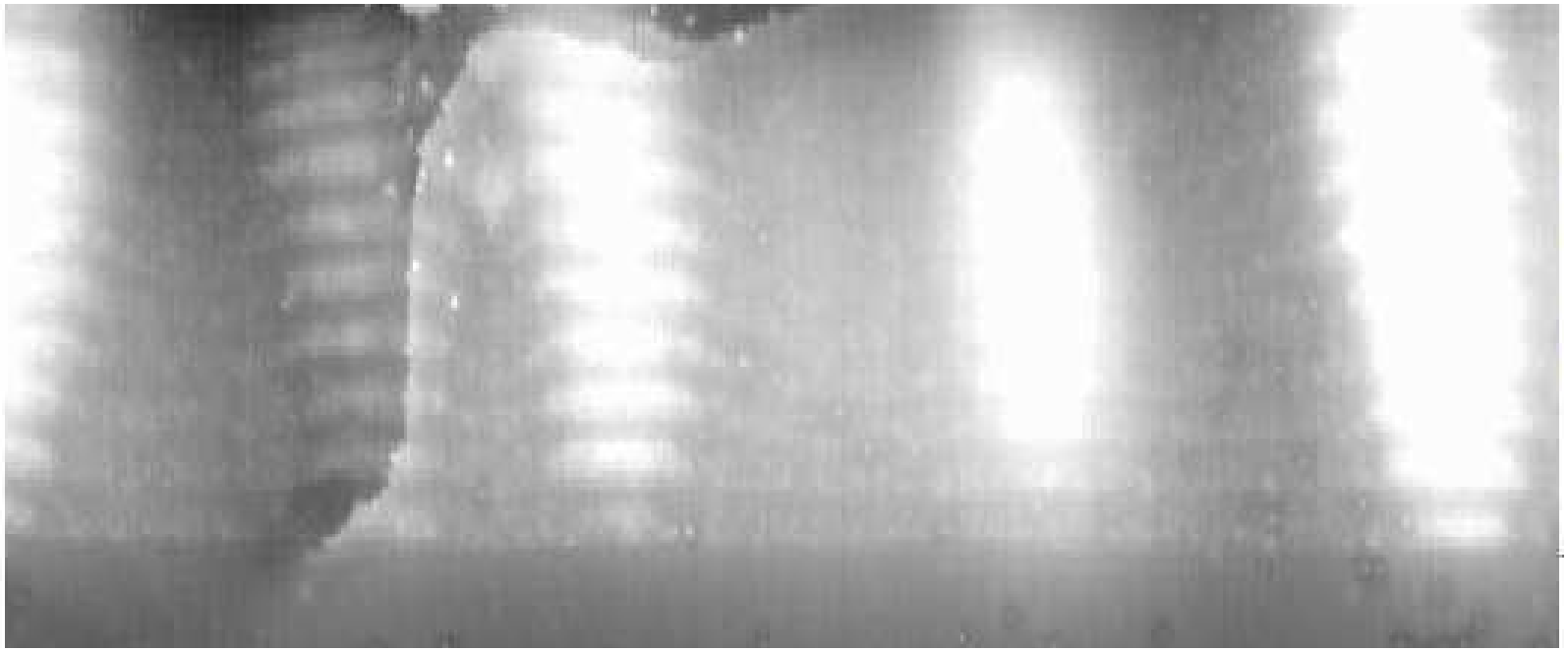
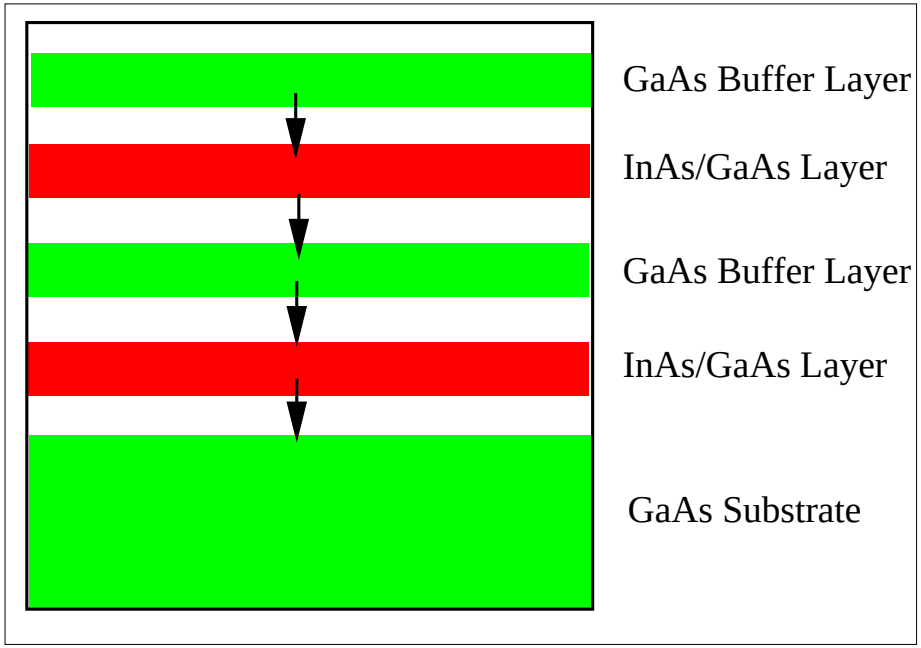


Figure 2: A quantum dot structure – InAs/GaAs on GaAs with GaAs buffers.

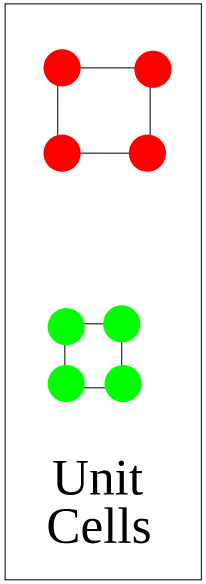
Lita, Goldman, Phillips, & Bhattacharya, Nanometer-scale studies of vertical organization and evolution of stacked self assembled InAs/GaAs quantum dots, *Appl. Phys. Lett.* (1999).

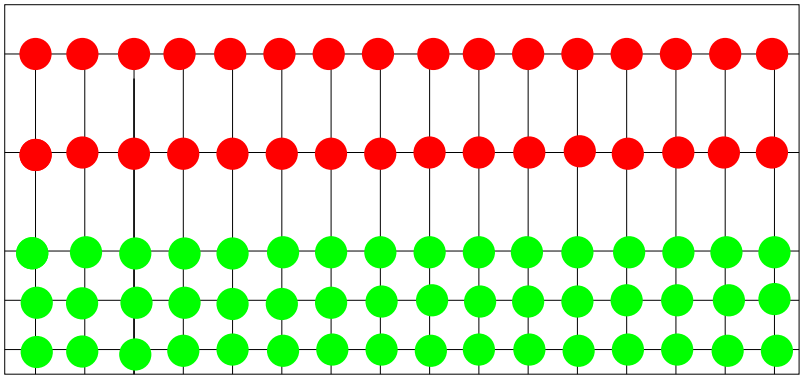
Stacked Quantum Dot Fabrication

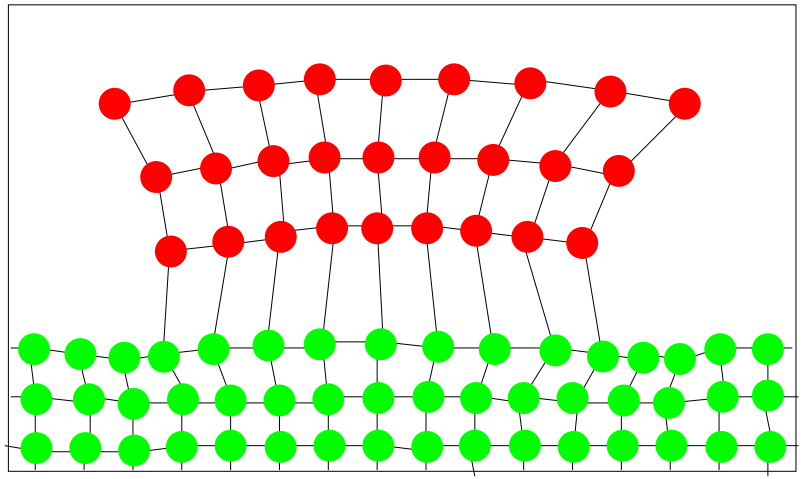


Stacked Quantum Dots are made by Molecular Beam Epitaxy. Alternating layers of different materials are deposited onto a substrate.

ELASTIC ENERGY

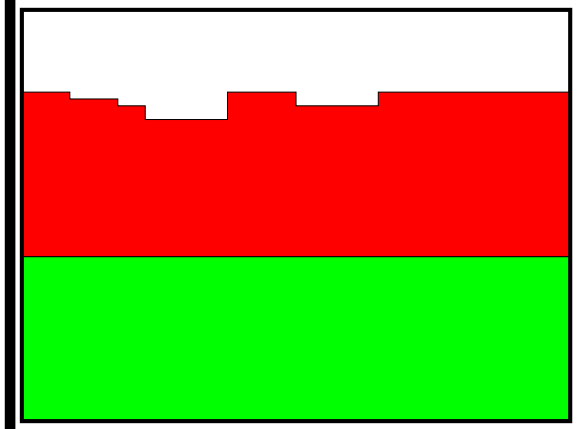






Due to misfit the bottom configuration has less elastic energy than the top one.

