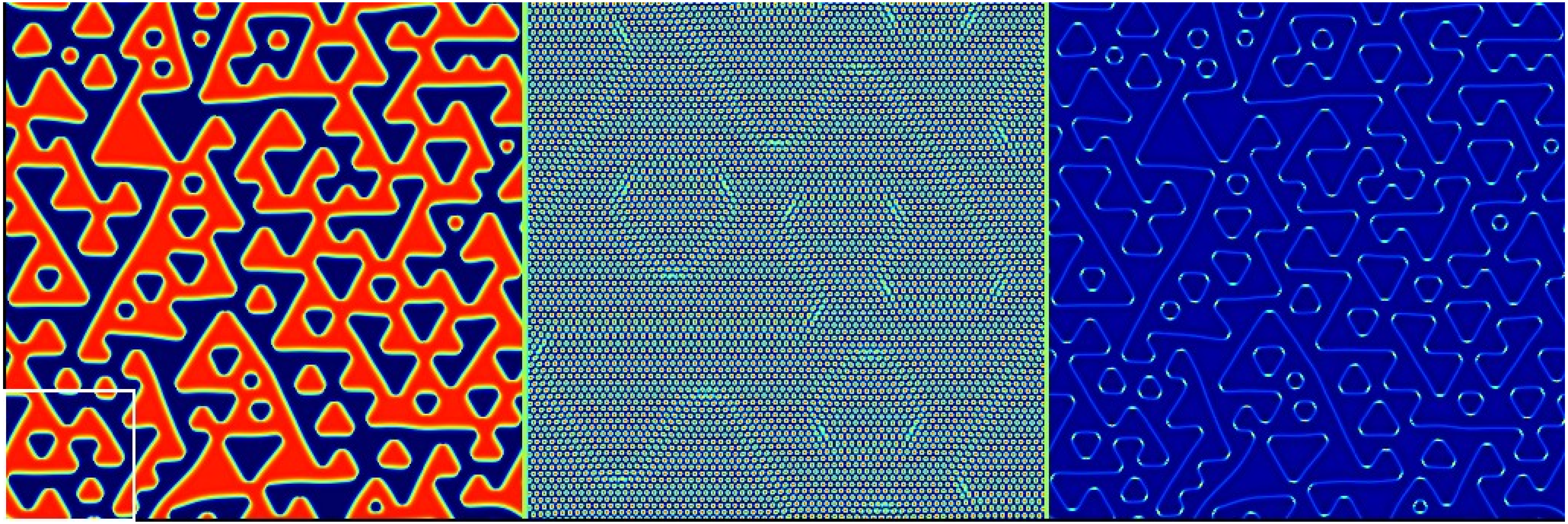
Ordering of nano-scale structures on micron length scales

Ken Elder, Oakland University



Alemi, UBC, June 8th 2011

Collaborators

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Princeton U., Mikko Haataja,

Wayne State U. Zhi-Feng Huang,

U. of Western Ontario, Mikko Kartunnen,

NSF Division of Materials Research

Oakland University

Length Scales and Modelling

Atomistic:

DFT (density functional theory): ab-initio calculation of binding (**E_o**) and activation energies (**E_A**) of solutes at α-γ interface

MD (molecular dynamics): Use DFT results to build suitable potentials for simulations of diffusion (**D_b**) across and mobility (**M**) of α-γ interface

PFC (phase field crystal): Provide linkage from atomistic to continuum modelling using MD length scale and PFM time scale, translate interaction potentials to two-point correlation function (**c_2**)

Mesoscale:

PFM (phase field model): Use DFT/MD/PFC (**c_2**) results for binding energy (**E_o**), interfacial diffusion (**D_b**) and mobility (**M**) to simulate **solute drag** and overall transformation kinetics

Macroscale:

JMAK (Johnson-Mehl-Avrami-Kolmogorov): Translate PFM **solute drag** model into suitable **JMAK rate parameters** for overall **transformation model**

Validation Experiments: **Validate transformation model** with experimental data

Length Scales and Modelling

Atomistic:

Classical

DFT (density functional theory):
--- mechanical properties

MD (molecular dynamics):
Use DFT results to build suitable potentials for simulations of diffusion (**D_b**) across and mobility (**M**) of α-γ interface

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Provide linkage from atomistic to continuum modelling using MD length scale and PFM time scale, translate interaction potentials to two-point correlation function (**c_2**)

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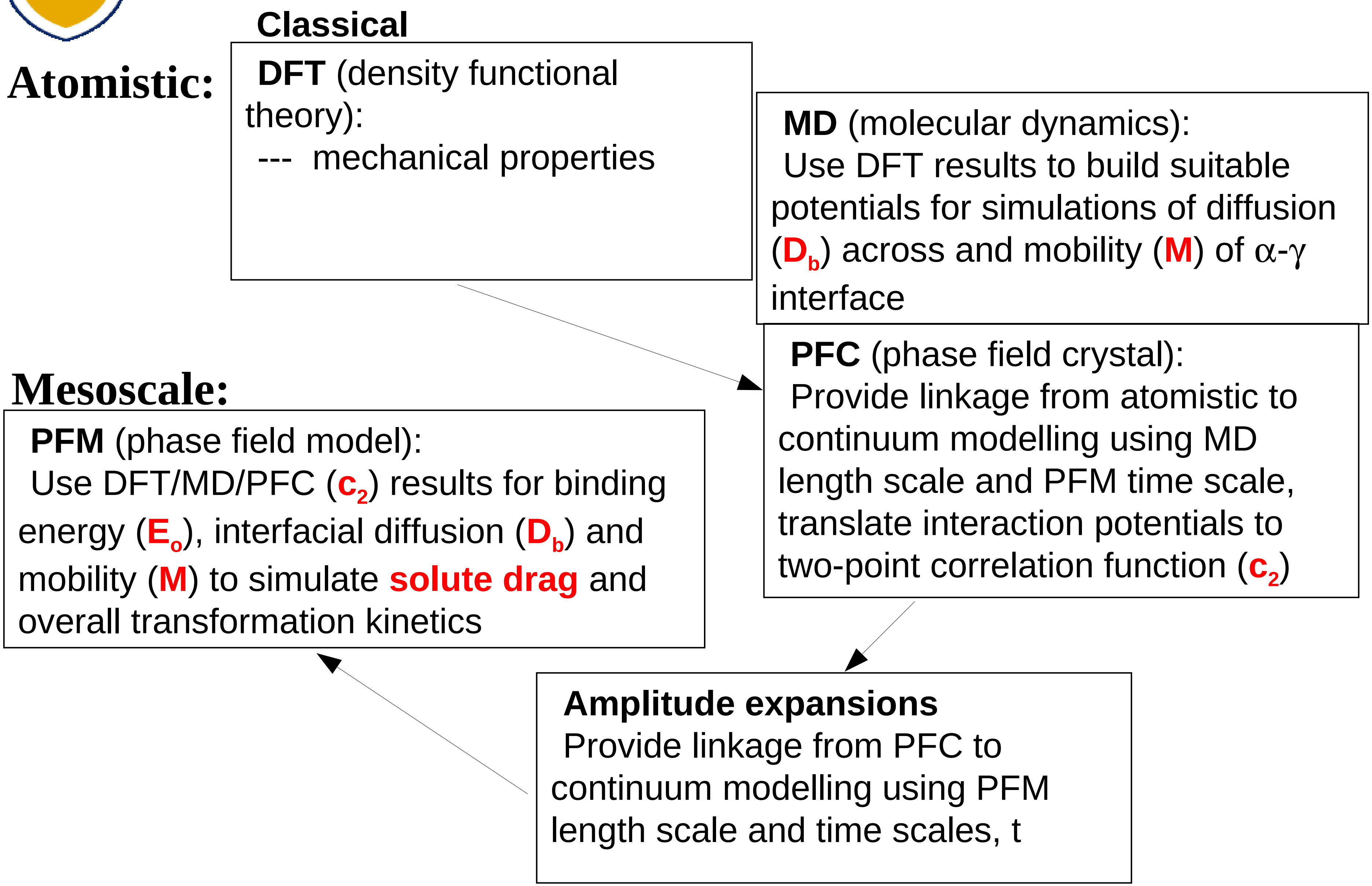
Length Scales and Modelling



Classical

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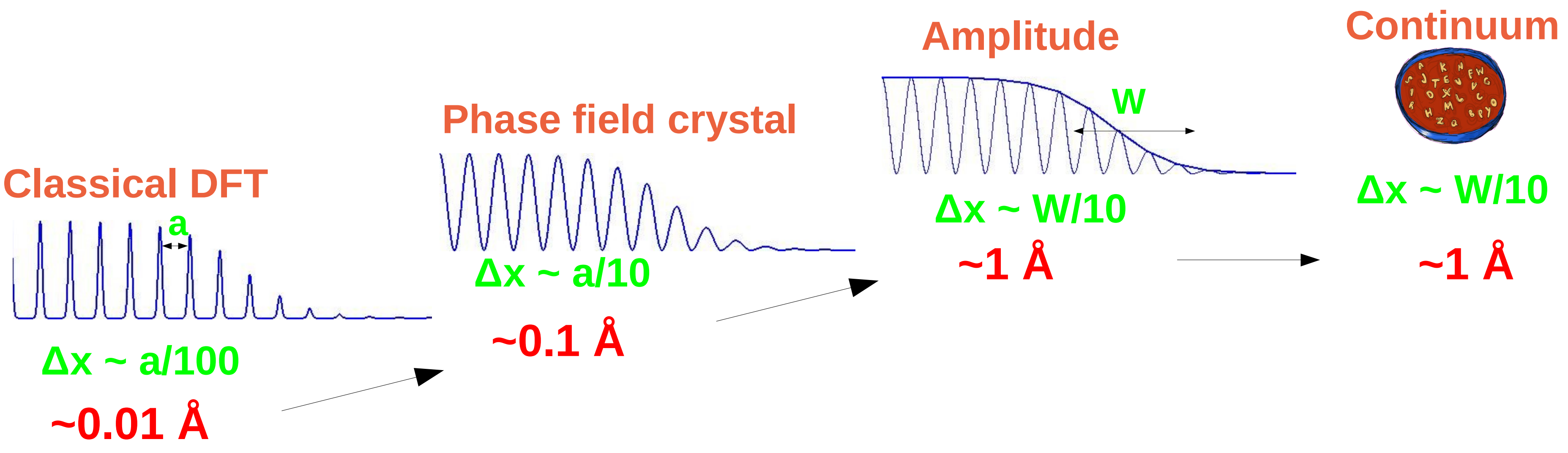
Use DFT/MD/PFC (**c_2**) results for binding energy (**E_o**), interfacial diffusion (**D_b**) and mobility (**M**) to simulate **solute drag** and overall transformation kinetics

Amplitude expansions
Provide linkage from PFC to continuum modelling using PFM length scale and time scales, t

