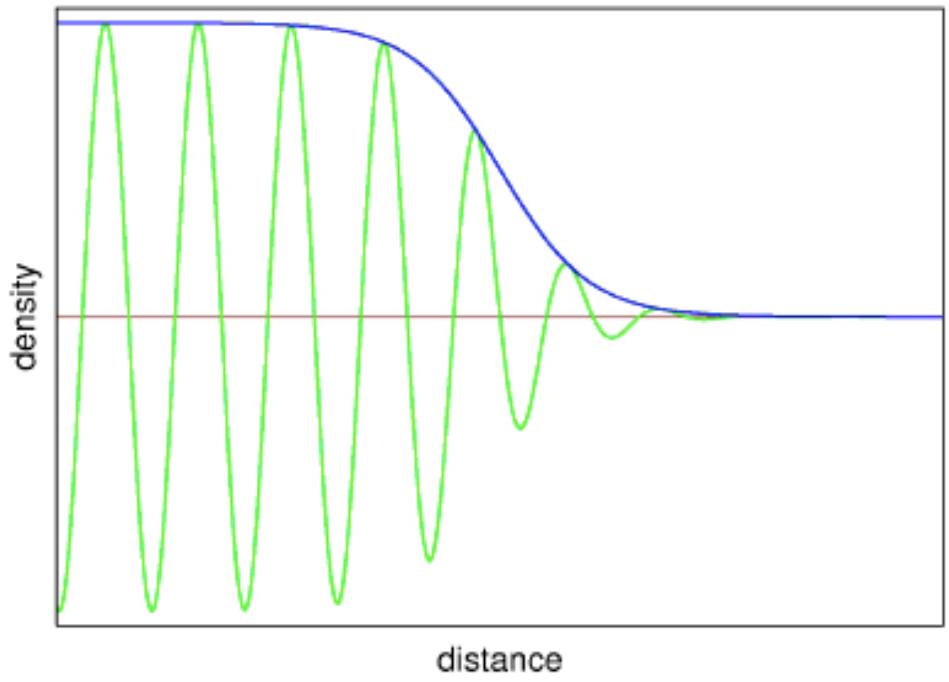
The Phase Field Crystal Model



Idea: Free energy formulation for number density ρ

Phase Field Crystal Model

$$\phi = (\rho - \rho_{eq})$$

$$\partial_t \phi = \nabla \cdot (M(\phi) \nabla \mu)$$

Mobility

$$\mu := \delta_\phi E(\phi)$$

Temperature

$$E(\phi) = \int_\Omega \left\{ \frac{1}{4}\phi^4 + \frac{1-\epsilon}{2}\phi^2 - \mid \nabla\phi \mid^2 + \frac{1}{2}(\Delta\phi)^2 \right\} d\mathbf{x}$$

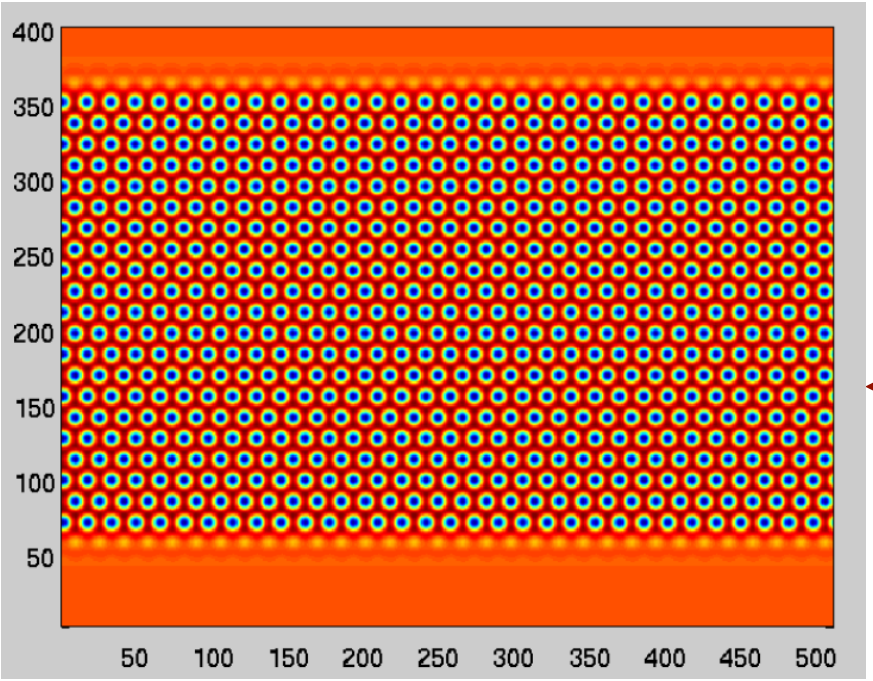
$$\epsilon \leq 1, \epsilon \in \mathbb{R}$$