GROWTH MODES

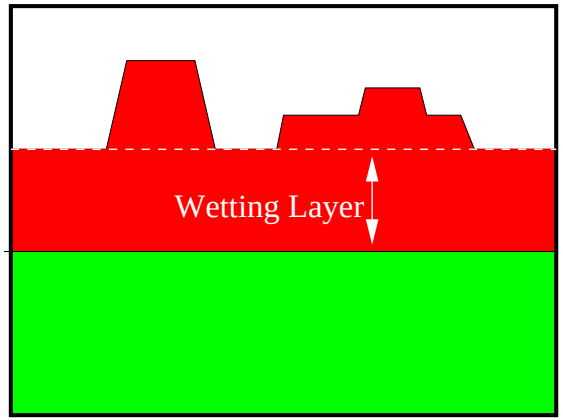


Layer-by-Layer (FM)

-observed when elastic effects are negligible

-surface forces dominate

-minimize surface area

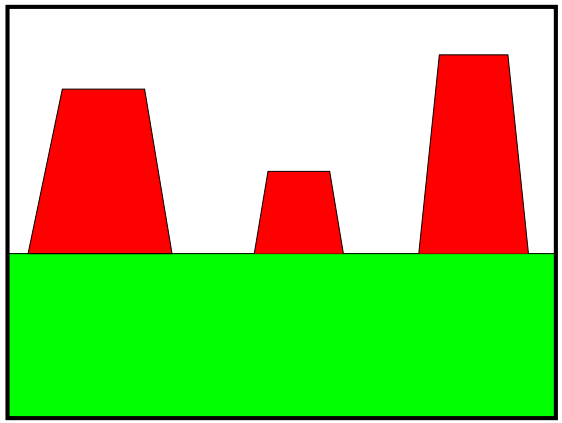


Stranski-Krastanov (SK)

-expected when elastic effects are significant.

-commonly observed in experiments

-results from an interplay between elastic and surface forces



Volmer-Weber (VM)

-expected when elastic effects are overwhelming

-not commonly observed in experiments

Modeling and Computational Approaches

- Molecular Dynamics
- Kinetic Monte Carlo (Temporally Coarse Grained MD)
- Semi-Discrete –Step flow Models (Level Set Methods, Phase Field)
- Full Continuum (Phase Field, Sharp Interface)

Our Focus

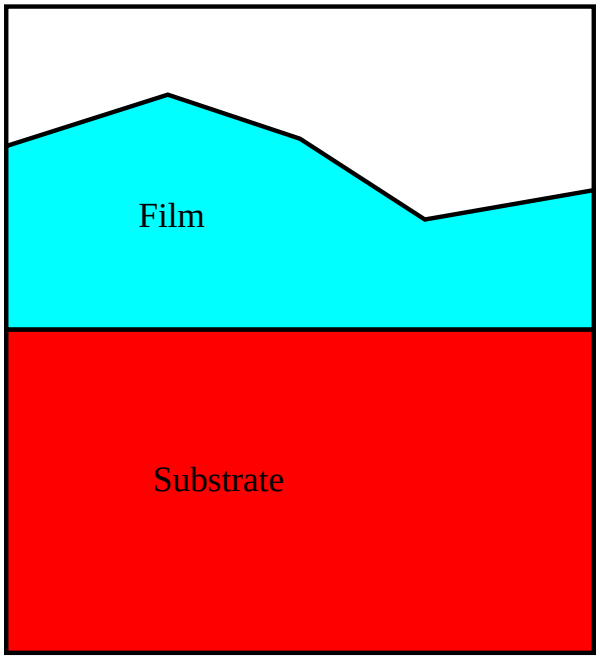
- This talk will focus on Kinetic Monte Carlo.
- As a point of comparison we will briefly review a well used continuum model.

Continuum Model for Film Growth with Elastic Effects

Continuum Model

- Film is assumed to be in:
  - mechanical equilibrium
  - local thermodynamic equilibrium
- Free Energy: F= Elastic energy + Surface energy
- $F = F[h]$; $h = h(x,t)$ where h is the film profile

Continuum Model



Ω = Film + Substrate

$\partial\Omega$ = Film/Vacuum Interface

χ_F = characteristic function of the film

Elastic Energy

$$W = \int_\Omega w(x,y)dxdy$$

$$w = \sum_{ij} c_{ij}(e_{ij} - \chi_F e^0_{ij})^2$$

e_{ij} =strain tensor, e^0_{ij} misfit strain

Surface Energy

$$S = \int_{\partial\Omega} \gamma(n)ds$$

Free Energy

$$F = S + W$$

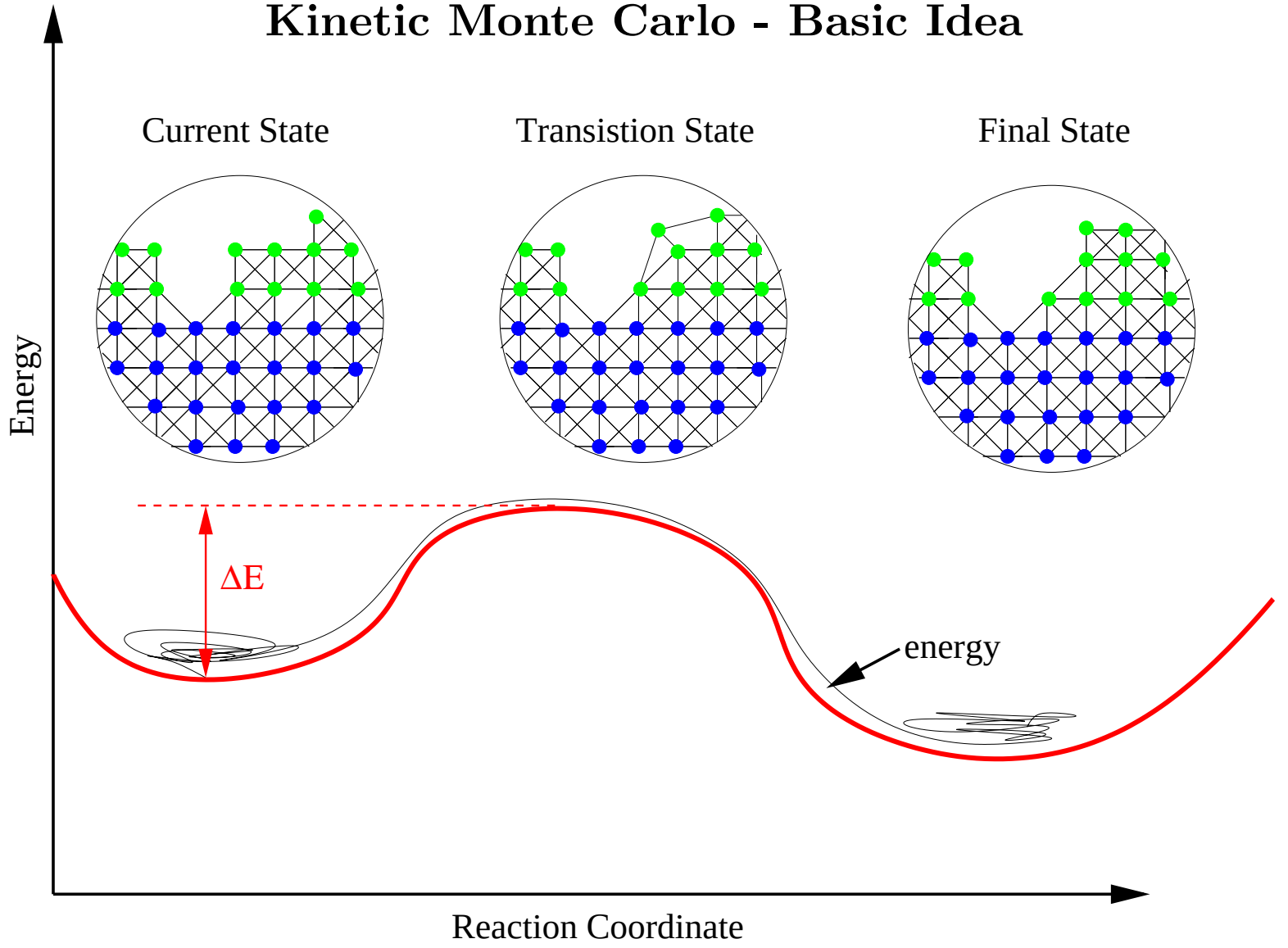
Continuum Model

- Surface Chemical Potential: F - F(one surface atom removed)
- Chemical Potential: $\mu = \mu(x) = v_a \frac{\delta F}{\delta h}$
- Flux of Atoms: $\mathbf{j} = -\frac{\nu D}{kT} \nabla_s \mu$ (Herring's Law)
- Mass Conservation: $h_t + v_a \nabla_s \cdot \mathbf{j} = 0$

where ∇_s is the surface gradient operator, D is the surface diffusivity, ν is the number density of surface atoms, and v_a is the atomic volume.

Kinetic Monte Carlo Model for Film Growth with Elastic Effects

Kinetic Monte Carlo - Basic Idea

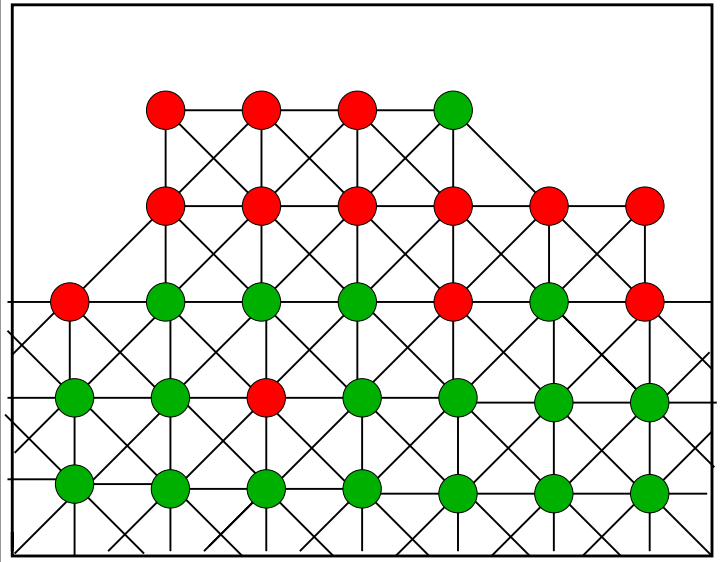


KMC is based on transition state theory

Kinetic Monte Carlo - Basic Idea

- Rates are based on transition state theory which gives $R = \omega \exp(-\Delta E/kT)$
- $\Delta E = E(\text{current state}) - E(\text{transition state})$
- ω is the attempt frequency, kT is the thermal energy
- One needs to know or assume what are the important events