Overview

Part 1: Multiscale Modeling



Classical DFT

Δx ~ a/100

~0.01 Å

Phase field crystal

Δx ~ a/10

~0.1 Å

Amplitude

Δx ~ W/10

~1 Å

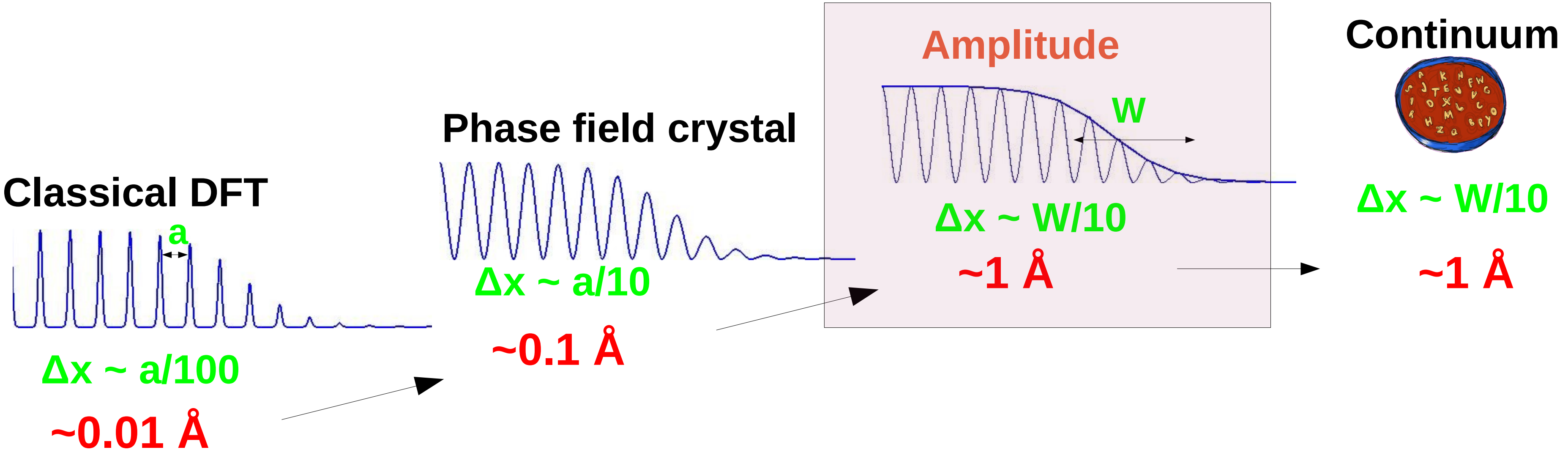
Continuum

Δx ~ W/10

~1 Å

Overview

Part 1: Multiscale Modeling



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Phase field crystal

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Amplitude

Δx ~ W/10

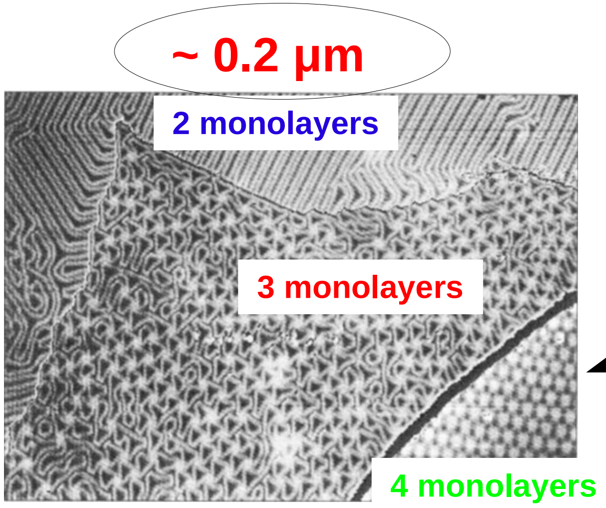
~1 Å

Continuum

Δx ~ W/10

~1 Å

Part 2: Application: Surface ordering

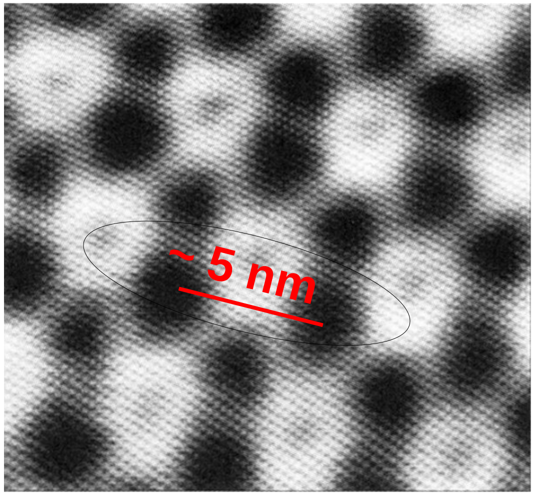


~ 0.2 µm

2 monolayers

3 monolayers

4 monolayers



~ 5 nm

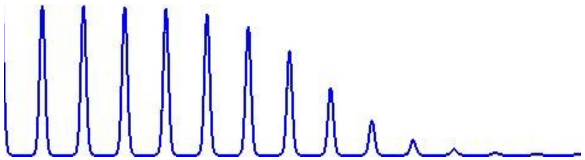
nm objects ordering on µm scales

Part 1: Multiscale Modeling: CDFT

Classical Density functional theory of freezing

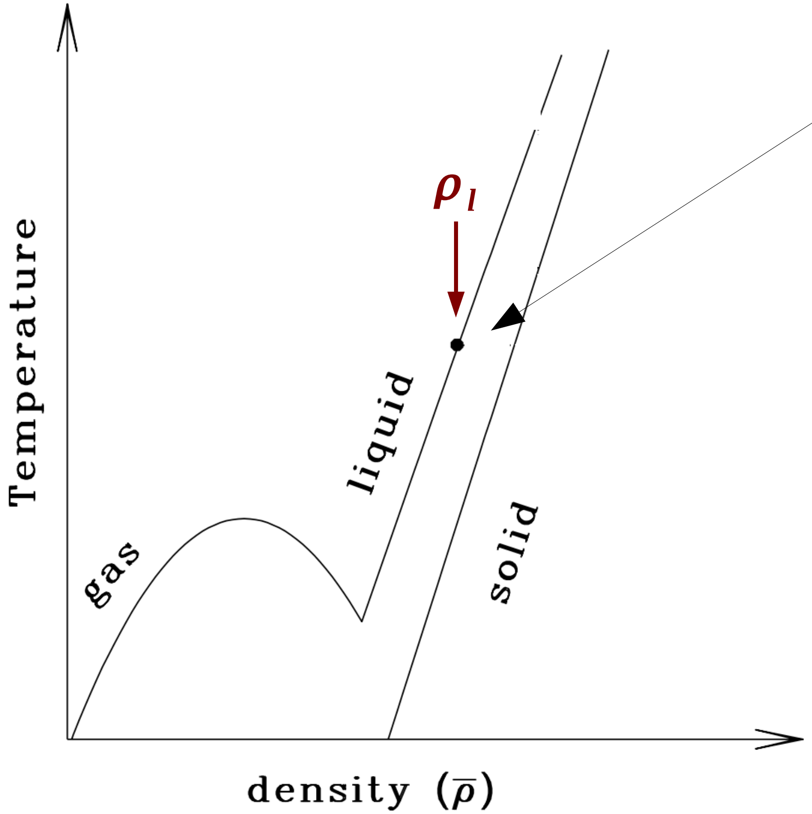
Ramakrishnan and Yussouff, PRB **19**, 2775 (1979), Singh Phys. Rep. **207**, 351 (1991)

$\rho(\vec{x},t)$



Liquid/Solid transition
Mechanical properties

atomic number density field



Free energy functional $F\{\rho(\vec{x},t)\}$

Expand in density/density correlations

1st term – no interaction: entropy

$$\frac{\Delta F_1}{k_B T} = \int d\vec{r}\left[\rho \ln\left(\frac{\rho}{\rho_l}\right) - \delta\rho\right]$$

where $\delta\rho \equiv \rho - \rho_l$

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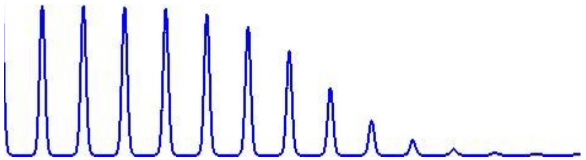

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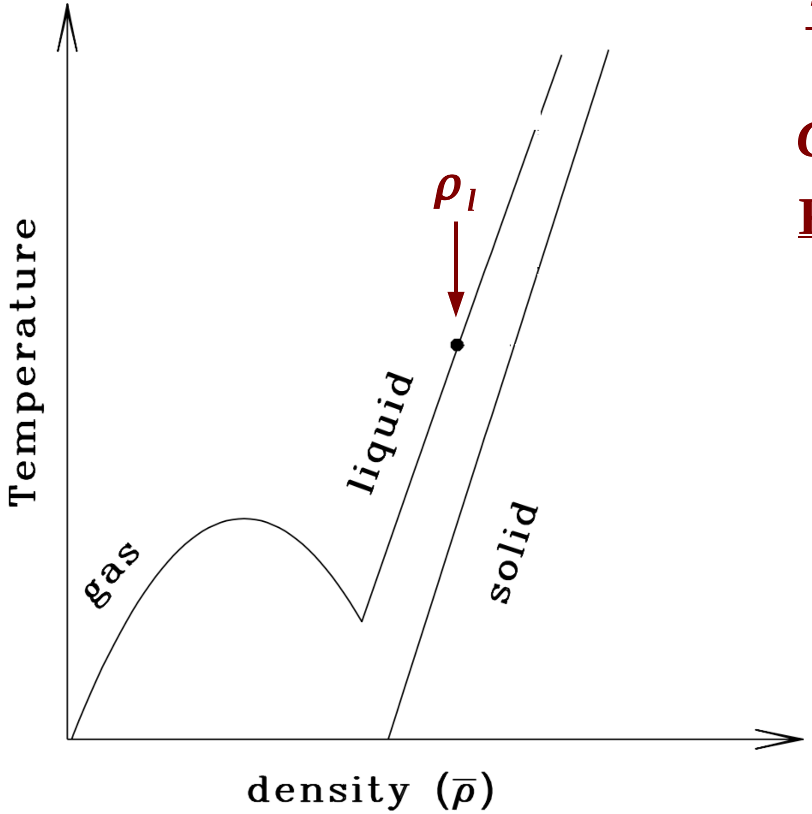


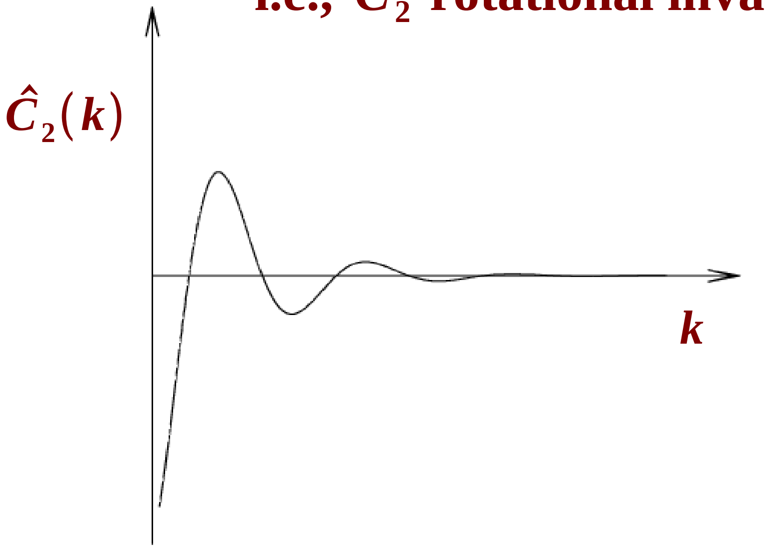
2^{nd} term – two body interactions

$$\frac{\Delta F_2}{k_B T} = -\frac{1}{2!}\iint d\vec{r}_1 d\vec{r}_2 \left[\rho(\vec{r}_1)\rho(\vec{r}_2)C_2(\vec{r}_1,\vec{r}_2)\right]$$

$C_2(\vec{r}_1,\vec{r}_2) \equiv$ 2-point direct correlation function

Key point : in liquid $C_2(\vec{r}_1,\vec{r}_2) \equiv C_2(|\vec{r}_1-\vec{r}_2|)$

i.e., C_2 rotational invariant



Part 1: Multiscale Modeling: CDFT

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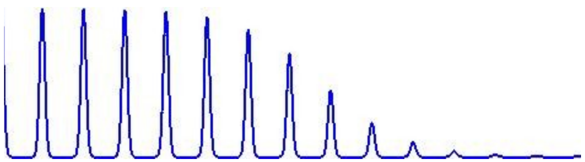
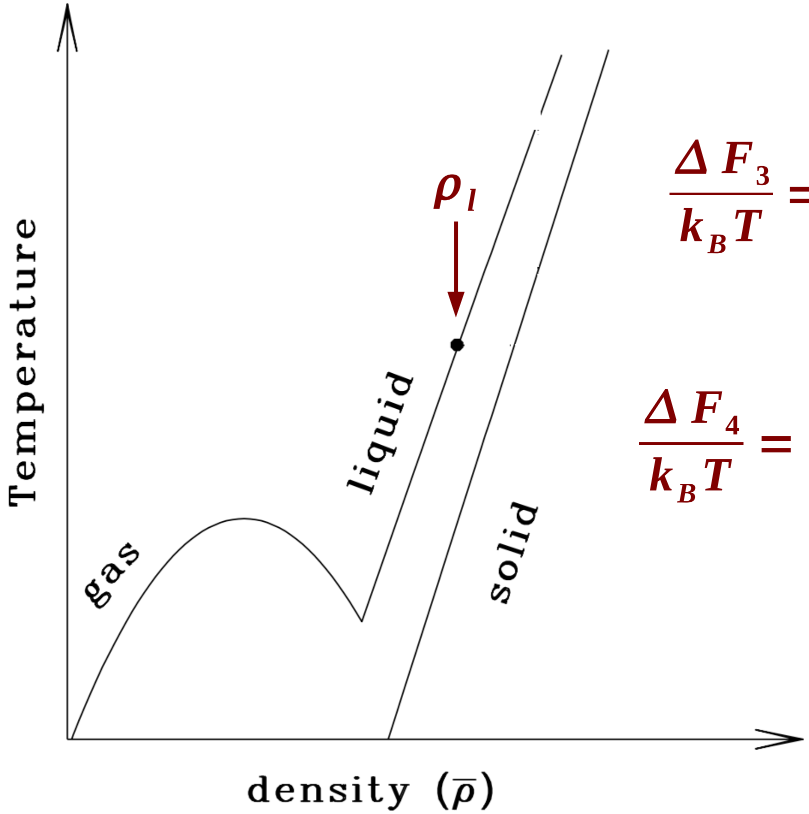
$\rho(\vec{x},t)$



Liquid/Solid transition
Mechanical properties

atomic number density field



3rd term – three body interactions

$$\frac{\Delta F_3}{k_B T} = -\frac{1}{3!}\iint d\vec{r}_1 d\vec{r}_2 \left[\rho(\vec{r}_1)\rho(\vec{r}_2)\rho(\vec{r}_3)C_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)\right]$$

4th term – four body interactions

$$\frac{\Delta F_4}{k_B T} = -\frac{1}{4!}\iint d\vec{r}_1 d\vec{r}_2 \left[\rho(\vec{r}_1)\rho(\vec{r}_2)\rho(\vec{r}_3)\rho(\vec{r}_4)C_4(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)\right]$$

etcetera ....