Swift-Hohenberg

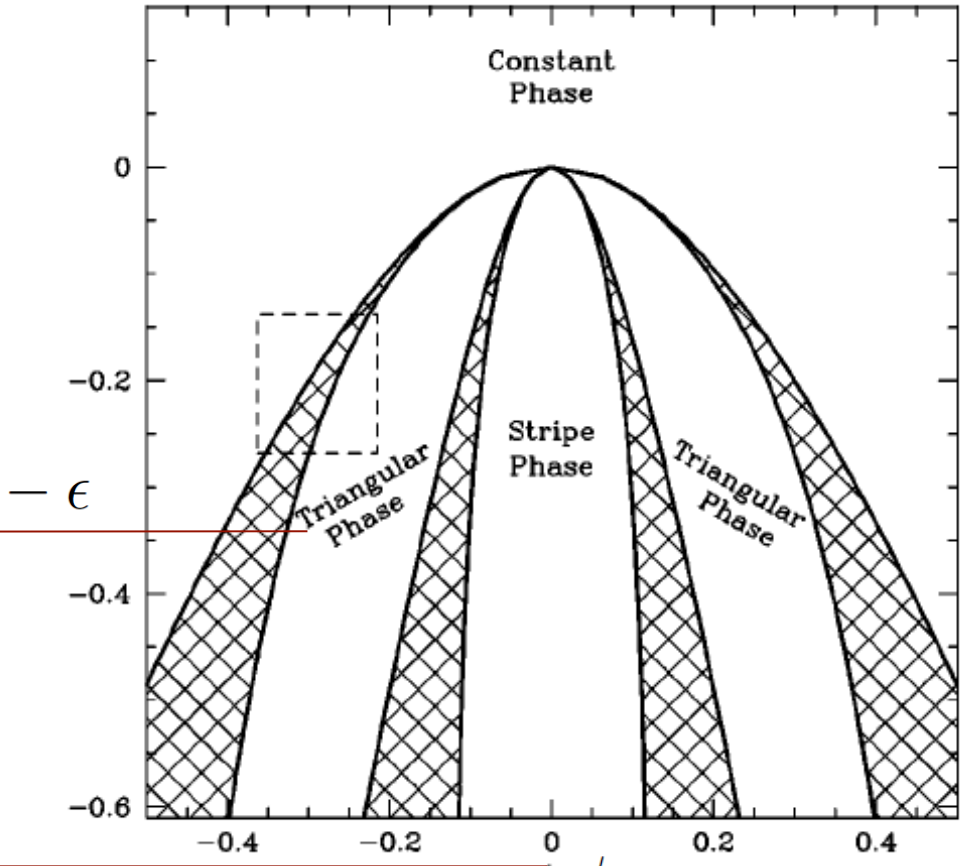
$$-\epsilon \approx \Delta T$$

Elder et al [PRE 051606 (2004)]

Phase Diagram



Elder et al [PRE 051606 (2004)]