Ball and Spring Model [Baskaran, Devita, Smereka, (2010)]



- Atoms are on a square lattice
- Semi-infinite in the y-direction
- Periodic in the x-direction
- Nearest and next to nearest neighbor bonds with strengths: $\gamma_{SS}, \gamma_{SG}, \gamma_{GG}$
- Nearest and next to nearest neighbor springs with contants: k_L and k_D
- System evolves by letting the surface atoms hop: Surface Diffusion

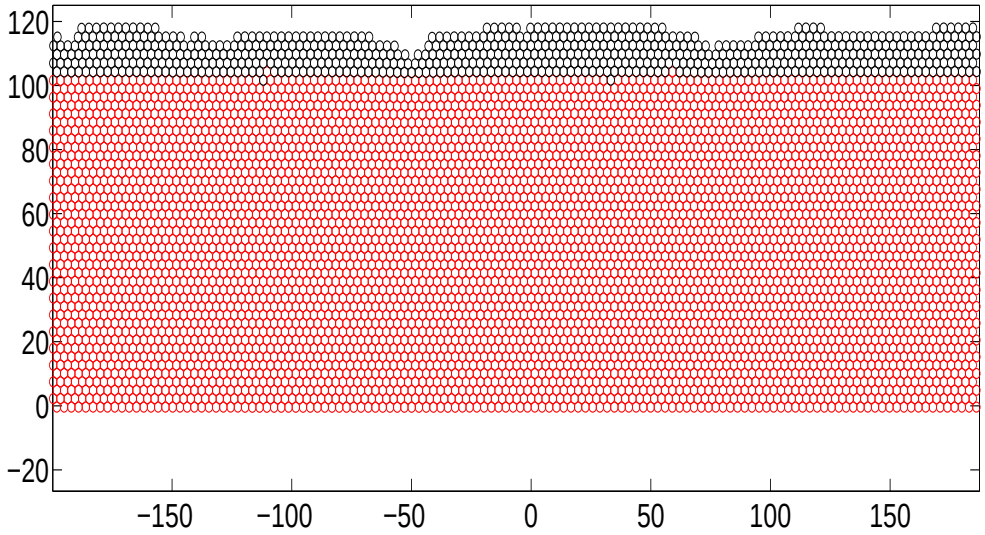
Red = "Germanium"
Green = "Silicon"

* without intermixing this model is due to:
Orr, Kessler, Snyder, and Sander (1992)
Lam, Lee and Sander (2002)

The Model

- Hopping Rate $R_p = \omega \exp\left[(U - U_p)/k_B T\right]$
- U = total energy, $\quad U_p$=total energy without atom p
- $U = \sum_{i>j}^{N} \phi(r_{ij}) \quad$ where $\quad \phi(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$
- ω is a prefactor, $k_B T$ is the thermal energy
- r_{ij} is the distance between atoms i and j
- $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$
- $\epsilon_{Si} = 0.4$, $\epsilon_{Ge} = 0.3387$, $\sigma_{Si} = 2.731$, $\sigma_{Ge} = (1 + \mu)\sigma_{Si}$
- $\mu = \frac{\sigma_{Si} - \sigma_{Ge}}{\sigma_{Si}}$, μ is the *misfit*
- Periodic in the x-direction
- Semi-infinite in the y-direction

Rejection-Free Kinetic Monte Carlo



- Make a list of hopping rates, R_p, for all surface atoms
- $s(j) = \sum_{p=1}^{j} R_p$, array of partial sums
- $R_{\rm tot} = R_d + \sum_{p=1}^{N} R_p$: total rate for all processes, R_d : deposition rate
- Draw a random number r between $(0, R_{\rm tot})$
- The first atom j for which $s(j) > r$ is the atom that hops.
- If $r > s(N)$, deposit an atom

KMC Computational Bottlenecks

- In principle we need to compute $R_p = \omega \mathrm{e}^{(\Delta U/kT)}$ for all atoms.
- This means removing each surface atom and relaxing the full system with nonlinear conjugate gradient (NlCG)
- Relax the whole system after each hop or deposition
- NlCG involves a hessian matrix with dimension $D \times D$ where $D = 2 \times N_{Si} + N_{Ge}$. $N_{Si} = 256 \times 40$
- Thus full on computations of heteroepitaxy are very time consuming and memory intensive.
- We perform local relaxation (local NlCG) in a small region around hopped/deposited atom
- Global relaxations periodically, also triggered by a flag
- Approximate R_p using local distortion around atom p. 97% accuracy.

Previous Work Using The Lennard-Jones Potential

- F. Much, M. Ahr, M. Biehl, and W. Kinzel, *Europhys. Lett*, 56 (2001) 791-796
- F. Much, M. Ahr, M. Biehl, and W. Kinzel, *Comput. Phys. Commun*, 147 (2002) 226-229
- M. Biehl, M. Ahr, W. Kinzel, and F. Much *Thin Solid Films*, 428 (2003) 52-55
- F. Much, and M. Biehl *Europhys. Lett*, 63 (2003) 14-20
- They compute saddle points but we do not.
- They use a substrate depth of 6 monolayers which is not ideal

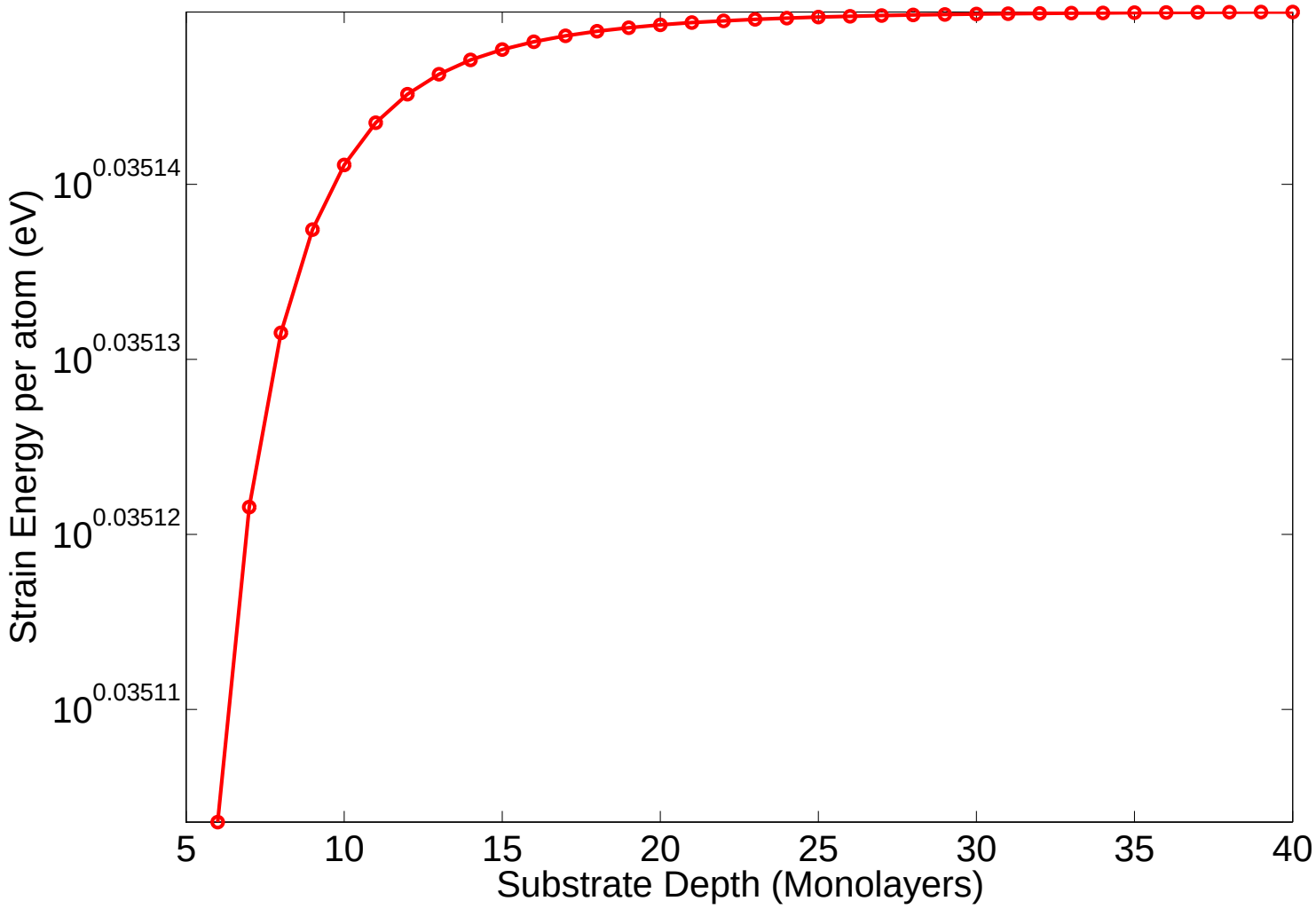


Figure 3: Strain Energy per atom vs Substrate Depth. $\mu = -0.04$.