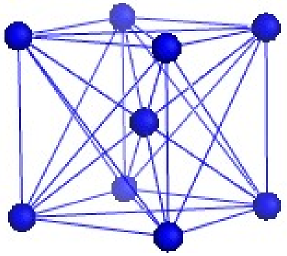
Part 1: Multiscale Modeling: CDFT

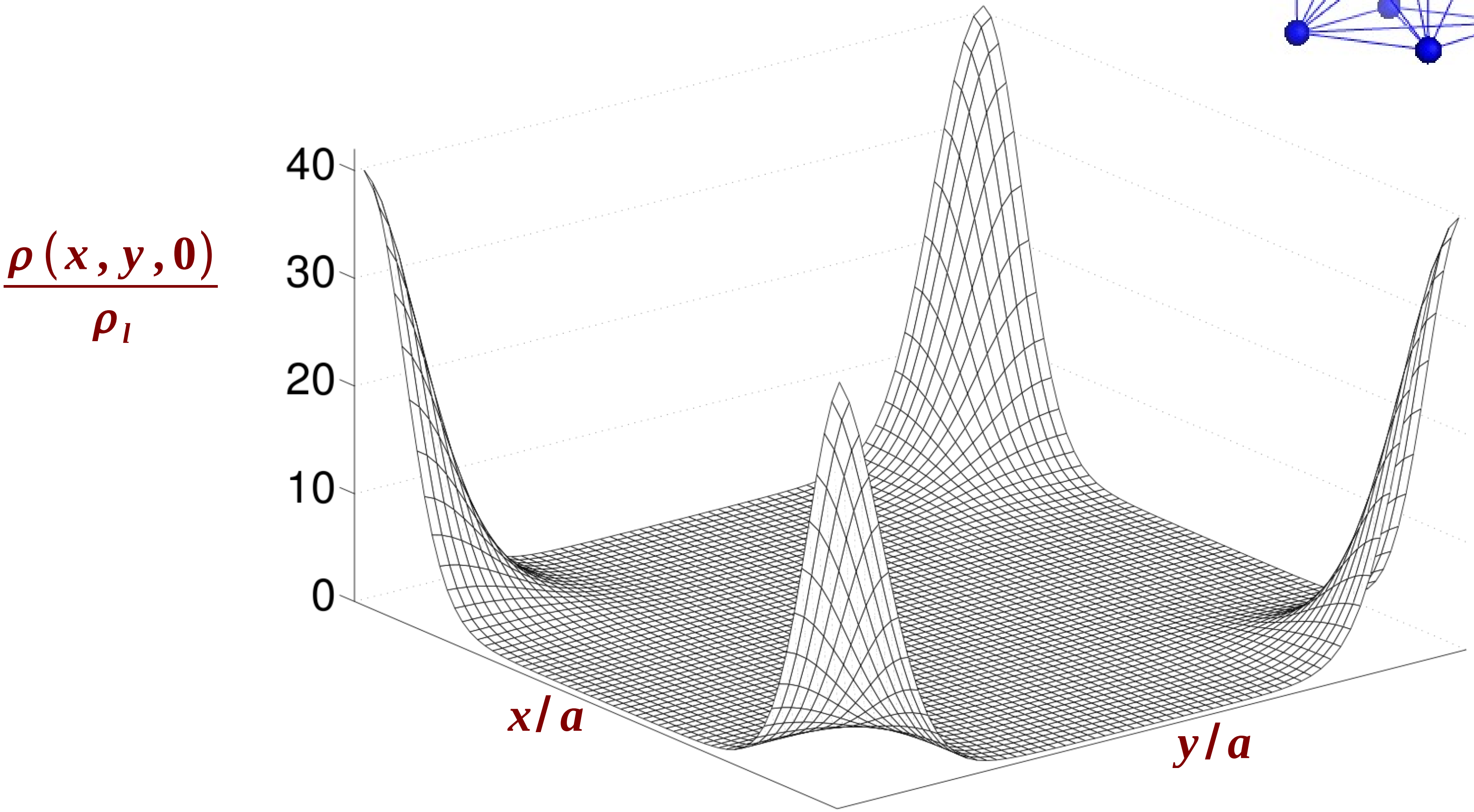
Classical Density functional theory of freezing

Ramakrishnan and Yussouff, PRB **19**, 2775 (1979), Singh Phys. Rep. **207**, 351 (1991)

Example Iron, 1833 K: BCC symmetry

Jaatinen, Achim, Elder, Ala-Nissilä, PRE **80**, 031602 (2009)

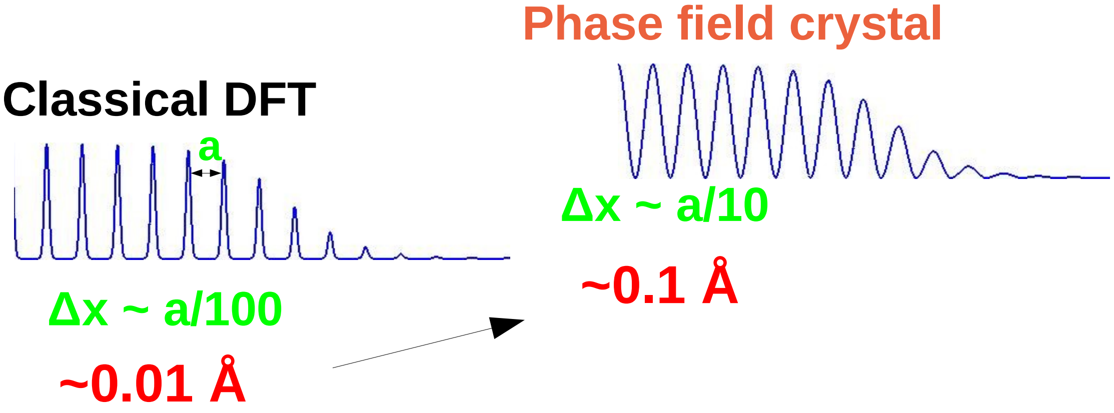




Problem: density very sharply peaked Δx << a

Part 1: Multiscale Modeling: PFC

CDFT to Phase Field Crystal (PFC) in three easy steps

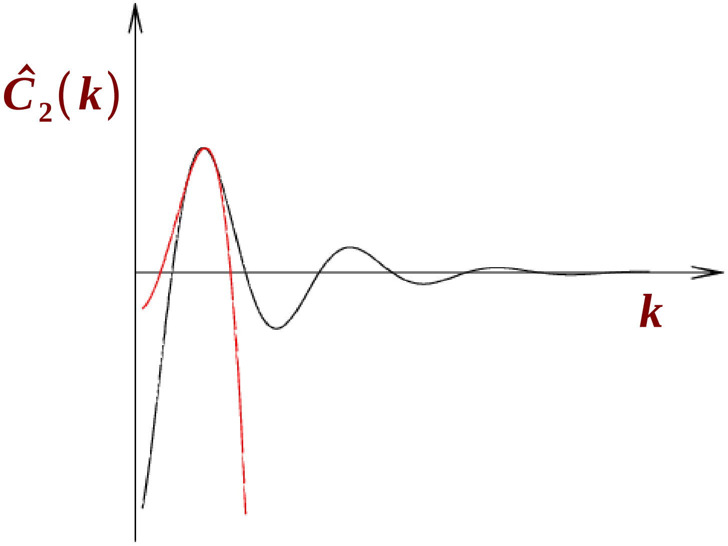


1) Expand in $n \equiv (\rho - \bar{\rho})/\bar{\rho}$ to order n^4

2) Truncate at C_2: $\dfrac{\Delta F}{k_B T} \approx \dfrac{\Delta F_1}{k_B T} + \dfrac{\Delta F_2}{k_B T}$

3) Expand C_2 in fourier space up to k^4, i.e.,

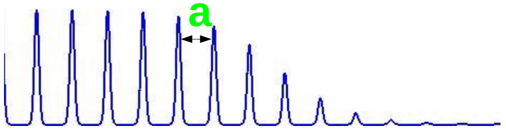
$$\hat{C}_2(k) \approx -\hat{C}_0 + \hat{C}_2 k^2 - \hat{C}_4 k^4$$



Part 1: Multiscale Modeling: PFC

CDFT to Phase Field Crystal (PFC) in three easy steps

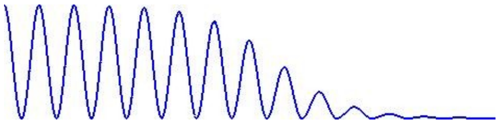
Classical DFT



Δx ~ a/100

~0.01 Å

Phase field crystal



Δx ~ a/10

~0.1 Å

Result (in dimensionless units $\vec{r} \equiv \vec{x}/R\,,\quad R \equiv \sqrt{2\left|\hat{C}_4\right|/\hat{C}_2}$)

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \frac{R^d}{V}\int d\vec{r}\left[\frac{n}{2}\left(B^l + B^x\left(2\nabla^2 + \nabla^4\right)\right)n - \frac{n^3}{6} + \frac{n^4}{12}\right]$$