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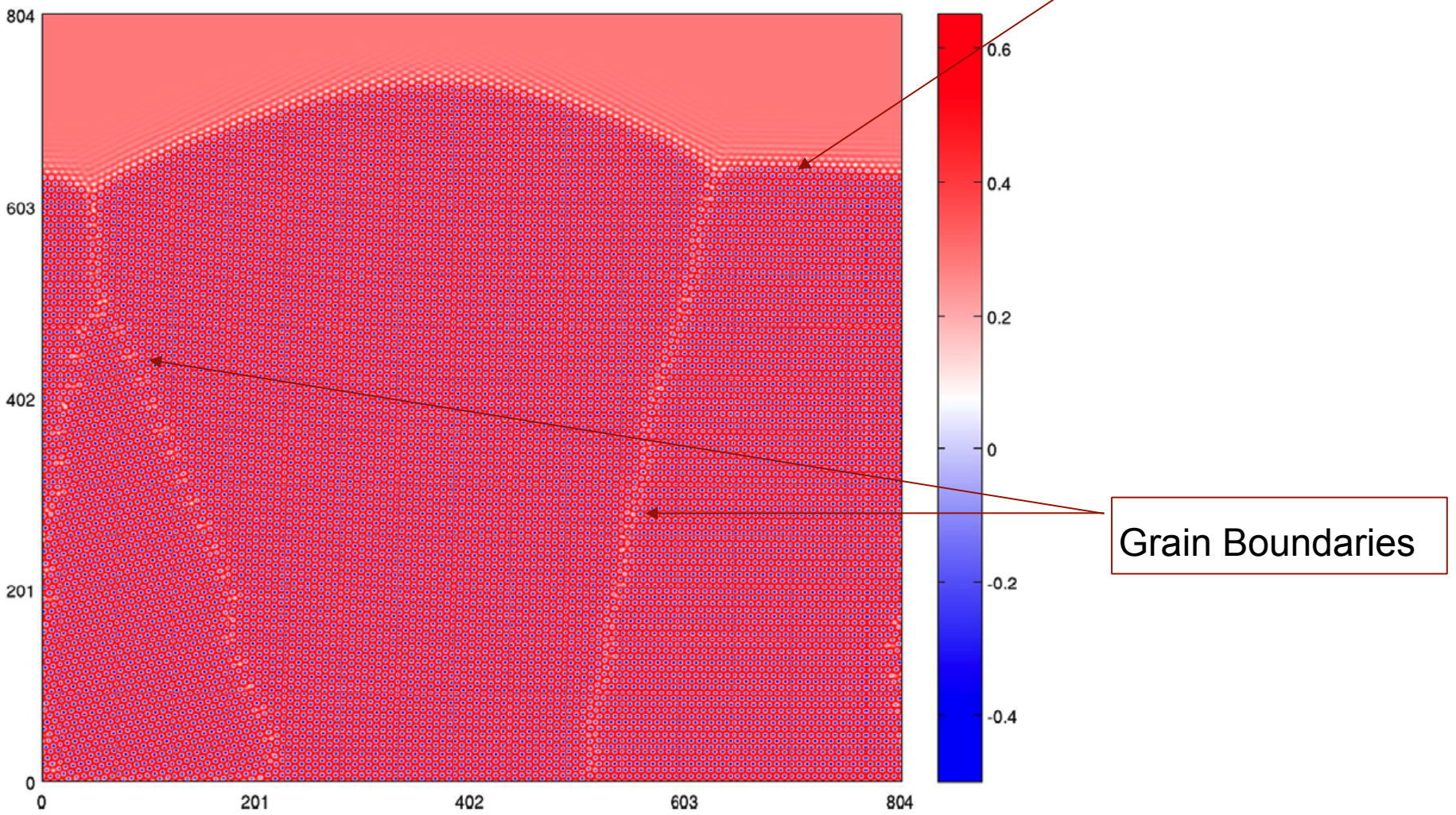
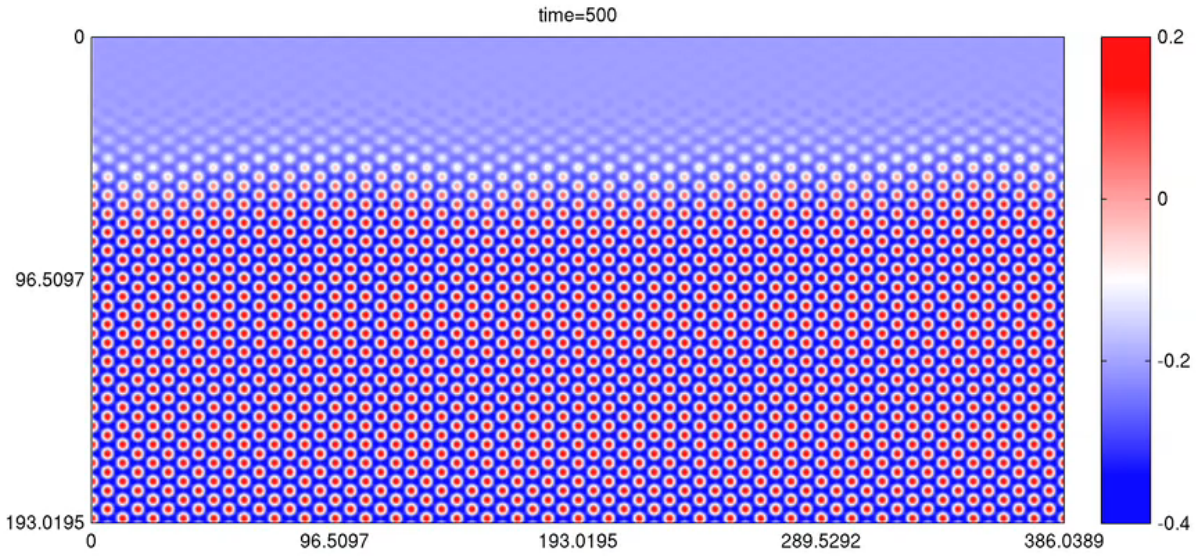
Phase Field Crystal