$\kappa = C\frac{\mu h_f}{h_s^2}$, $C > 0$

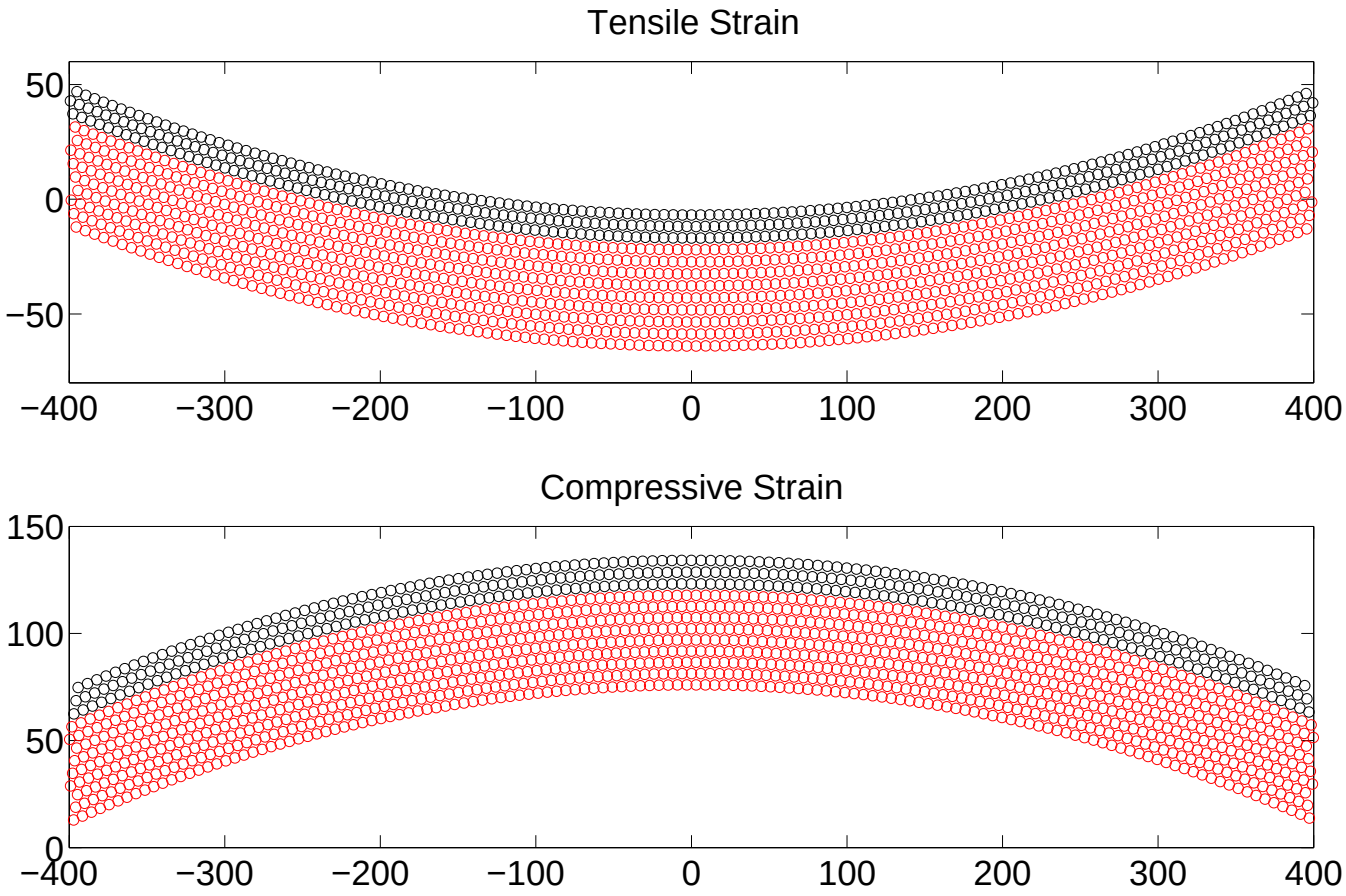


Figure 4: Curvature (κ) –9 ML of substrate and 3ML of film. $\mu = \pm 0.04$

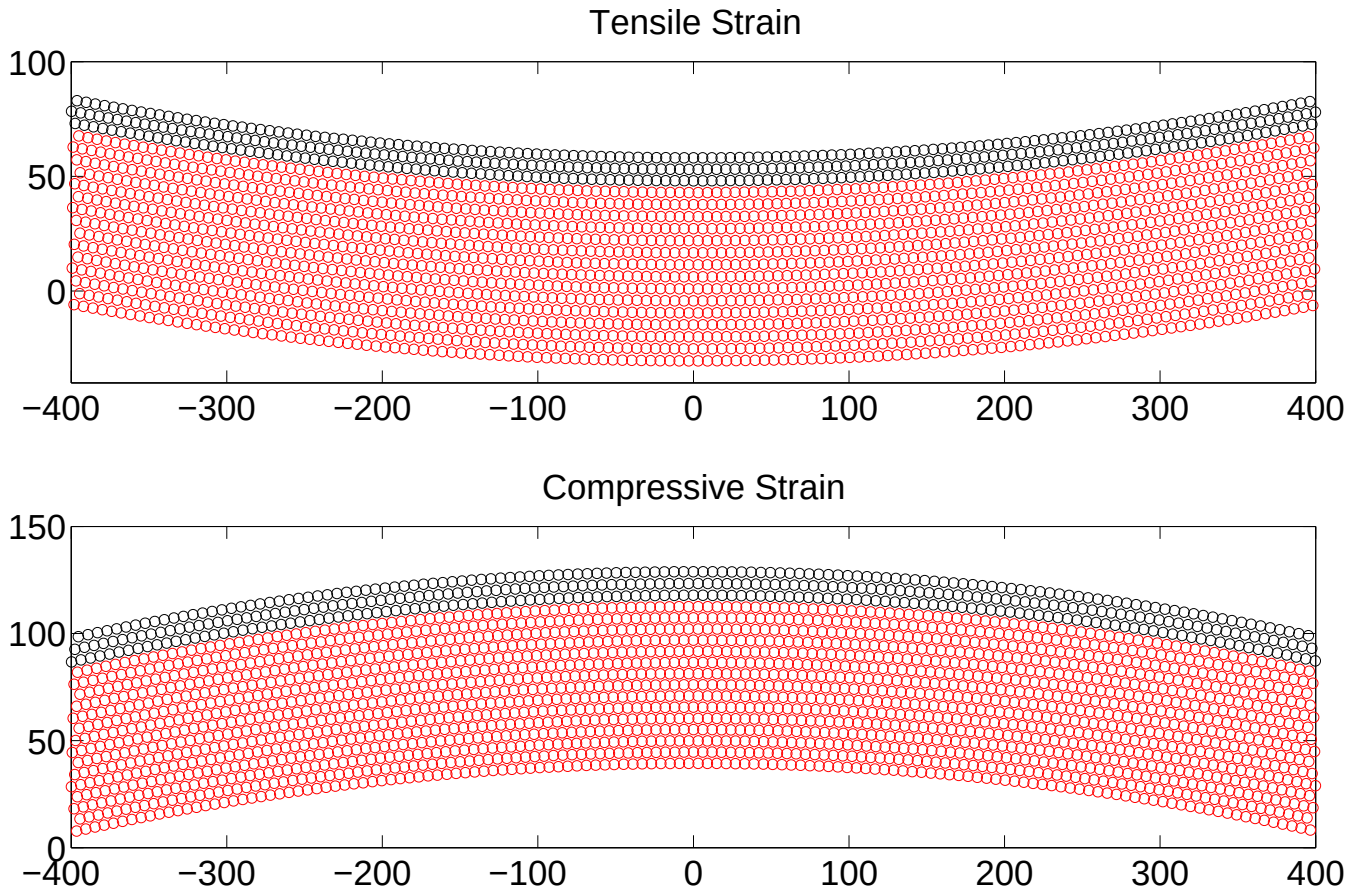


Figure 5: Curvature (κ)–15 ML of substrate and 3ML of film. $\mu = \pm 0.04$

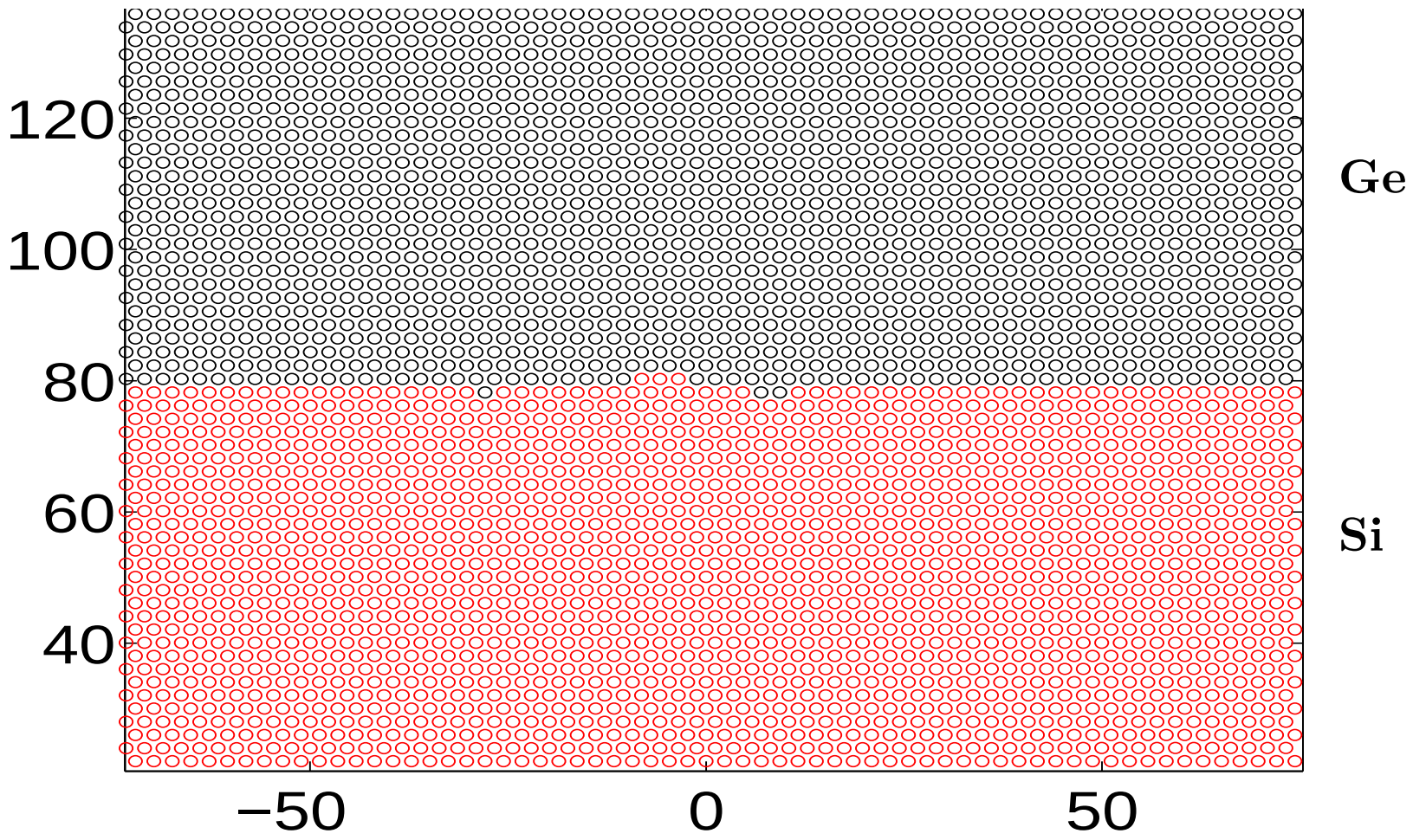