$$B^l \equiv 1 - \bar{\rho}\hat{C}_0$$

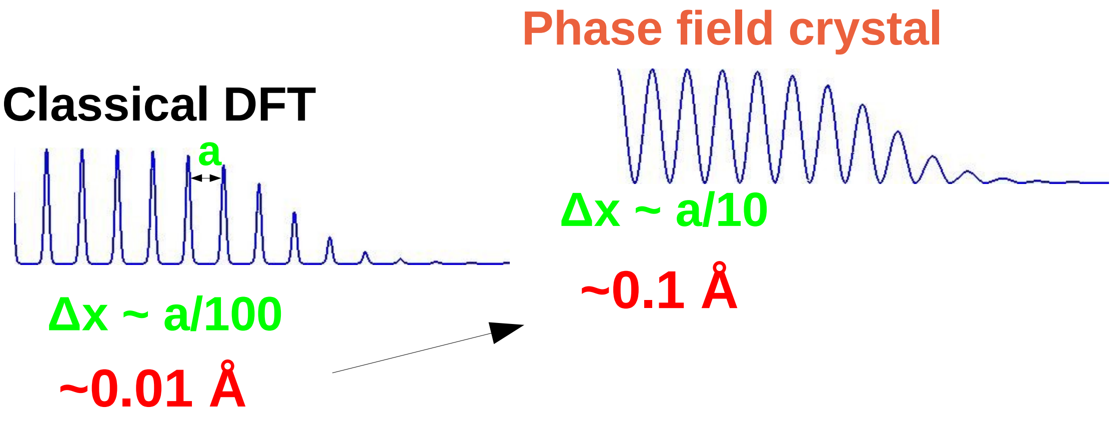
$= \text{liquid bulk modulus}$

$$B^x \equiv \bar{\rho}\left(\hat{C}_2\right)^2/4\hat{C}_4$$

$\sim \text{crystal bulk moduli}$

Part 1: Multiscale Modeling: PFC

CDFT to Phase Field Crystal (PFC) in three easy steps



Assume dissipative dynamics of a conserved field

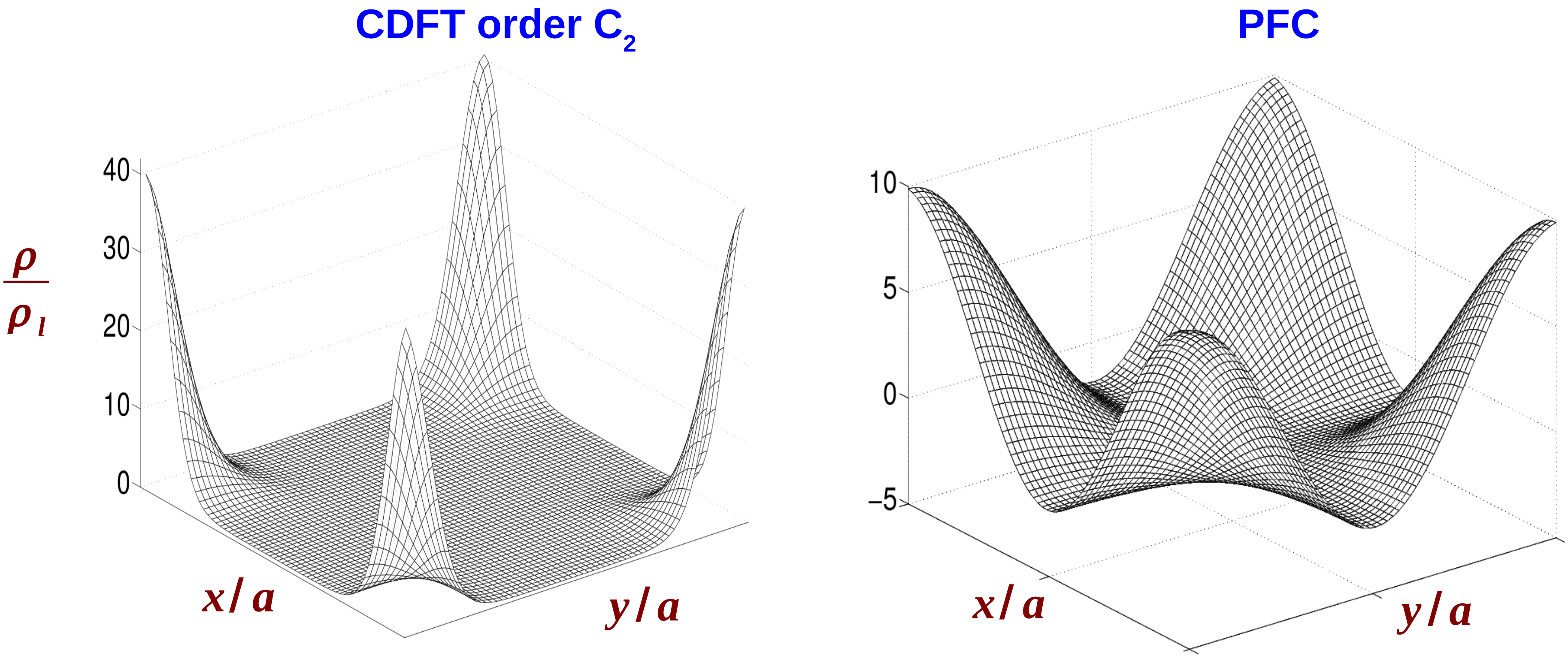
$$\frac{\partial n}{\partial dt} = D\nabla^2 \frac{\delta F}{\delta t} = D\nabla^2\left(\left[B^l + B^x\left(-2\nabla^2+\nabla^4\right)\right]n - tn^2 + v\,n^3\right)$$

Part 1: Multiscale Modeling: PFC

Comparison of CDFT to PFC solutions

Jaatinen, Achim, Elder, Ala-Nissilä, PRE **80**, 031602 (2009)

Density Profiles Iron, 1833 K



CDFT order C_2

PFC

PFC much smoother : Good and Bad

Good Δx_{PFC} >> Δx_{CDFT}

Bad approximation to CDFT

Oakland UNIVERSITY

* Can PFC parameter be fit?

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \frac{R^d}{V} \int d\vec{r} \left[\frac{n}{2} \left(B^l + B^x \left(2\nabla^2 + \nabla^4 \right) \right) n - \frac{n^3}{6} + \frac{n^4}{12} \right]$$

Physics: elasticity, dislocations,
Multiple crystal orientations

3 (2) parameters

* PFC parameter fitting

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \frac{R^d}{V} \int d\vec{r} \left[\frac{n}{2} \left(B^l + B^x \left(2\nabla^2 + \nabla^4 \right) \right) n - t \frac{n^3}{6} + v \frac{n^4}{12} \right]$$

Physics: elasticity, dislocations,
Multiple crystal orientations

3 (2) parameters

Fitting : **5 parameters** , Iron
Wu, Karma, PRB, **76**, 184107 (2007) (t,v)
liquid/solid surface energy + anisotropy

6 parameters, Iron
Jaatinen, Achim, Elder, Ala-Nissilä, PRE, **80**, 031602 (2009)
liquid/solid surface energy + anisotropy
Miscibility gap, bulk moduli,
Liquid state isothermal compressibility

Fitting : **4 parameters**, Colloids
Van Teeffelen, Backofen, Voigt, Löwen, PRE **79**, 051404 (2009)
Solidification rates - dynamics

* PFC parameter fitting

,

Fitting to Iron, T = 1772 K

Quantity	Experiment/ MD	5 parameter [1]	6 parameter [2]
surface energy (100) (J/m²)	0.177 [1]	0.207	0.166
surface energy (110) (J/m²)	0.174 [1]	0.202	0.162
surface energy (111) (J/m²)	0.173 [1]	0.195	0.157
Anisotropy (%)	1.0 [1]	1.3	1.3
Expansion upon melting (Å³/atom)	0.38 [3]	2.07	0.43
Solid bulk modulus (GPa)	105.0 [4]	22.2	94.5
Liquid bulk modulus (GPa)	96.2 [5]	18.6	93.2

[1] Wu, Karma, PRB, **76**, 174107 (2007)
[2] Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009).
[3] Mendelev, Han, Srolovitz, Ackland, Sun, Asta, Phil. Mag. **83**, 3977 (2003)
[4] Dever, J. Appl. Phys., **43**, 3293 (1972):
Adams, Agosta, Leisure, Ledbetter, J. Appl. Phys. **100**, 113530 (2006)
[5] Tsu, Takano, 88th Spring Conference (Japan Institute of Metals, Sendai 1981), **88**, p. 86:
Itami, Shimoji, J. Phys. F: Met. Phys, **14**, L15 (1984).

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surface energy (111) (J/m^2)	0.173 [1]	0.195 12%	0.157 9%
Anisotropy (%)	1.0 [1]	1.3 30%	1.3 30%
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percent error

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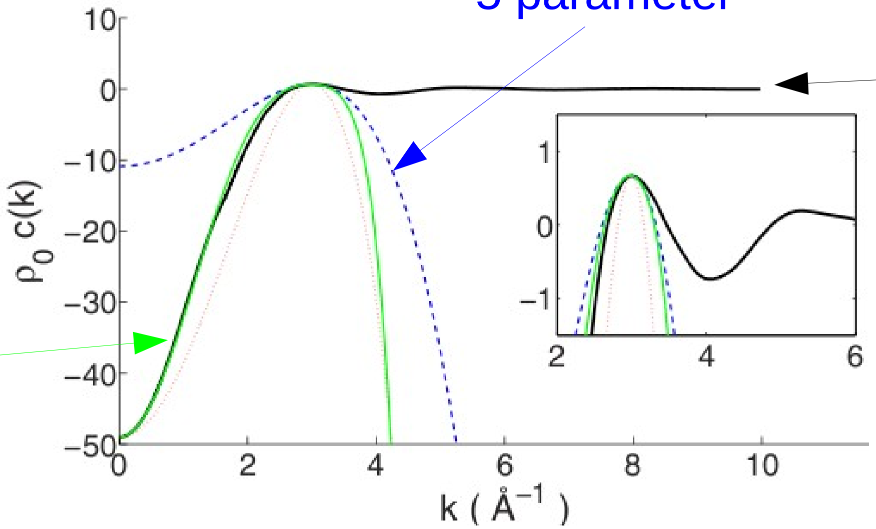
percent error

Difference between 5 and 6 parameter fits...

k = 0 mode of C(k)



5 parameter

full

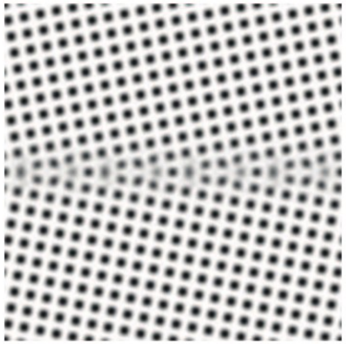
6 parameter

Iron grain boundary energy <100> symmetric tilt boundary

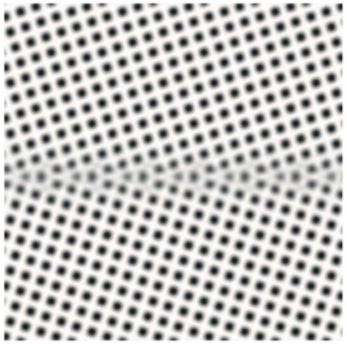
Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009): Tech. Mech, **30**, 169 (2010)

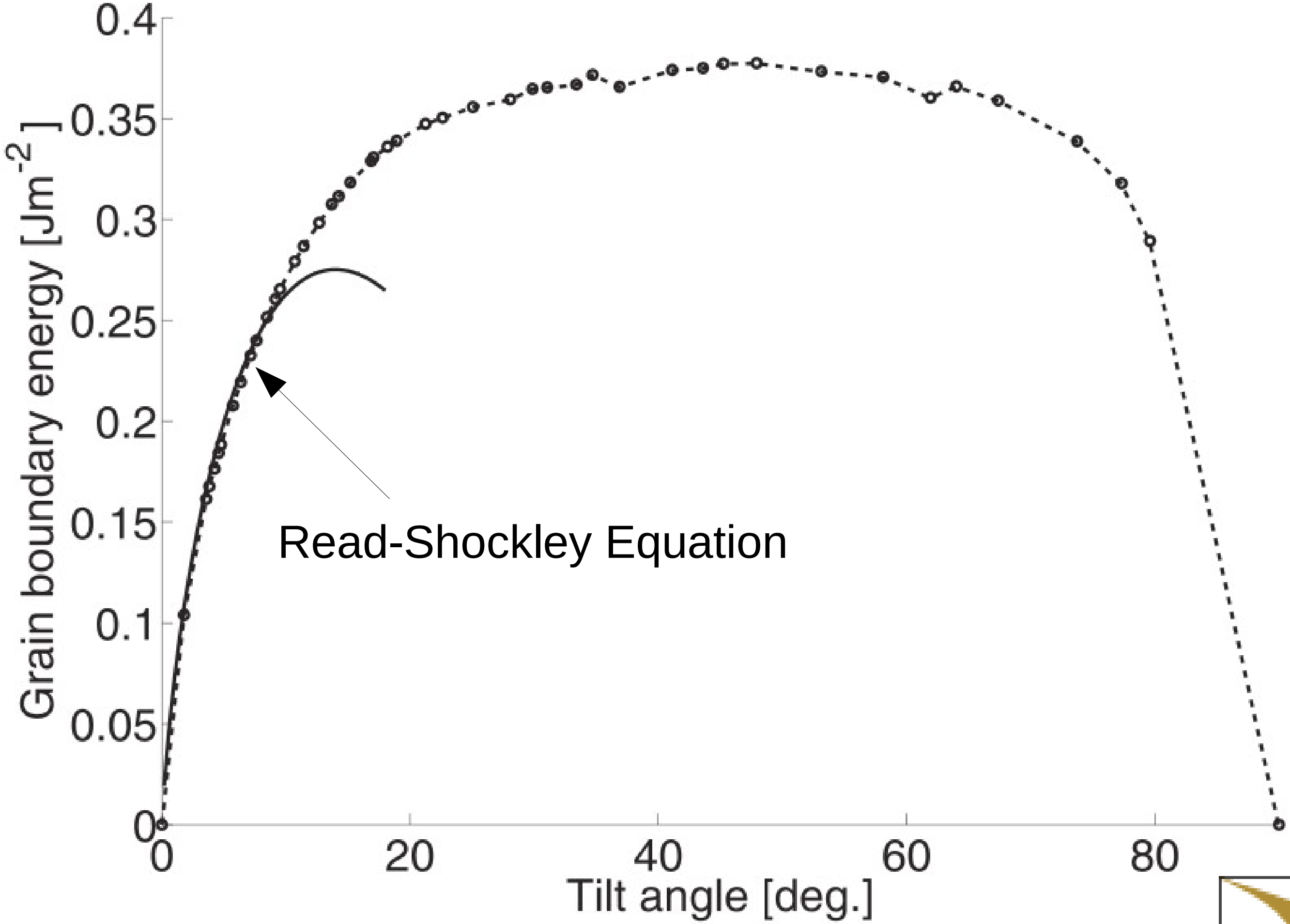
mismatch, θ=1.79°

mismatch, θ=22.62°



mismatch, θ=36.87°

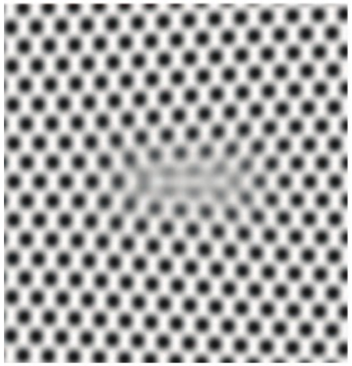




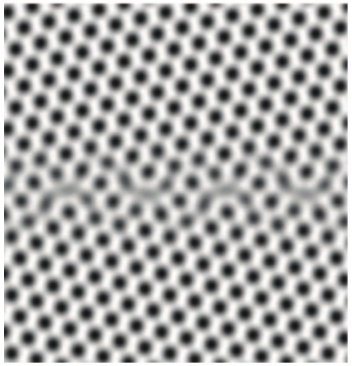
Iron grain boundary energy <110> symmetric tilt boundary

Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009): Tech. Mech, **30**, 169 (2010)

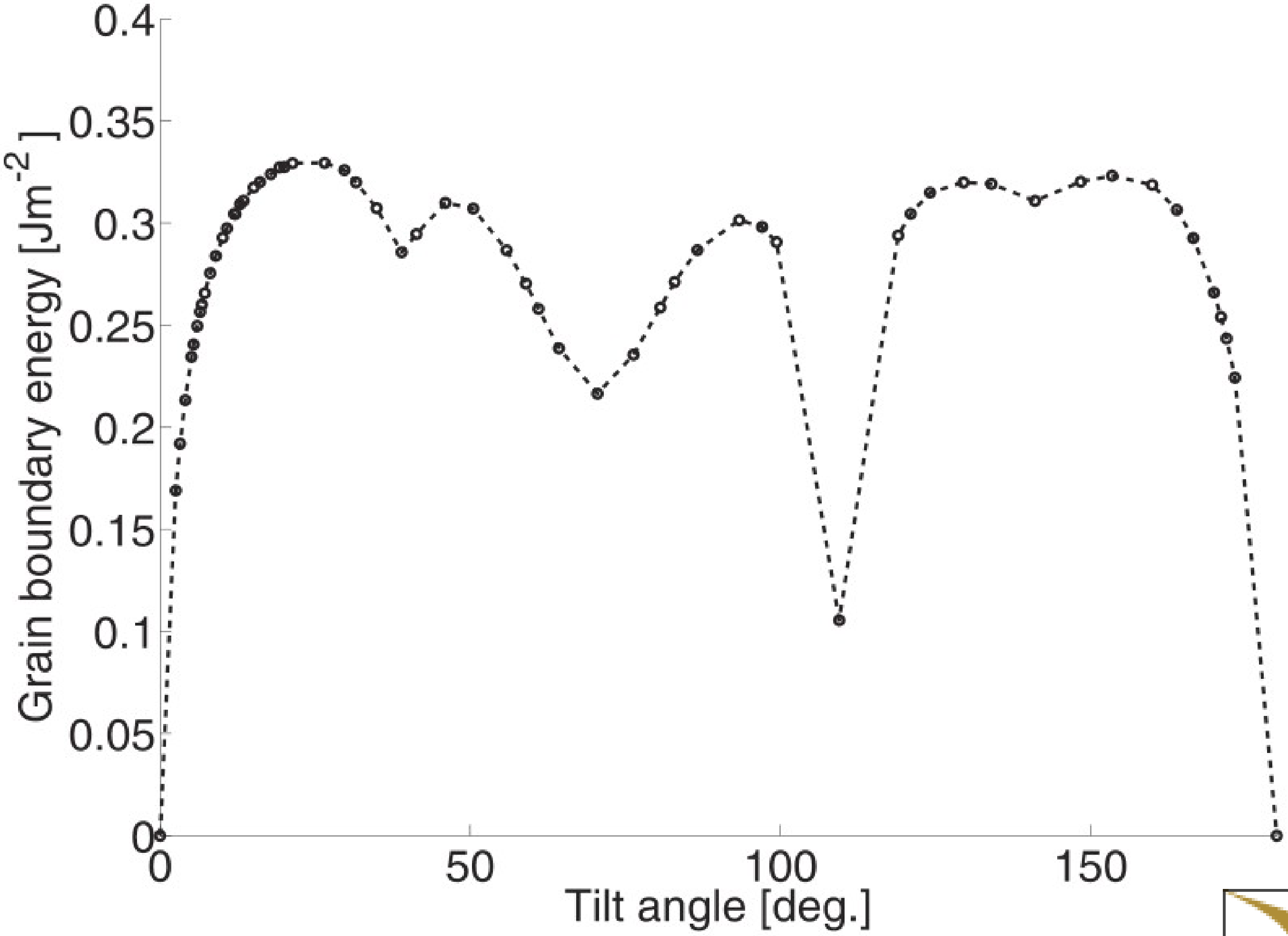
mismatch, $\theta=2.53^{o}$



mismatch, $\theta=26.52^{o}$



mismatch, $\theta=50.47^{o}$



Iron grain boundary energy <100> symmetric tilt boundary

Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009): Tech. Mech, **30**, 169 (2010)

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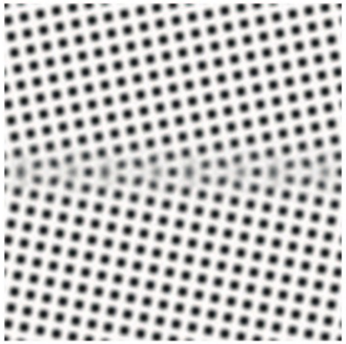
mismatch, θ=22.62°



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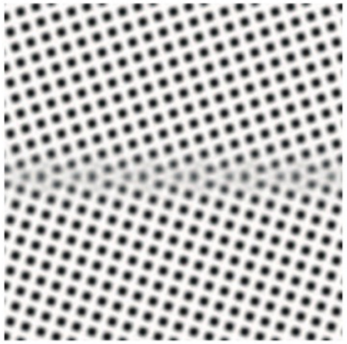


Comparison with other work

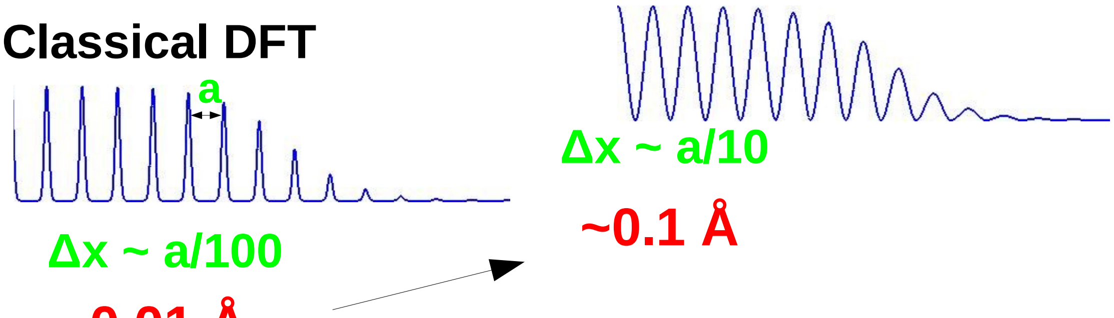
Method	Maximum GB energy	Ratio : GB energy to Liq/Sol energy
Current work	0.37 Jm^{-2}	2.2
Experiment[1]	0.46 Jm^{-2}	2.6
Embedded atom (T=0)[2]	10.0 Jm^{-2}	
MD[3]	1.6 Jm^{-2}	

[1] Muir *Interfacial Phenomena in Metals and Alloys* Addison Wesley, New York (1975)

[2] Zhang, Huang, Wu, Xu, Appl. Surf. Sci. 252, 4936 (2005)

[3] Shibuta, Takamoto, Suzuki, ISIJ Int. 48 1582 (2008)

Part 1: Multiscale Modeling



Phase field crystal

Classical DFT

a

Δx ~ a/10

~0.1 Å

Δx ~ a/100

~0.01 Å

PFC bad approximation to CDFT – but parameters can be adjusted

or

PFC field ≠ DFT field

Jaatinen and Ala-Nissila, PRE, **82**, 061602 (2010)

$$n(\vec{r}) = \frac{1}{\rho_l} \int d\vec{r}\,' w(|\vec{r} - \vec{r}\,'|) \left[\rho(\vec{r}) - \rho_l \right]$$

$$\text{where } \hat{w}(k) = \sqrt{\frac{1 - \hat{C}_{DFT}(k)}{1 - \hat{C}_{PFC}(k)}}$$

* PFC applications

Grain boundary melting

Mellenthin, Karma, Plapp PRB (2008); Berry, Elder, Grant PRB (2008);

Strained films / Epitaxial growth

Wu, Voorhees PRB (2009); Elder, Katakowski, Haataja, Grant PRL (2002)
Huang, Elder PRB (2010), PRL (2009);

Strength of polycrystals

Stefanovic, Haataja, Provatas PRL (2006), PRE (2009);
Hirouchi, Takaki, Tomita Comput. Mater. Sci. (2009)
Elder, Grant PRE (2004); Elder, Katakowski, Haataja, Grant PRL (2002);

Surface ordering and growth

Achim, Ramos, Karttunen, Elder, Granato, Ala-Nissilä, Ying PRE (2010),(2009), (2008), (2006)
Backofen, Voight, Witkowski PRE (2010); Muralidharan Haataja PRL (2010)

Solidification

Tegze, Granasy, Toth, Podmaniczky, Jaatinen, Ala-Nissilä, Pusztai PRL (2009)
Van Teeffelen, Backofen, Voigt, Löwen, PRE **79**, 051404 (2009)
Galenko, Danilov, Lebedev PRE (2009); Backofen, Ratz, Voigt Phil Mag (2007);
Backofen, Voigt J. Cond. Mat. (2009); Berry, Elder, Grant PRE (2008)

Dislocation dynamics

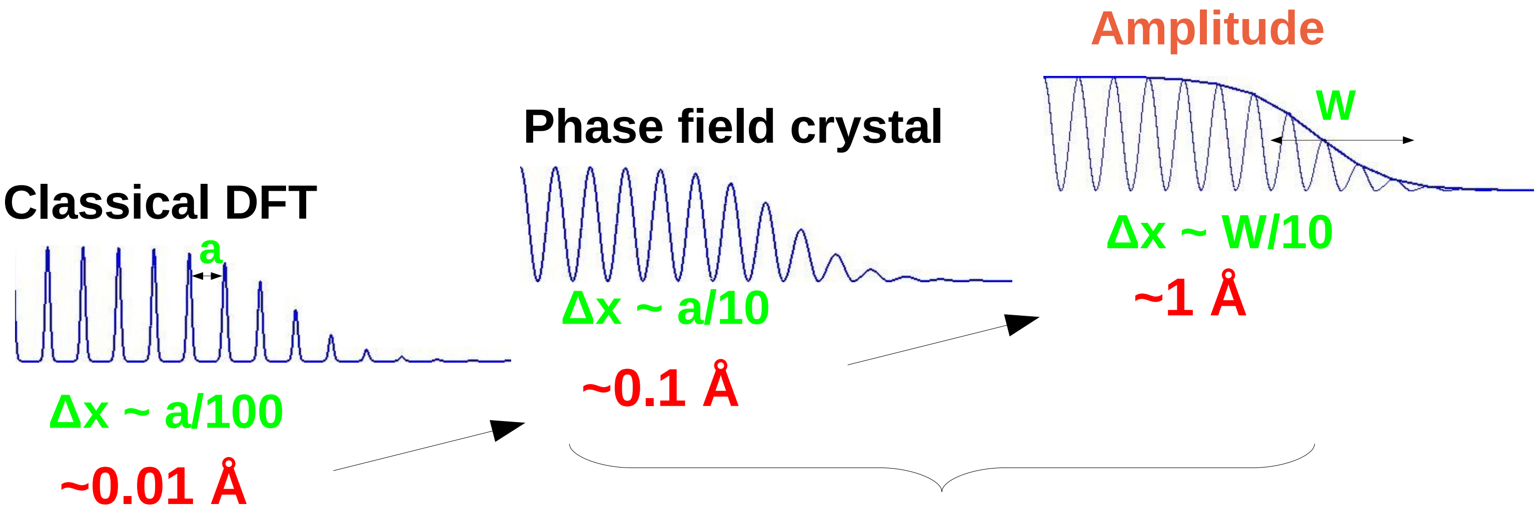
Chan, Tsekenis, Dantzig, Dahmen, Goldenfeld, PRL (2010)
Berry, Grant, Elder PRE (2006)