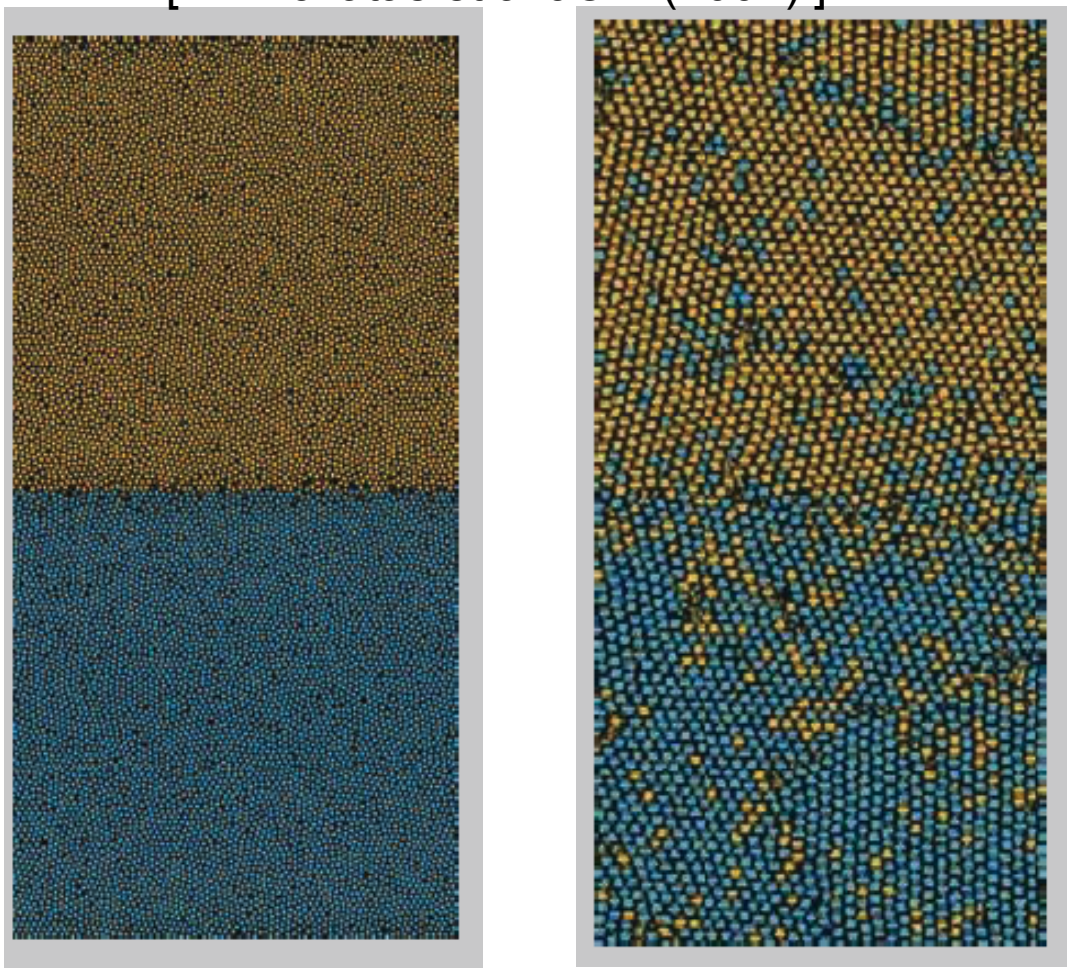
Strained Film



- Strain is applied to the film by changing the dimension of the film.
- Stained film has higher free energy
- To release the energy, the film produces undulation, or create dislocations.
- Film flattens after the stresses are relieved by the annihilation of dislocations.

Phase Field Simulation of Binary Alloy

[N Provatas et al JOM (2007)]



Elastic and Interfacial Energy

Elastic Interactions

$$\phi(\vec{x}) = \phi_{eq}(\vec{x} + \vec{u}) + \delta$$

$$E(\phi) = E(\phi_{eq}) + \int d\vec{x}(C_{ijkl}u_{ij}u_{kl}) \quad + \ldots$$

→ Hook's Law

Anisotropic Interfacial Energy

R. Backofan and A. Voigt J. Phys. Condens. Matter 21. (2009) 464109

PFC Advantages :

1 Efficient numerical evolution though straight forward finite difference schemes

2 Captures the basic energetics
   a) Elastic Energy (Linear Elasticity)
   b) Anisotropic Interfacial Energy

3 Captures Atomistic details including
   a) Grain Boundaries
   b) Defect formation

PFC Disadvantages :