Figure 6: $\mu = -0.02$, deposition flux (F) = 1ML/s

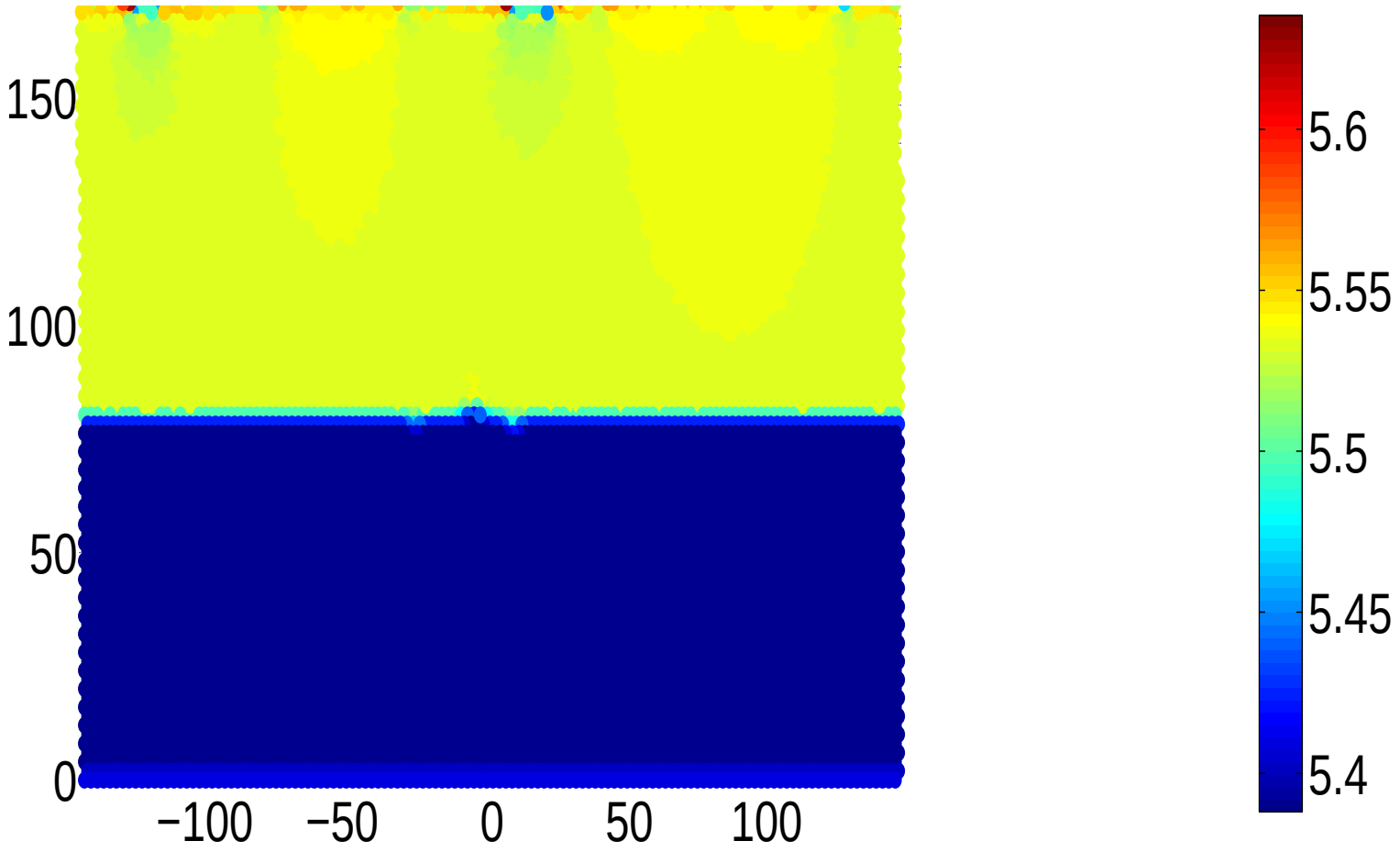


Figure 7: $\mu = -0.02$, $\bar{r}_{ij}$ to nearest neighbors

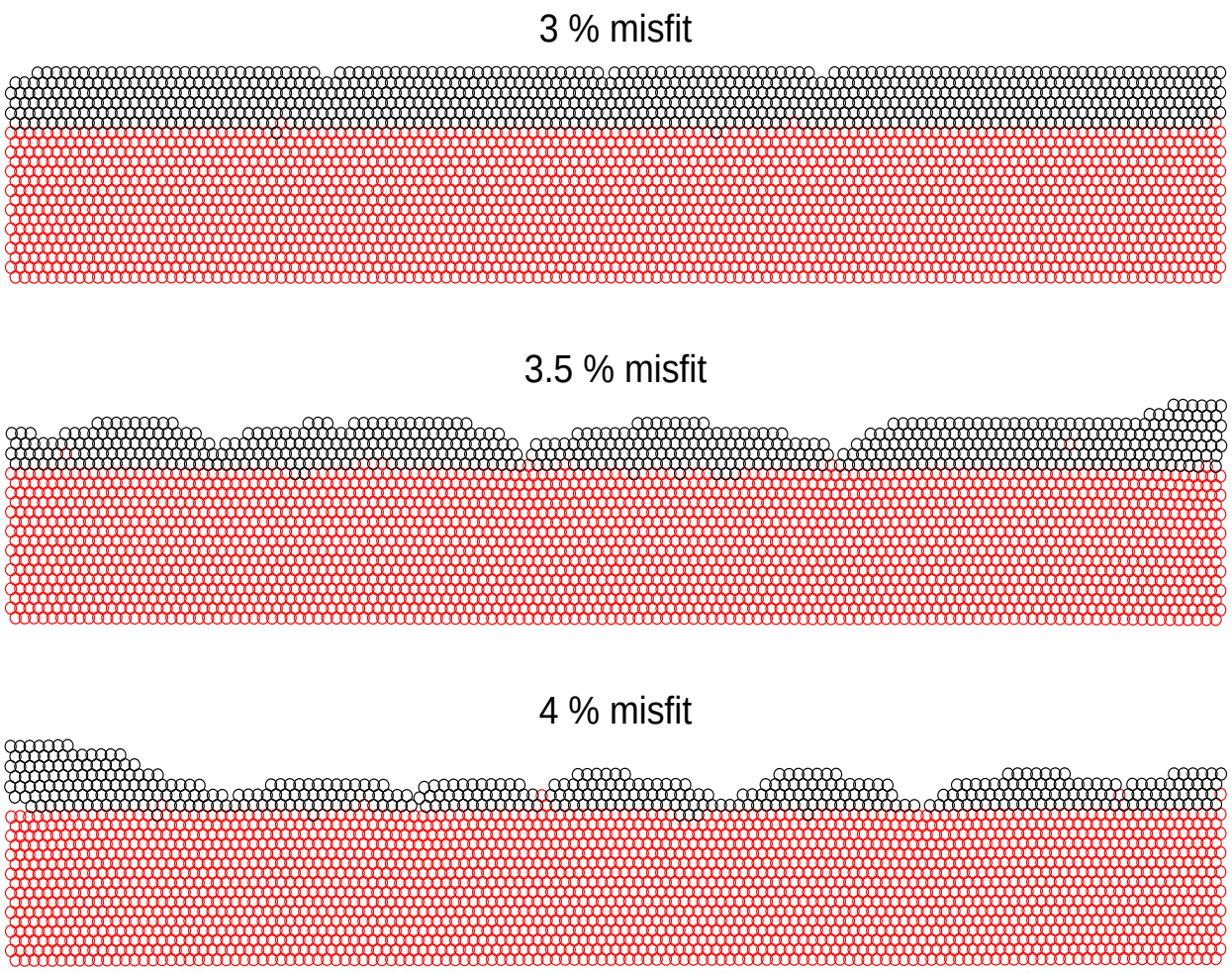


Figure 8: FM, SK and VW growth, $\mu = -0.04$, $F = 0.1ML/s$

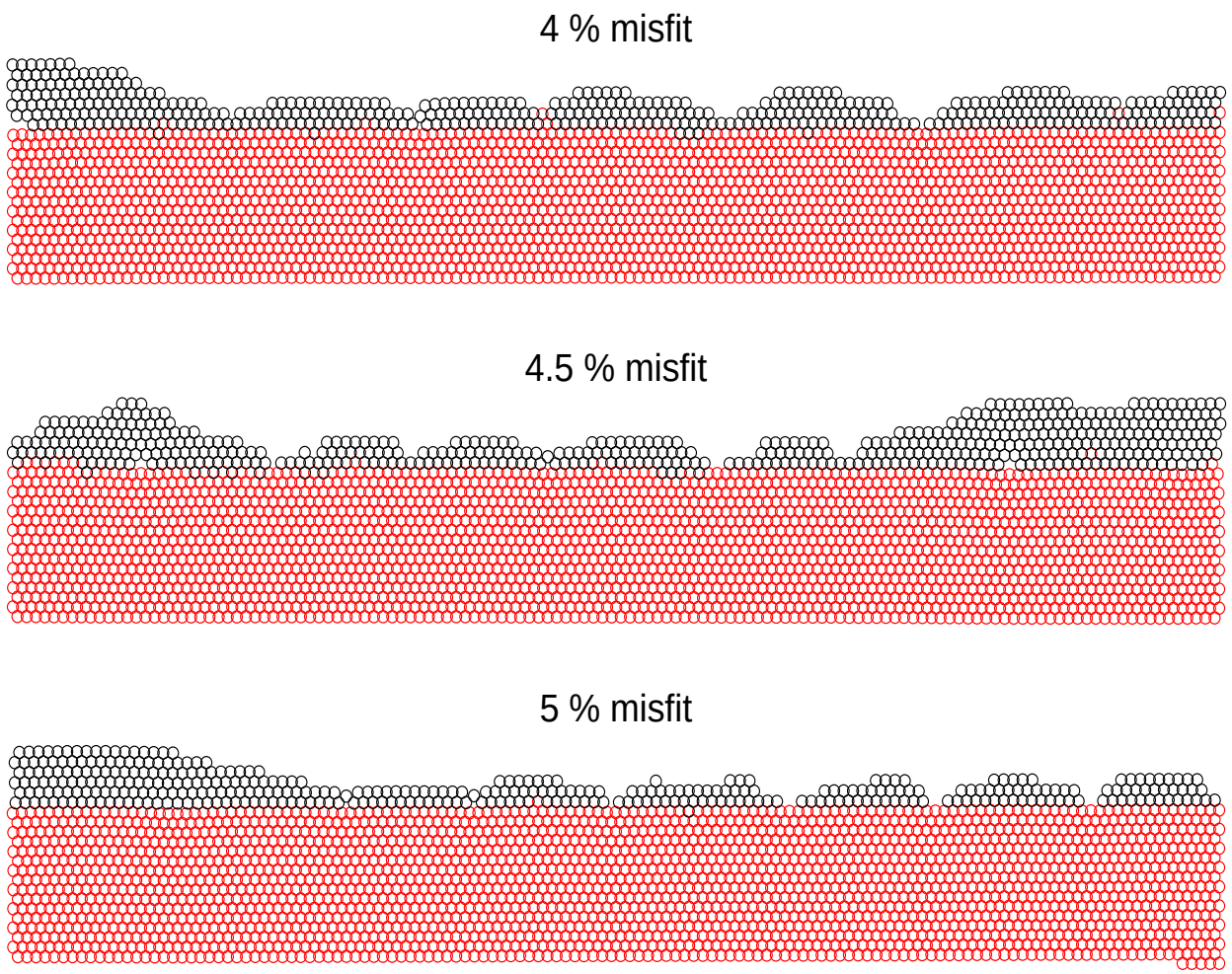