Kirkendall Effect

Elder, Hoyt, Thornton Phil Mag (2010)

Overview

Part 1: Multiscale Modeling: Amplitude



Classical DFT

$\Delta x \sim a/100$

~0.01 Å

Phase field crystal

$\Delta x \sim a/10$

~0.1 Å

Amplitude

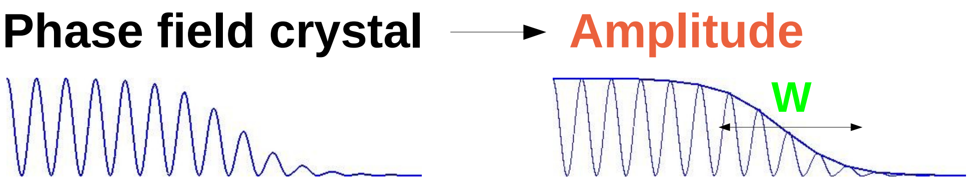
$\Delta x \sim W/10$

~1 Å

References

pure systems
Goldenfeld, Athreya, Dantzig, PRE (2005)
Athreya, Goldenfeld, Dantzig, PRE (2006)
Athreya, Goldenfeld, Dantzig, Greenwood, Provatas PRE (2007)
Chan, Goldenfeld PRE (2009)
Yeon, Huang, Elder, Thornton, Phil Mag (2010)
binary systems
Elder, Huang, Provatas PRE (2010)
Huang, Elder, Provatas PRE (2010)
Spatschek, Karma PRB (2010)

PFC to Amplitude expansions


Phase field crystal → **Amplitude**

PFC free energy functional

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \frac{R^d}{V} \int d\vec{r} \left[\frac{n}{2} \left(\Delta B + B^x \left(1 + \nabla^2 \right)^2 \right) n - t \frac{n^3}{3} + v \frac{n^4}{4} \right]$$

Amplitude formulation: a poor man's PFC

$$\boxed{n = \sum_{\vec{G}} \left(\eta_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} + \eta^*_{\vec{G}} e^{-i\vec{G}\cdot\vec{r}} \right)}$$

$$\vec{G} \equiv l\vec{q}_1 + m\vec{q}_2 + n\vec{q}_3$$

$$\left(\vec{q}_1, \vec{q}_2, \vec{q}_3 \right) \equiv \text{principle reciprocal lattice vectors}$$

$$\left(l, m, n \right) \equiv \text{Miller indices}$$

Goal – derive

$$\boxed{\frac{\partial \eta_{\vec{G}}}{\partial t} = ?}$$

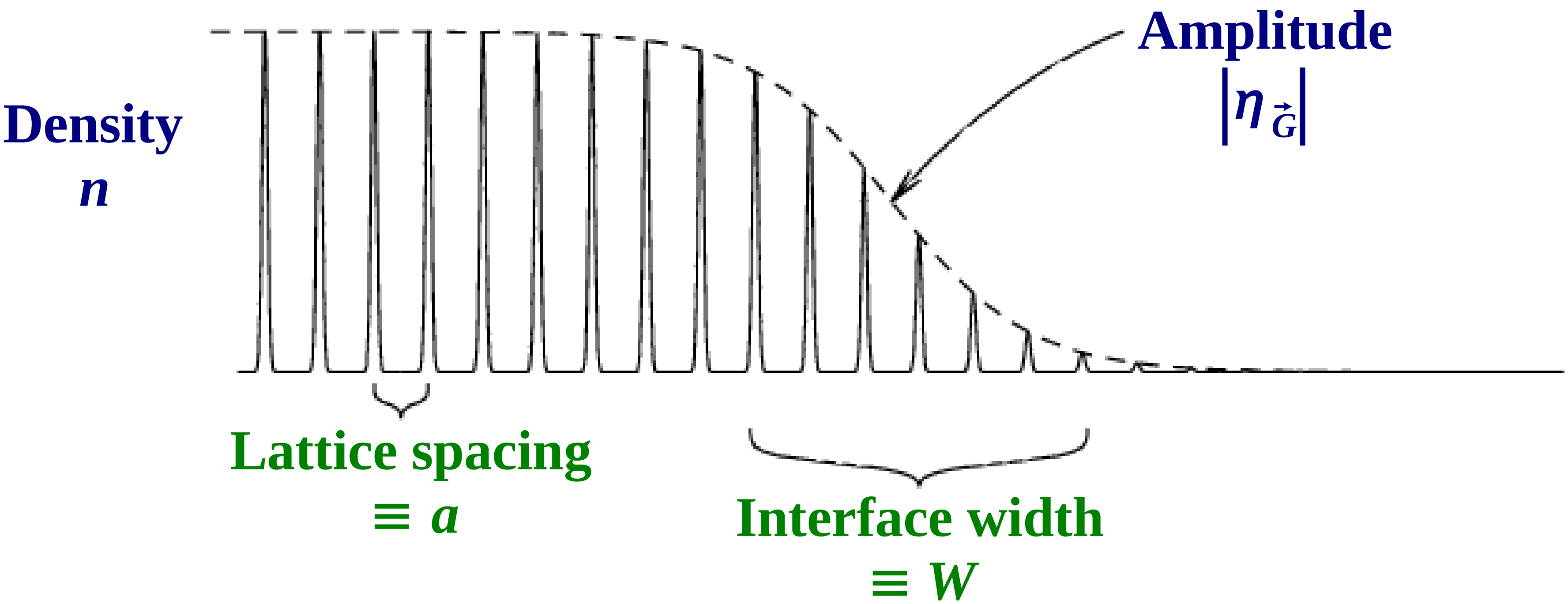
* Amplitude expansion: multiple scales approximation

$$n = \sum_{\vec{G}} \left(\eta_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}} + \eta^{*}_{\vec{G}}\, e^{-i\vec{G}\cdot\vec{r}} \right)$$

$$\frac{\partial \eta_{\vec{G}}}{\partial t} = ?$$

2 fields *(n, η_G)* – **2 length scales (*a*,*W*)**

Consider schematic of liquid/solid interface



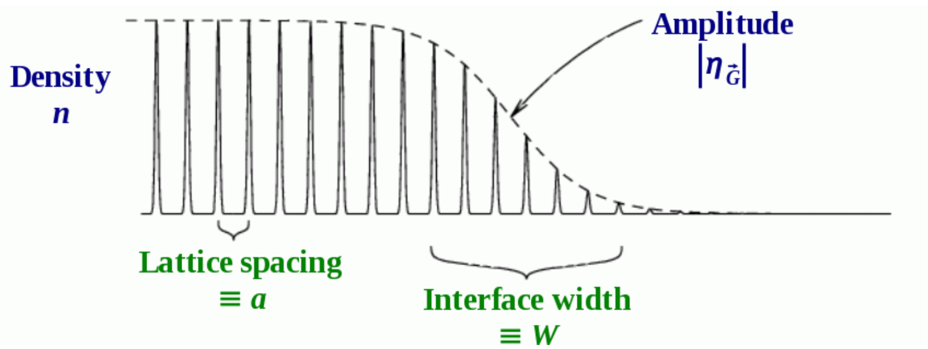
Multiple scales approximation

$W \gg a$ → Phase field limit

* Amplitude expansion: multiple scales approximation

$W \gg a$

Phase field limit



If valid then

$$\int_{x-a/2}^{x+a/2} d\vec{r}\, |\eta_{\vec{G}}|^2 \approx |\eta_{\vec{G}}|^2, \quad \int_{x-a/2}^{x+a/2} d\vec{r}\, e^{i\vec{G}\cdot\vec{r}} |\eta_{\vec{G}}|^2 \approx 0, \text{ etc.}$$

$$\frac{\partial \eta_{\vec{G}}}{\partial t} = ? \longrightarrow \int d\vec{r}\; e^{i\vec{G}\cdot\vec{r}} \frac{\partial n}{\partial t} = \ldots$$

“Quick and dirty” method,
Goldenfeld, Athreya, Dantzig, PRE **72**, 020601 (2005)

More rigorous approaches, renormalization group,
multiple scales perturbation analysis – similar results
Athreya, Goldenfeld, Dantzig, PRE 74, 011601 (2006)

Oakland UNIVERSITY

* Amplitude expansion: technical details

1) substitute $n = \sum \eta_G \exp(iG_j r)$ + c.c. into equation of motion
2) multiply by $\exp(iG_m r)$ and integrate using 'quick + dirty' approx.
3) make 1 mode approximation

* Amplitude expansion: Two dimensions

2d: triangular lattice, principle reciprocal lattice vectors

$$\vec{q}_1 = -\frac{1}{2}\left(\sqrt{3}\,\hat{x} + \hat{y}\right) \;;\; \vec{q}_2 = \hat{y}$$

$$\frac{\partial \eta_j}{\partial t} = \Im_j \frac{\delta F_{2d}}{\delta \eta_j^*} \approx -\left[\left(\Delta B + B^x \Im_j^2 + 3\mathrm{v}\left(A^2 - |\eta_j|^2\right)\right)\eta_j - 2\mathrm{t}\prod_{i\neq j}\eta_i^*\right]$$

$$\boxed{F_{2d} = \int d\vec{r}\left[\frac{\Delta B}{2}A^2 + \frac{3\mathrm{v}}{4}A^4 + \sum_{j=1}^{3}\left(B^x|\Im_j\eta_j|^2 - \frac{3\mathrm{v}}{2}|\eta_j|^4\right) - 2\mathrm{t}\left(\prod_{j=1}^{3}\eta_j + c.c.\right)\right]}$$

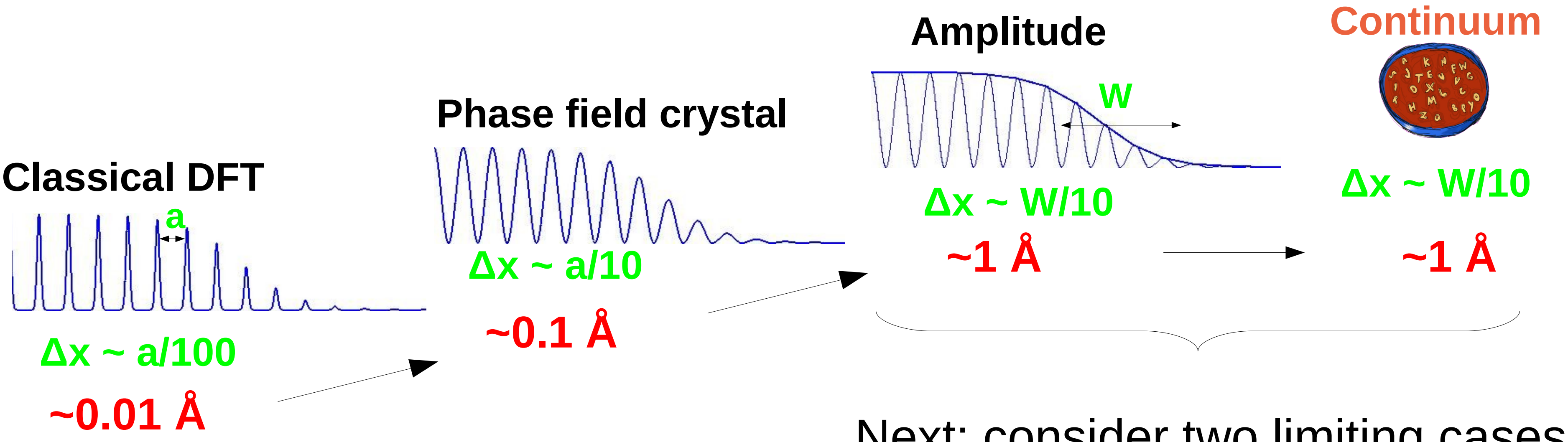
where $A^2 \equiv 2\sum|\eta_j|^2, \;\; \Im_j \equiv \nabla^2 + 2i\,\vec{q}_j\cdot\vec{\nabla}$