1 Modeling Pyrite Structure is difficult

Random arrangement of the two species on the lattice in Binary alloys

2 Surface rearrangement of atoms is hard to model

3 Determining the elastic field of the crystal is hard (computationally expensive)

4 Lack of resolution of difference on relaxation and diffusion time scale

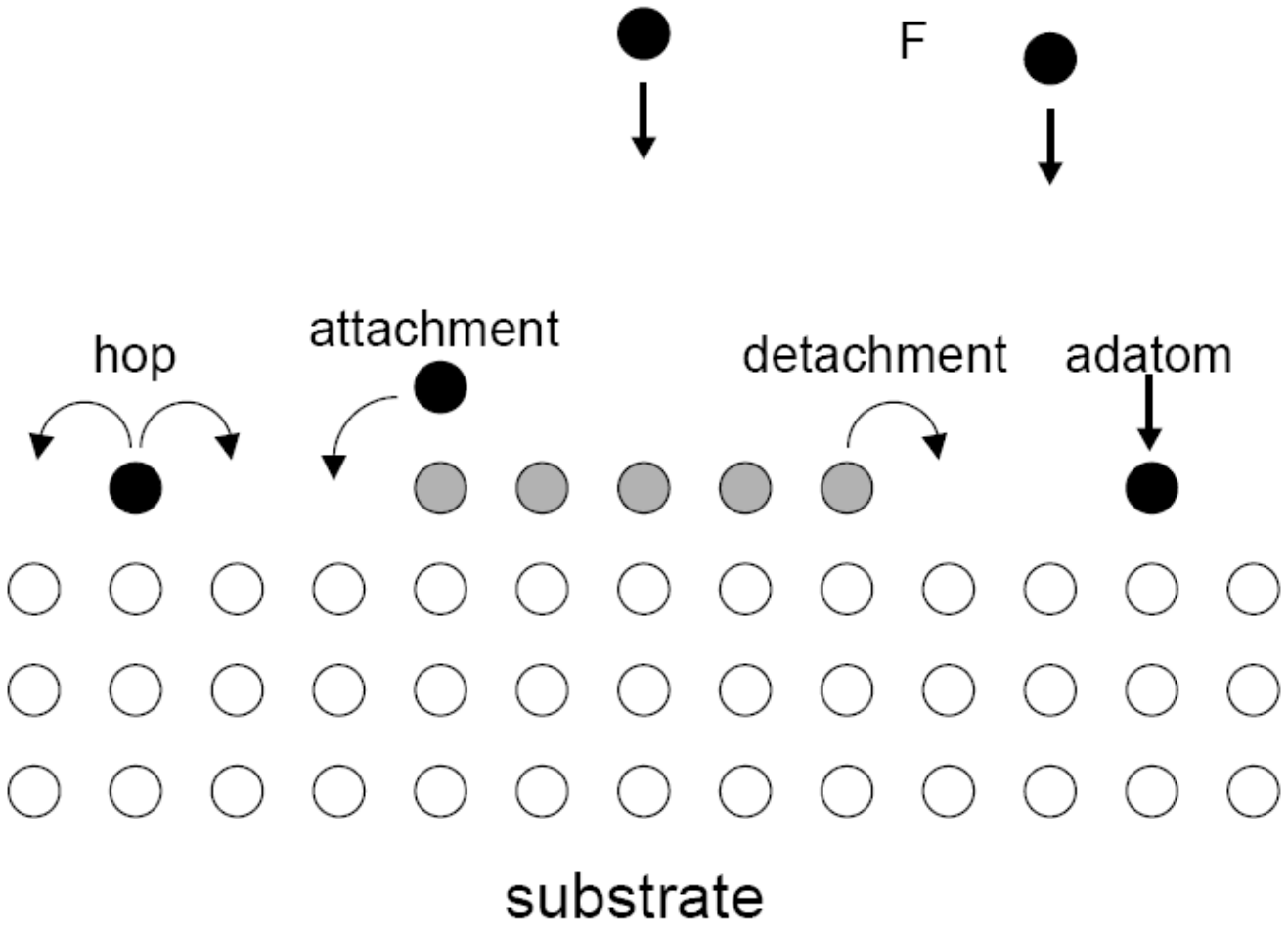
$$\frac{\mathcal{F}}{k_B T} = \int d\vec{r}\left[\rho_A \ln\left(\frac{\rho_A}{\rho_L^A}\right) - \Delta\rho_A + \rho_B \ln\left(\frac{\rho_B}{\rho_L^B}\right) - \Delta\rho_B\right] - \frac{1}{2}\int d\vec{r}_1 d\vec{r}_2 [\Delta\rho_A(\vec{r}_1) C_{AA}(\vec{r}_1,\vec{r}_2)\Delta\rho_A(\vec{r}_2)$$
$$+ \Delta\rho_B(\vec{r}_1) C_{BB}(\vec{r}_1,\vec{r}_2)\Delta\rho_B(\vec{r}_2) + 2\Delta\rho_A(\vec{r}_1) C_{AB}(\vec{r}_1,\vec{r}_2)\Delta\rho_B(\vec{r}_2)],$$

Expand 2-particle correlation function.

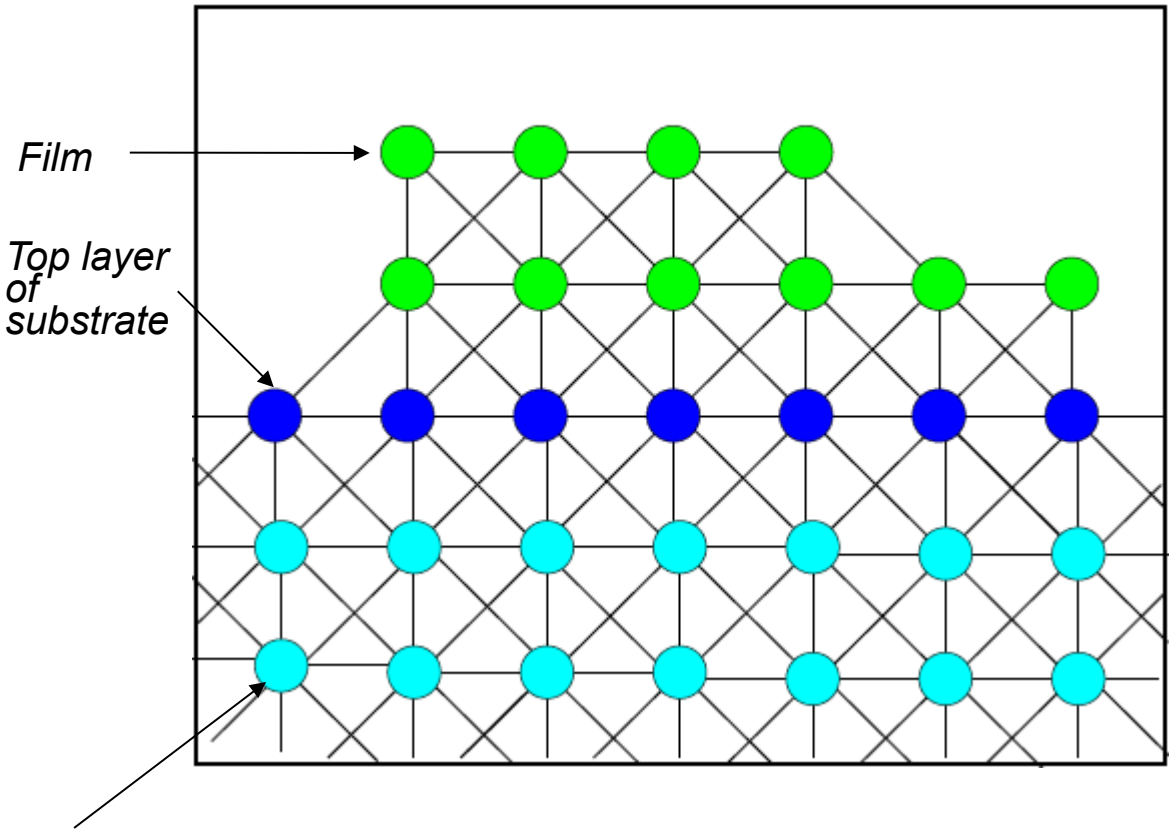
$$C_{ij} = [C_{ij}^0 - C_{ij}^2\nabla^2 + C_{ij}^4\nabla^4]\delta(\vec{r}_1 - \vec{r}_2)$$