Figure 9: SK and VW growth, $\mu = -0.04$, $F = 0.1ML/s$

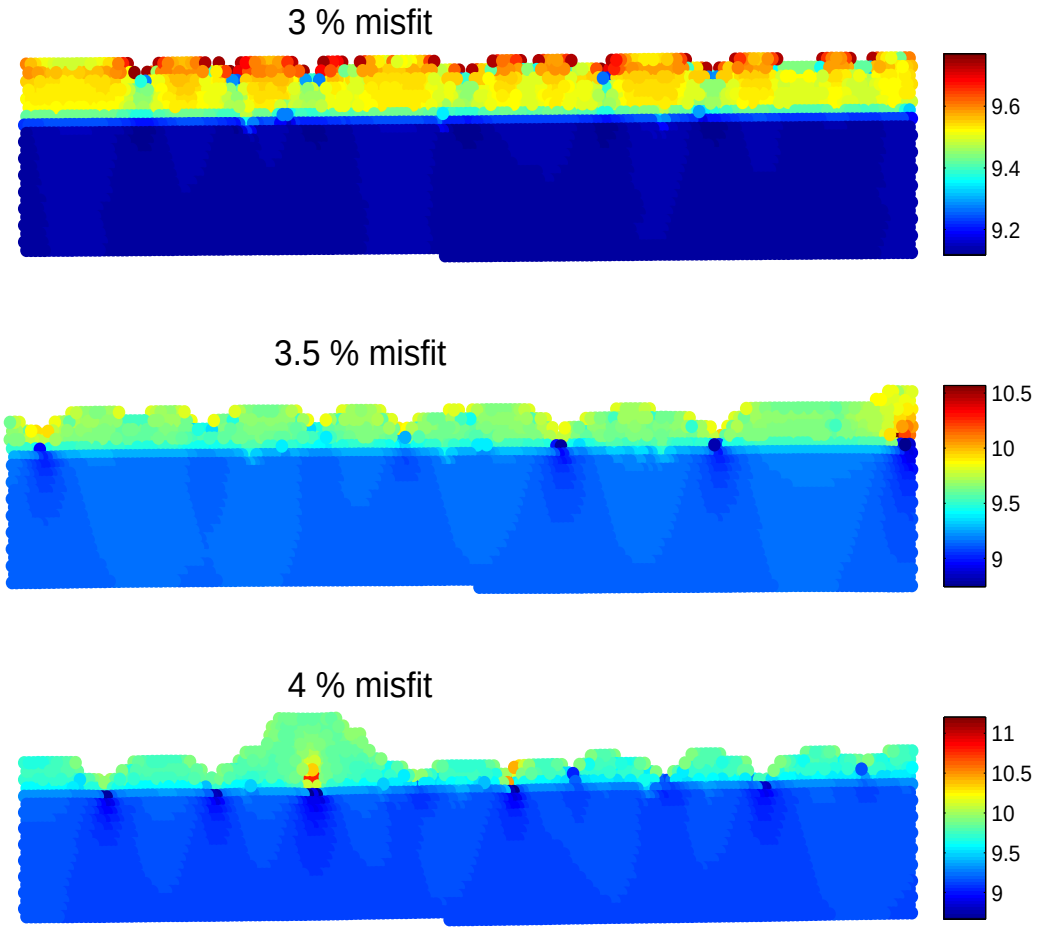


Figure 10: , $\bar{r}_{ij}$ to nearest neighbors, F = 0.1ML/s

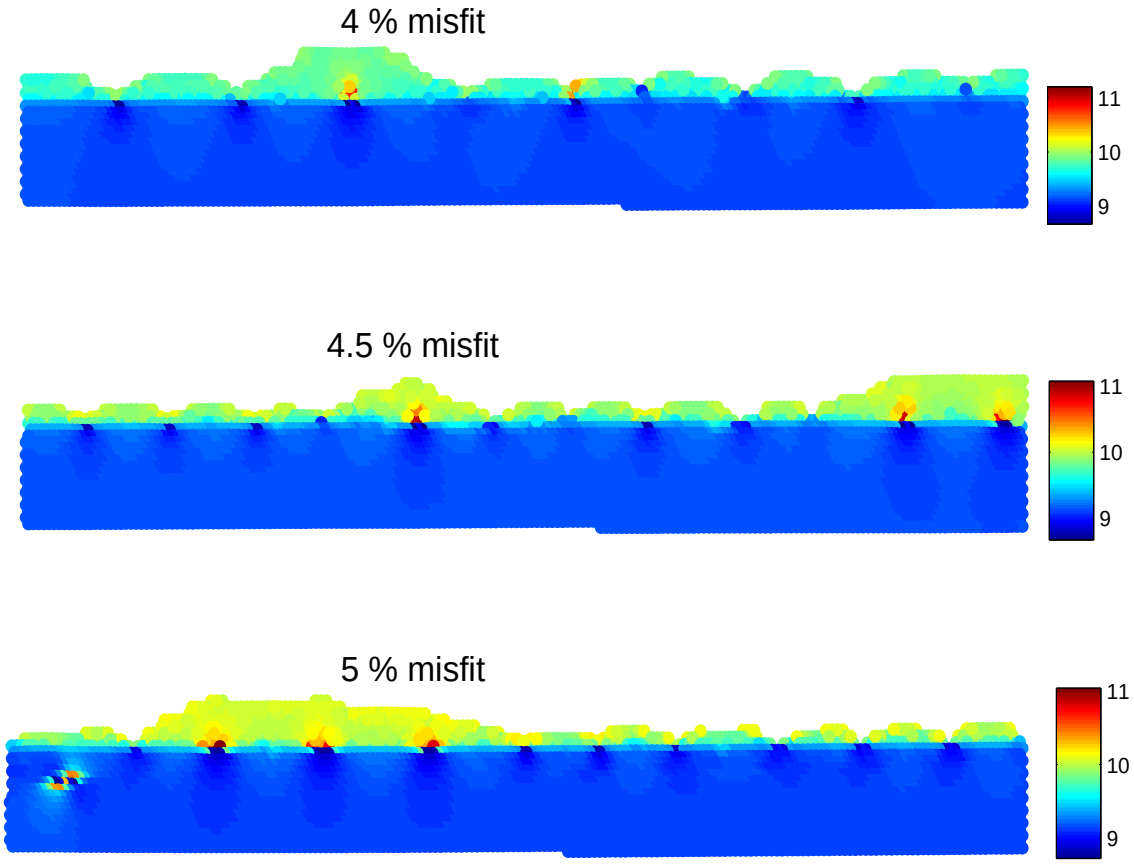


Figure 11: , $\bar{r}_{ij}$ to nearest neighbors, $F = 0.1ML/s$

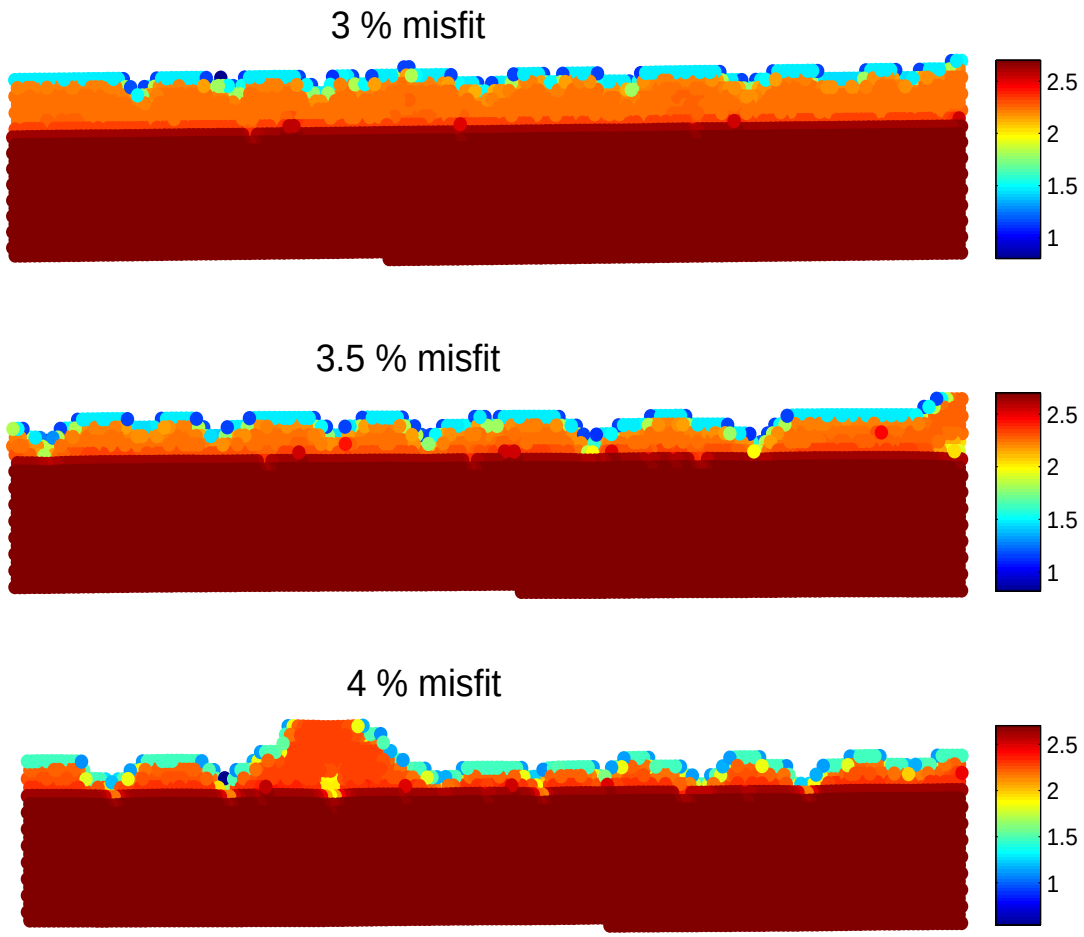