→ **Now 6 equations (3 complex)**

→ **Still includes elasticity, dislocations, multiple crystal orientations**

Overview

Part 1: Multiscale Modeling: Continuum



Classical DFT

a

Δx ~ a/100

~0.01 Å

Phase field crystal

Δx ~ a/10

~0.1 Å

Amplitude

W

Δx ~ W/10

~1 Å

Continuum

Δx ~ W/10

~1 Å

Next: consider two limiting cases:

1) $\eta_j = \phi$ real number

2) $\eta_j = \phi\, e^{i\vec{G}_j\cdot\vec{u}}$,

where, $\vec{u}$= displacement field

* Continuum limit of amplitude equations

Limiting Case 1) $\eta_j = \phi$ (real): substitute into free energy - F

Free energy $$\boxed{\frac{F}{A} = \int d\vec{r} \left(\underbrace{3\Delta B \phi^2 - 4t\phi^3 + \frac{45v}{2}\phi^4}_{\text{First order phase transition}} + \underbrace{6B^x |\vec{\nabla}\phi|^2}_{\text{Surface energy}} \right)}$$

where $\Delta B \equiv B^l - B^x$

Surface energy

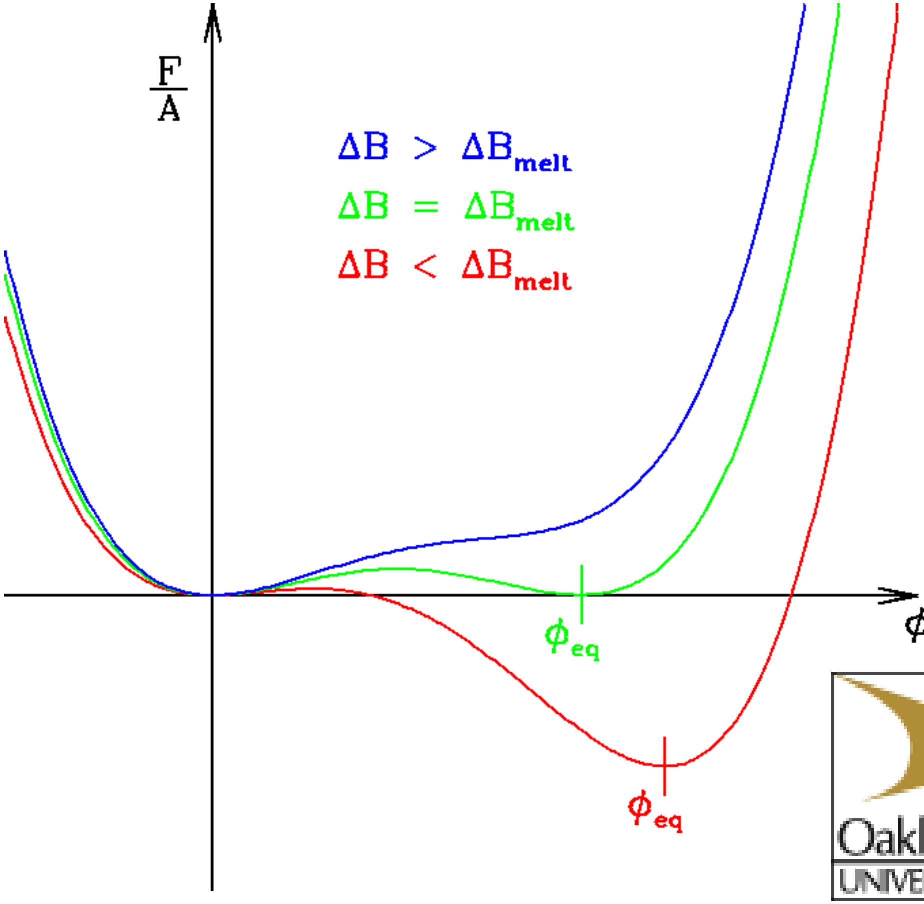
First order phase transition

$\Delta B > \Delta B_{melt}$ liquid state $\phi = 0$

$\Delta B < \Delta B_{melt}$ Crystalline state $\phi = \phi_{eq}$

Minimize with respect to ϕ

$$\frac{dF/A}{d\phi} = 0 \quad \text{gives } \phi_{eq} = \frac{t + \sqrt{t^2 - 15\Delta B v}}{15v}$$



* Continuum limit of amplitude equations

Limiting Case 1) $\eta_j = \phi$ (real): substitute into free energy - F

Free energy $$\frac{F}{A} = \int d\vec{r}\left(3\Delta B\phi^2 - 4t\phi^3 + \frac{45v}{2}\phi^4 + 6B^x\left|\vec{\nabla}\right|\phi^2\right)$$

where $\Delta B \equiv B^l - B^x$

Dynamics

$$\frac{\partial\phi}{\partial t} = -\frac{\delta F}{\delta\phi} = -6\left(\Delta B\phi - 2t\phi^2 + 15v\phi^3 - 2B^x\nabla^2\phi\right)$$

Model A: non-conserved dynamics

Halperin/Hohenberg Rev. Mod. Phys. **49**, 435 (1977)

* Continuum limit of amplitude equations

Limiting case 2) $\eta_j = \phi\, e^{i\vec{G}_j\cdot\vec{u}}$, where, $\vec{u}$= displacement field

Small deformation limit

Recover continuum elasticity

consider deformation $\rho(\vec{r}) \rightarrow \rho(\vec{r}+\vec{u})$: $\vec{u}$=displacement vector

$$n=\sum_j \eta_j e^{i\vec{G}_j\cdot\vec{r}} + c.c. \rightarrow \sum_j \eta_j e^{i\vec{G}_j\cdot(\vec{r}+\vec{u})} + c.c. \quad : \quad \eta_j \rightarrow \eta_j e^{i\vec{G}_j\cdot\vec{u}}$$

Write η_j as real amplitude and phase, i.e.,

$$\eta_j = \phi \exp(i\vec{G}_j\cdot\vec{u})$$

* Continuum limit of amplitude equations

Limiting case 2) $\eta_j = \phi \, e^{i\vec{G}_j\cdot\vec{u}}$, where, $\vec{u}$ = displacement field

Small deformation limit

ϕ → 1^{st} order liquid/solid transition, $\vec{u}$ → continuum elasticity theory ¿

$$F_{2d} = \int d\vec{r}\left[\underbrace{3\Delta B\phi^2 - 4t\phi^3 + \frac{45}{2}v\phi^4}_{\text{1st order phase transition}} + \underbrace{6B^x\left|\vec{\nabla}\phi\right|^2}_{\text{surface energy}} + \underbrace{3\mathrm{B}^x\phi^2\left\{\frac{3}{2}\sum_{i=1}^{2}U_{ii}^2 + U_{xx}U_{yy} + 2\mathrm{U}_{xy}^2\right\}}_{\text{linear elastic energy}}\right]$$

(as before)

elastic constants

$$\underbrace{\begin{aligned} C_{11} &= 9\mathrm{B}^x\phi^2 \\ C_{12} = C_{44} &= C_{11}/3 \end{aligned}}$$

Continuum elasticity

Where U_{ij} = stress tensor $\approx \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$

* Continuum limit of amplitude equations

Repeat for binary alloy model:

- substitutional binary alloy A and B atoms, densities ρ_A and ρ_B define two fields,

$$\psi \;=\; 2c-1 \;,\; n \;=\; (\rho-\rho_l)/\rho_l, \;\; \text{where } \rho \equiv \rho_A + \rho_B, \quad c \equiv \rho_A/\rho$$

- free energy (see Elder, Provatas, Berry, Stefanovic, Grant, PRB **75**, 064107 (2007))

$$\boxed{\frac{\Delta F}{k_B T \rho_l} = \int d\vec{r} \left[\underbrace{\frac{B^l}{2} n^2 + B^x \frac{n}{2}\left(2R^2\nabla^2 + R^4\nabla^4\right) n - \frac{t}{3} n^3 + \frac{v}{4} n^4}_{\text{usual PFC model}} + \underbrace{\frac{\omega}{2}\psi^2 + \frac{u}{4}\psi^4 + \frac{K}{2}\left|\vec{\nabla}\psi\right|^2}_{\text{Model B/Cahn Hilliard}} \right]}$$

$$\begin{aligned} \text{where } B^l &= B^l_0 + B^l_1\psi + B^l_2\psi^2 + \ldots &&\rightarrow \text{eutectics phase diagrams etc.} \\ B^x &= B^x_0 + B^x_1\psi + B^x_2\psi^2 + \ldots &&\rightarrow \text{elastic moduli} \sim \text{function of } \psi \\ R &= R_0 + R_1\psi + R_2\psi^2 + \ldots &&\rightarrow \text{lattice constant} \sim \text{function of } \psi \end{aligned}$$

- dynamics, for mobilities M_A and M_B

$$\frac{\partial n}{\partial t} = M_1\nabla^2\frac{\delta F}{\delta n} + M_2\nabla^2\frac{\delta F}{\delta \psi}$$

$$\frac{\partial \psi}{\partial t} = M_2\nabla^2\frac{\delta F}{\delta n} + M_1\nabla^2\frac{\delta F}{\delta \psi}$$

where

$$M_1 \equiv (M_A + M_B)/\rho_l^2$$

$$M_2 \equiv (M_A - M_B)/\rho_l^2$$

* Amplitude expansion: Binary alloys, statics

Small deformation limit $\eta_j = \phi \exp(i \vec{G}_j \cdot \vec{u})$

$\psi \equiv$ **concentration difference,** $\phi \equiv$ **liquid/solid order parameter**

Elder, Huang, Provatas, PRE, **81**, 011602 (2010)

$$
\begin{aligned}
F_{2\mathrm{d}} = \int d\vec{r} \Big[& \underbrace{3\Delta B \phi^2 - 4\mathrm{t}\phi^3 + \frac{45}{2} v \phi^4 + 6 B^x \left|\vec{\nabla}\phi\right|^2}_{\text{First Order Liquid/Solid transition with surface energy}} + \underbrace{3\mathrm{B}^x \phi^2 \left\{ \frac{3}{2} \sum_{i=1}^{2} U_{ii}^2 + U_{xx} U_{yy} + 2\mathrm{U}_{xy}^2 \right\}}_{\text{Elastic energy}} \\
& \underbrace{+ \left(\omega + 6\mathrm{B}_2^l \phi^2\right) \frac{\psi^2}{2} + \frac{u}{4}\psi^4 + \frac{K}{2} \left|\vec{\nabla}\psi\right|^2}_{\text{Phase Segregation, eutectic solidification, spindodal decomposition, etc.. with surface energy cost}} + 12\alpha B_0^x \Big(\underbrace{-\phi \nabla^2 \phi}_{\text{Segregation at surfaces, dislocations, etc.}} + \underbrace{\sum_{i=1} 2 U_{ii} \phi^2}_{\text{Vegard's Law } a = a_o(1+\alpha\Psi)} \Big) \psi \Big]
\end{aligned}
$$

First Order Liquid/Solid
transition with surface energy

Elastic energy

Phase Segregation, eutectic solidification,
spindodal decomposition, etc..
with surface energy cost

Vegard's Law
$a = a_o(1+\alpha\Psi)$

Segregation at surfaces,
dislocations, etc.