$$\frac{\partial n}{\partial t} = M_1\nabla^2\frac{\delta\mathcal{F}}{\delta n},$$
$$\frac{\partial(\delta N)}{\partial t} = M_2\nabla^2\frac{\delta\mathcal{F}}{\delta(\delta N)},$$

Evolution of KMC Model



Example : KMC Model for a Si/Ge system to study Stranski - Krastanov Growth



What is a Crystal?

- Atoms on a square lattice
- Semi-infinite in the y direction
- Infinite in the x direction (We use a periodic boundary...)
- Nearest and next to nearest neighbour bonds
- Nearest and next to nearest neighbour springs

How does it evolve?

- *"Surface atoms are allowed to hop to neighbouring vacant surface site"* **Surface Diffusion**

Hopping Rates - Lam, Lee & Sander (2002)

$R = \omega \exp(-\Delta E / kT)$

ΔE= E(with the atom) – E(without atom)

ω is the attempt frequency

kT is the thermal energy

E = energy of the state (configuration)

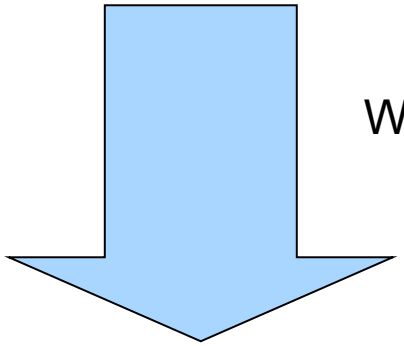
$E = E_{chem} + E_{elastic}$

E_{chem} bond energy (bond counting)

$E_{elastic}$ energy stored in springs

These rates satisfy :

- Detailed balance
- Ergodicity



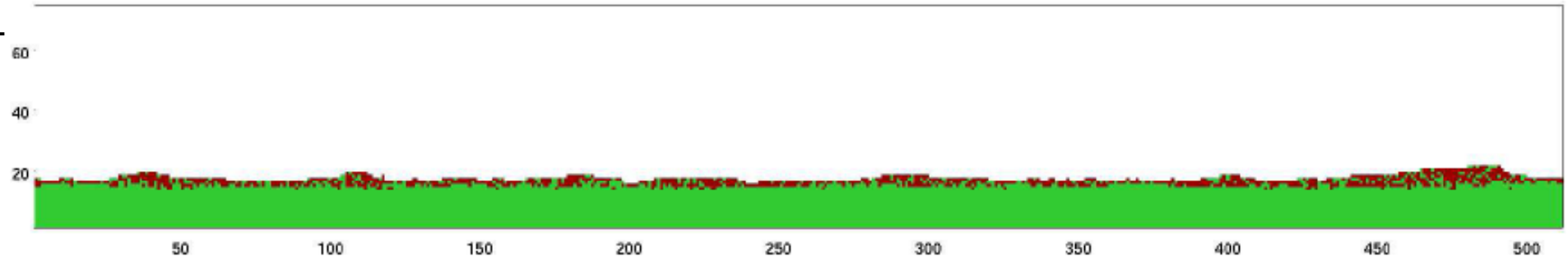
Wait long enough...

Boltzmann Equilibrium Distribution

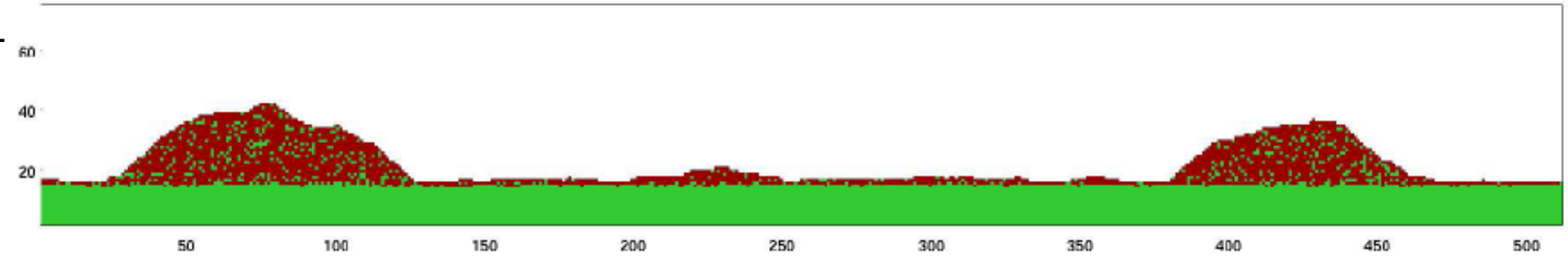
Crystal Grown with different bonds strengths