Figure 12: FM, SK and VW growth showing energy of each atom. $F = 0.1ML/s$

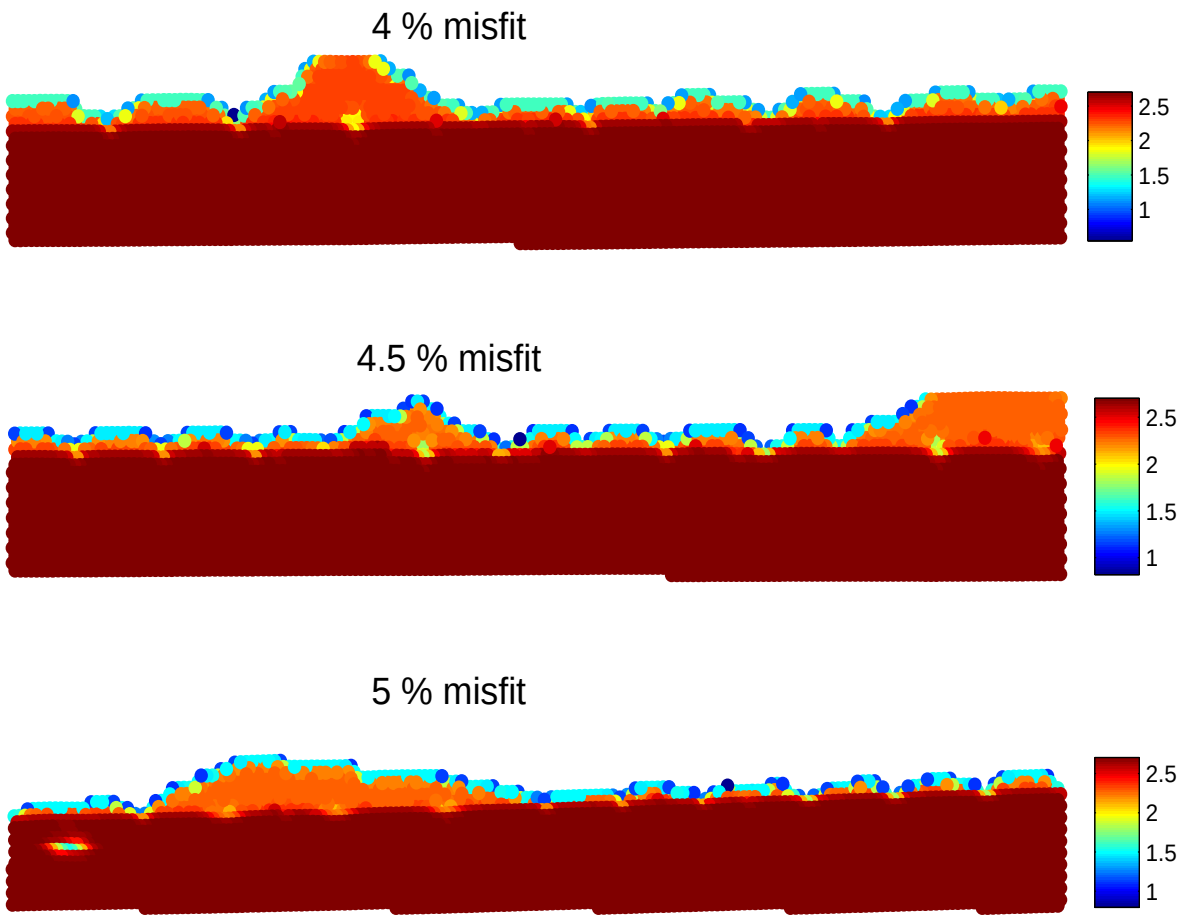


Figure 13: SK and VW growth showing energy of each atom. $F = 0.1ML/s$

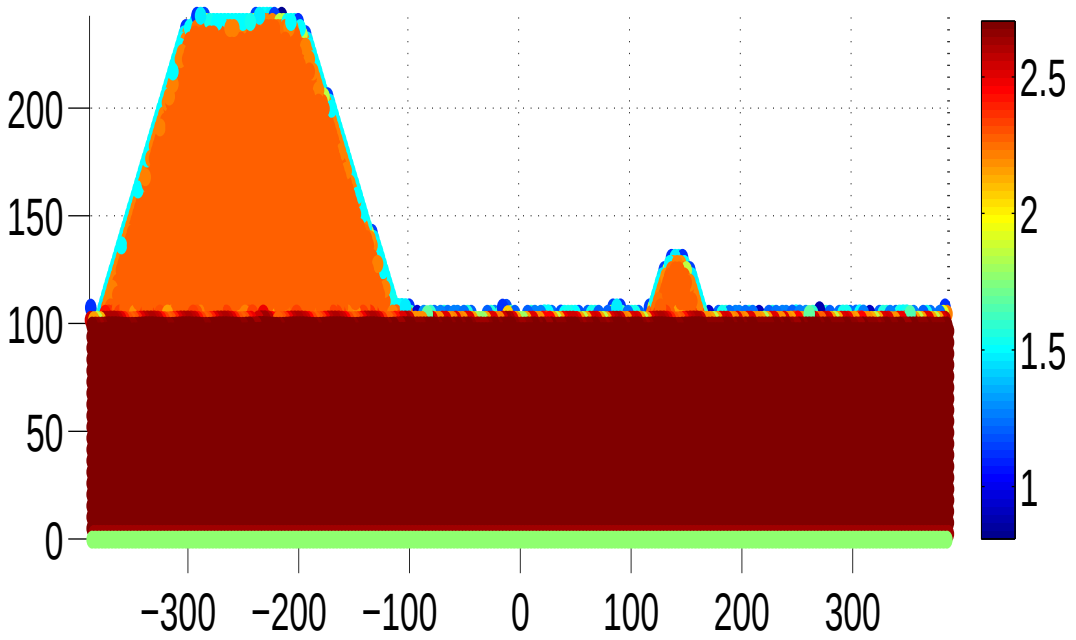


Figure 14: Volmer Weber growth showing energy of each atom. $\mu = -0.1$, $F = 1.0ML/s$

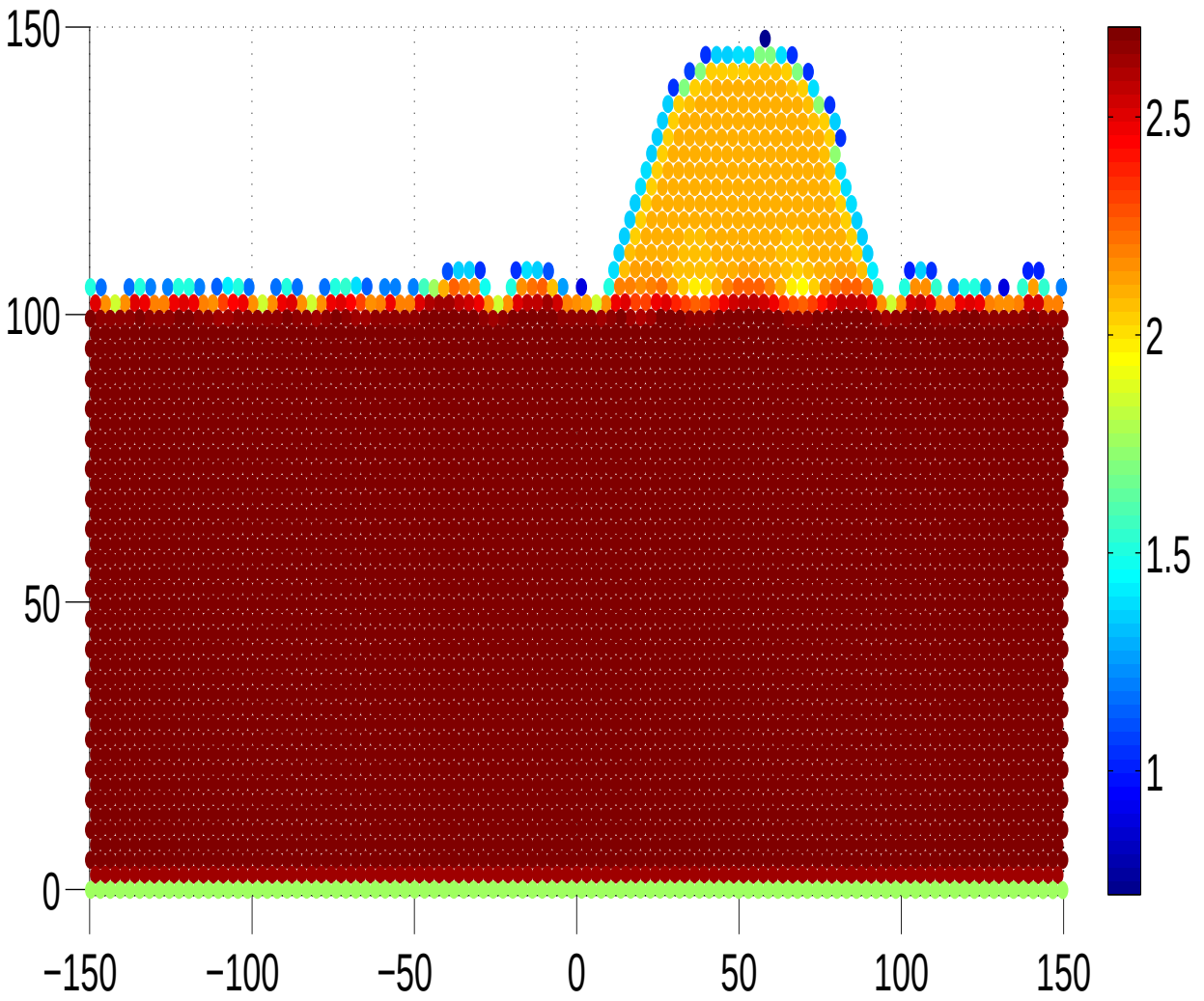


Figure 15: VM growth showing energy of each atom.
$\mu = -0.1$, $F = 0.25ML/s$

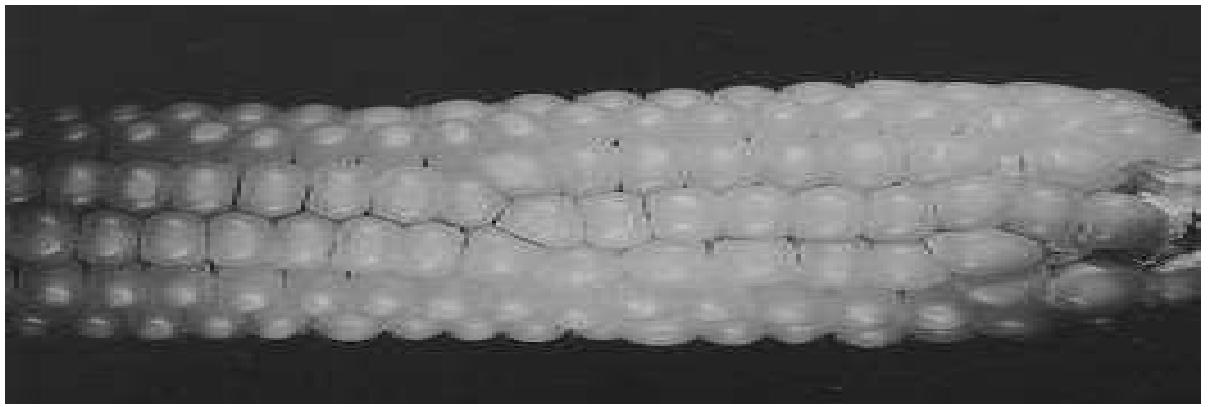


Figure 16: Edge dislocations in nature.

By Peter J. Goodhew, Dept. of Engineering, University of Liverpool

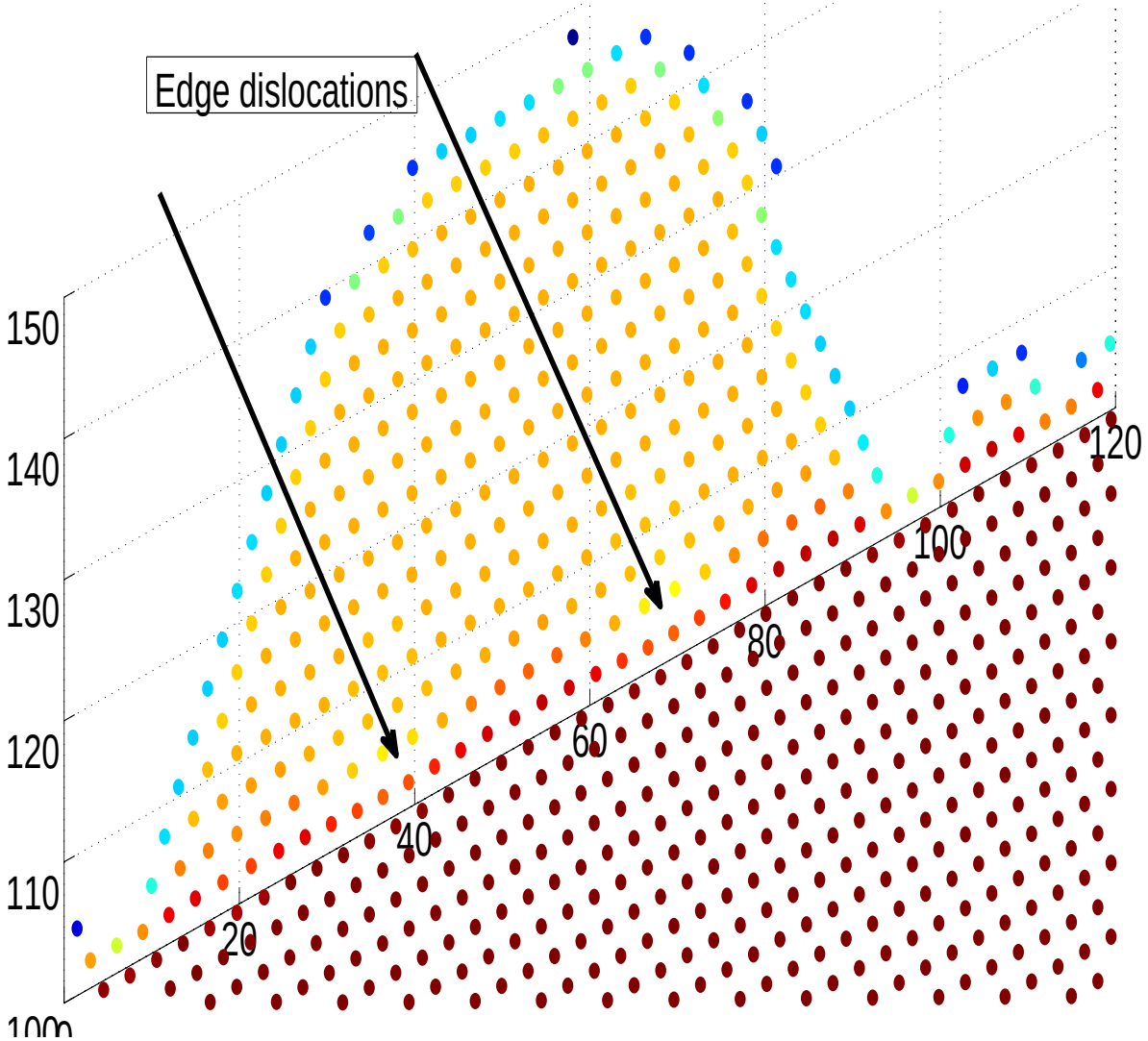


Figure 17: Edge dislocations

Summary

Our model

- Predicts the right curvature due to Stoney's formula
- Clearly captures the effect of misfit strength on the growth modes (FM, SK, VM)
- Captures dislocations and its physical effects
- Easily incorporates intermixing

Connection Between

Continuum Mechanics

and Kinetic Monte Carlo

Statistical Mechanics

- Consider Film in Thermodynamic Equilibrium
- Free Energy $F = -kT \log Z$ where $Z = \sum_{\text{states}} e^{-U(\text{state})/\text{kT}}$
- Ensemble Average $\langle g \rangle \equiv \frac{1}{Z} \sum_{\text{states}} g e^{-U(\text{state})/\text{kT}}$
- $\mu = F - F_0 = kT \log \langle \exp\left[(U - U_0)/kT\right] \rangle$
- $\Rightarrow \langle R \rangle = \omega e^{\mu/kT}$

Local Thermodynamic Equilibrium

- $\Rightarrow \langle R \rangle(x) = \omega e^{\mu(x)/kT}$
- Fick's Law $\Rightarrow \mathbf{j} = -M \nabla_s \langle R \rangle$
- M depends on the details of the hopping rules
- $\mathbf{j} = -\frac{M\langle R \rangle}{kT} \nabla_s \mu$
- $D = M\langle R \rangle / \nu$
- $\Rightarrow \mathbf{j} = -\frac{\nu D}{kT} \nabla_s \mu$ (same as continuum)

Summary

- The KMC formulation contains the same physics as this class of continuum models
- But KMC also captures other physical effects, stochastic in nature, such as:
  - Nucleation of Islands or Pits
  - Atomistic scale features that occur during intermixing
  - Promotion of intermixing due to surface roughness
- Main drawback of KMC is that it can be computationally slow