Si-Si = 0.37 eV Ge-Si =0.355 eV Ge-Ge = 0.34 eV

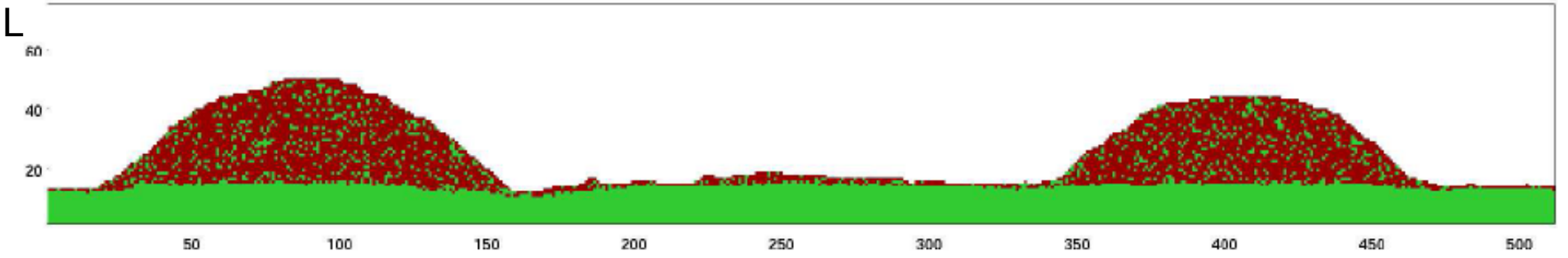
2ML



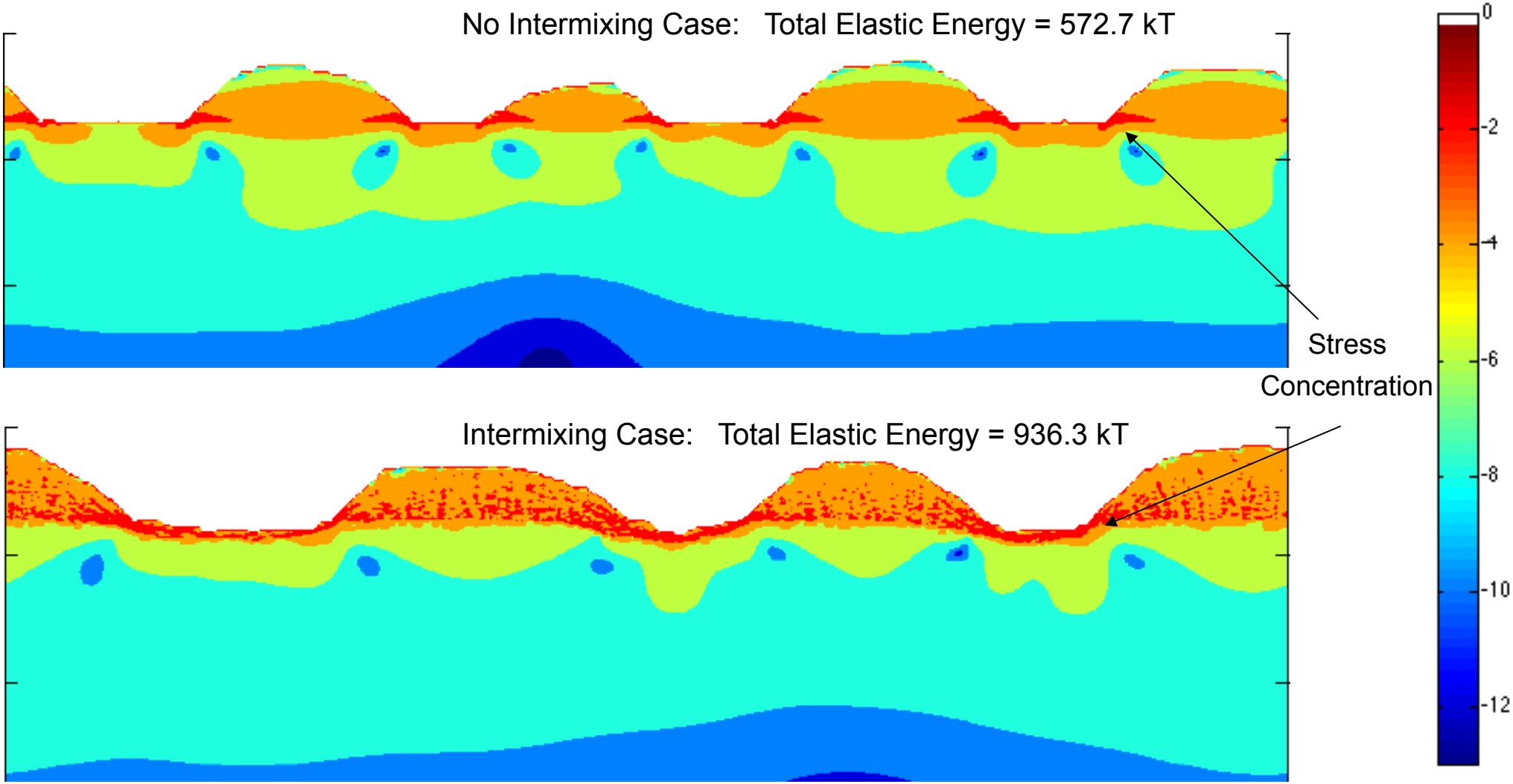
6ML



10ML

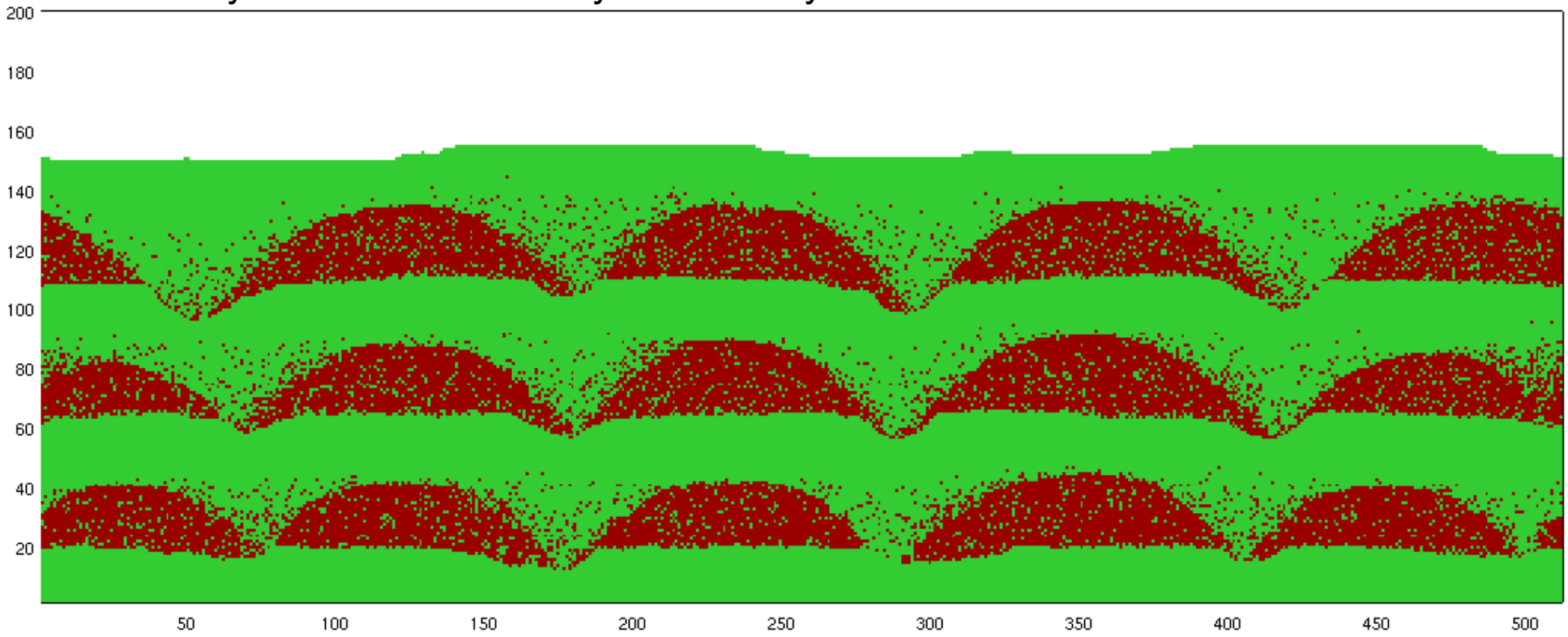


Elastic Energy Density with and without intermixing of Ge/Si



Stacked quantum dots

10 Monolayers of Ge followed by 15 Monolayers of Si



KMC Advantages :

1 Modeling Pyrite Structure will be straight forward

2 Surface rearrangement of atoms is modeled through introduction of new events

3 Determining the elastic field of the crystal is simple

4 The model is stochastic and captures entropy

It minimizes the Free energy rather than the energy of the system

PFC Disadvantages :

1 Developing a discrete elastic model for the pyrite structure is not straight forward

2 Numerical evolution for systems with misfit strain is expensive

Elastic computations are expensive

3 Lacks the ability to capture the Defects and Grain Boundaries.

	PFC	KMC
Grain Boundaries/Defects	Yes	No
Surface Rearrangements	No	Yes
Pyrite Structure	Needs to be modeled	Yes
Control over material Constants/ parameters	No	Yes
Elasticity interactions In pyrite configuration	Yes	No