* Amplitude expansion: Binary alloys, dynamics

Small deformation limit $\eta_j = \phi \exp(i \vec{G}_j \cdot \vec{u})$

$\psi \equiv$ concentration difference, $\phi \equiv$ liquid/solid order parameter

Elder, Huang, Provatas, PRE, **81**, 011602 (2010)

$$F_{2\mathrm{d}} = \int d\vec{r} \Big[3\Delta B \phi^2 - 4t\phi^3 + \frac{45}{2} v \phi^4 + 6B^x |\vec{\nabla}\phi|^2 + 3B^x \phi^2 \Big\{ \frac{3}{2} \sum_{i=1}^{2} U_{ii}^2 + U_{xx} U_{yy} + 2U_{xy}^2 \Big\}$$

$$+ (\omega + 6B_2^l \phi^2) \frac{\psi^2}{2} + \frac{u}{4} \psi^4 + \frac{K}{2} |\vec{\nabla}\psi|^2 + 12\alpha B_0^x \Big(-\phi \nabla^2 \phi + \sum_{i=1} 2U_{ii} \phi^2 \Big) \psi \Big]$$

$$\frac{\partial \phi}{\partial t} = -\frac{\delta F}{\delta \phi} \Big\}$$

Model **A**
Allen/Cahn

$$\frac{\partial \psi}{\partial t} = \nabla^2 \frac{\delta F}{\delta \psi} \Big\}$$

Model **B**
Cahn/Hilliard
Hillert

} Model **C**

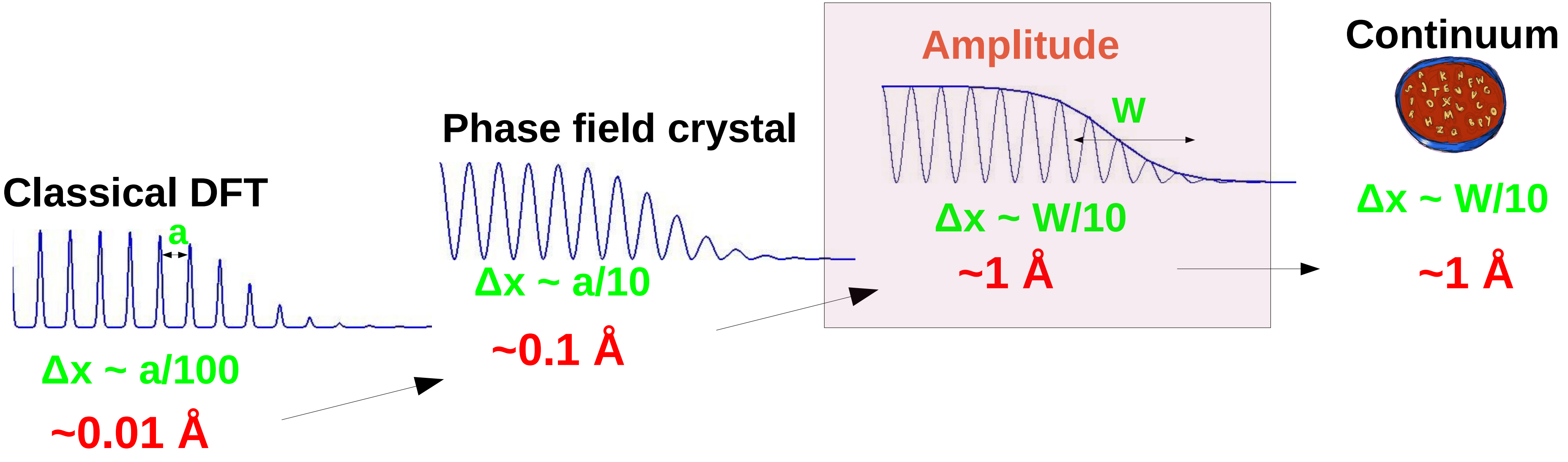
ABC's of pattern formation

$$\sum_i \frac{\partial}{\partial x_i} \frac{\delta F}{\delta U_{ij}} \approx 0 \Big\}$$

~~Mechanical
Equilibrium~~

Overview

Part 1: Multiscale Modeling



Classical DFT

a

Δx ~ a/100

~0.01 Å

Phase field crystal

Δx ~ a/10

~0.1 Å

Amplitude

W

Δx ~ W/10

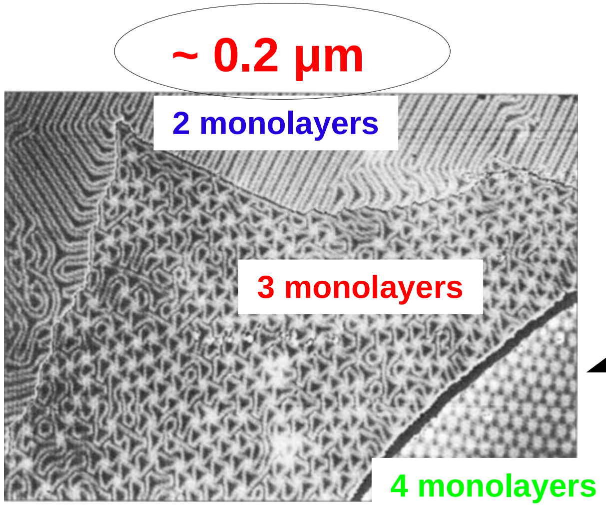
~1 Å

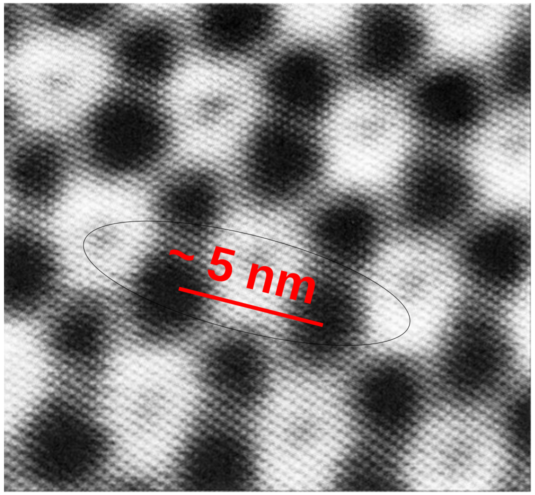
Continuum

Δx ~ W/10

~1 Å

Part 2: Application: Surface ordering





nm objects ordering on µm scales

* Amplitude expansion: Two dimensions

2d: triangular lattice, principle reciprocal lattice vectors

$$\vec{q}_1 = -\frac{1}{2}\left(\sqrt{3}\,\hat{x} + \hat{y}\right) \; ; \; q_2 = \hat{y}$$

$$\frac{\partial \eta_j}{\partial t} = \Im_j \frac{\delta F_{2d}}{\delta \eta_j^*} \approx -\left[\left(\Delta B + B^x \Im_j^2 + 3v\left(A^2 - |\eta_j|^2\right)\right)\eta_j - 2t\prod_{i\neq j}\eta_i^*\right]$$

$$\boxed{F_{2d} = \int d\vec{r}\left[\frac{\Delta B}{2}A^2 + \frac{3v}{4}A^4 + \sum_{j=1}^{3}\left\{B^x|\Im_j\eta_j|^2 - \frac{3v}{2}|\eta_j|^4\right\} - 2t\left\{\prod_{j=1}^{3}\eta_j + c.c.\right\}\right]}$$

where $A^2 \equiv 2\sum|\eta_j|^2$

→ **Now 6 equations (3 complex)**

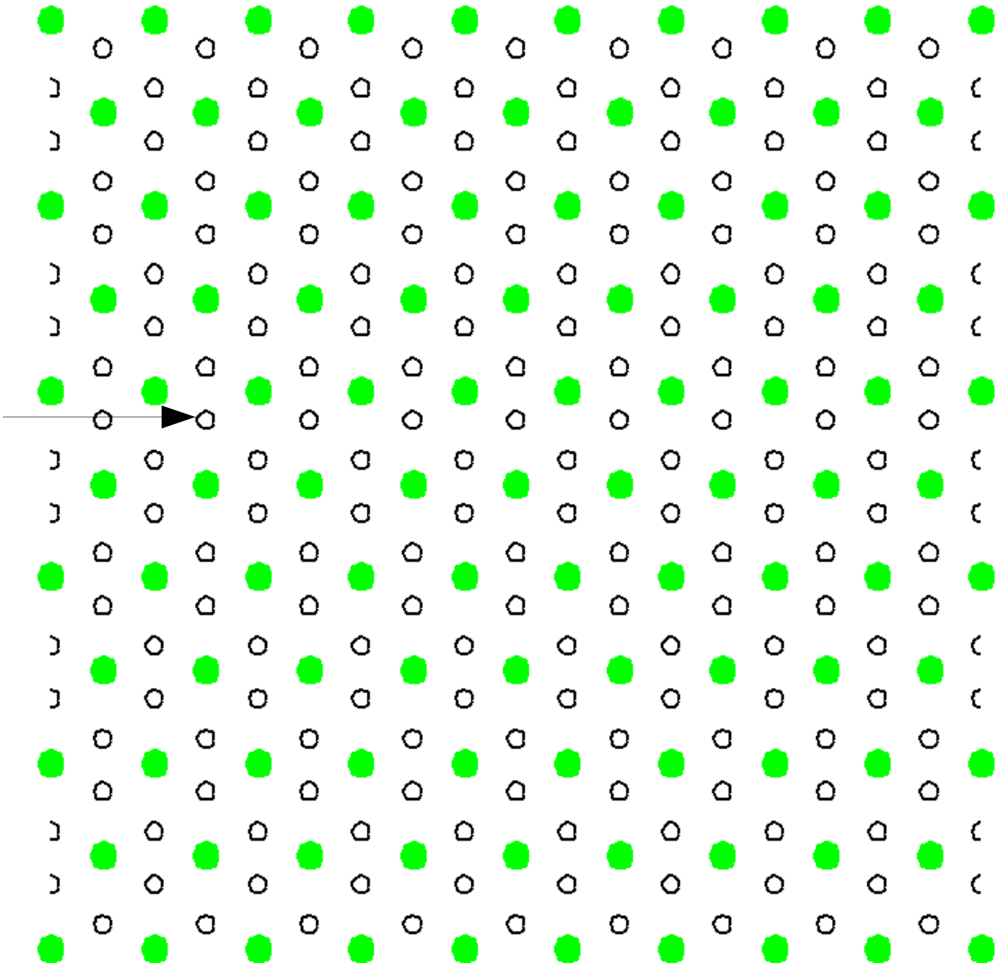
→ **Still includes elasticity, dislocations, multiple crystal orientations**

Next: applications of full model...

* Amplitude expansion: applications

Monolayer(s) ordering: Cu on Ru (0001)

Elder, Rossi, Kanerva, Sanches, Ala-Nissila, Elder, Ying, Granato in progress

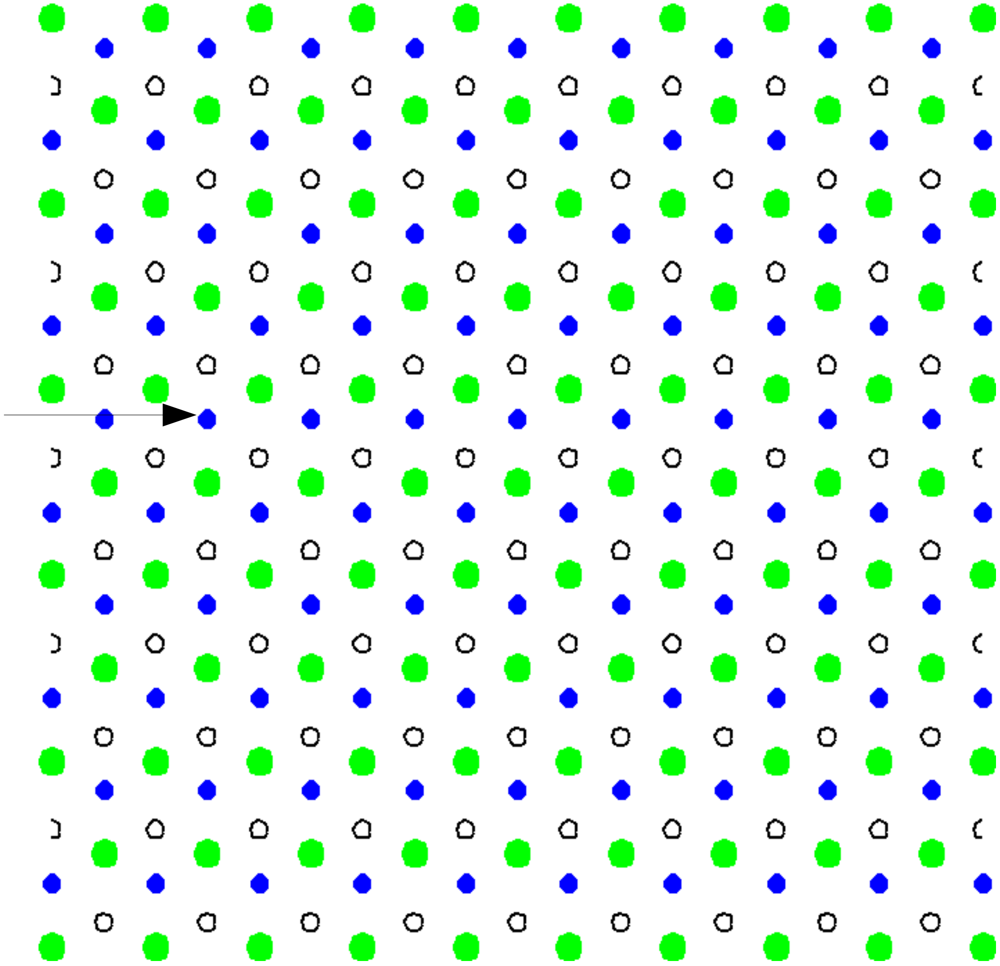


Ru substrate
triangular lattice

Cu binding site
honeycomb lattice

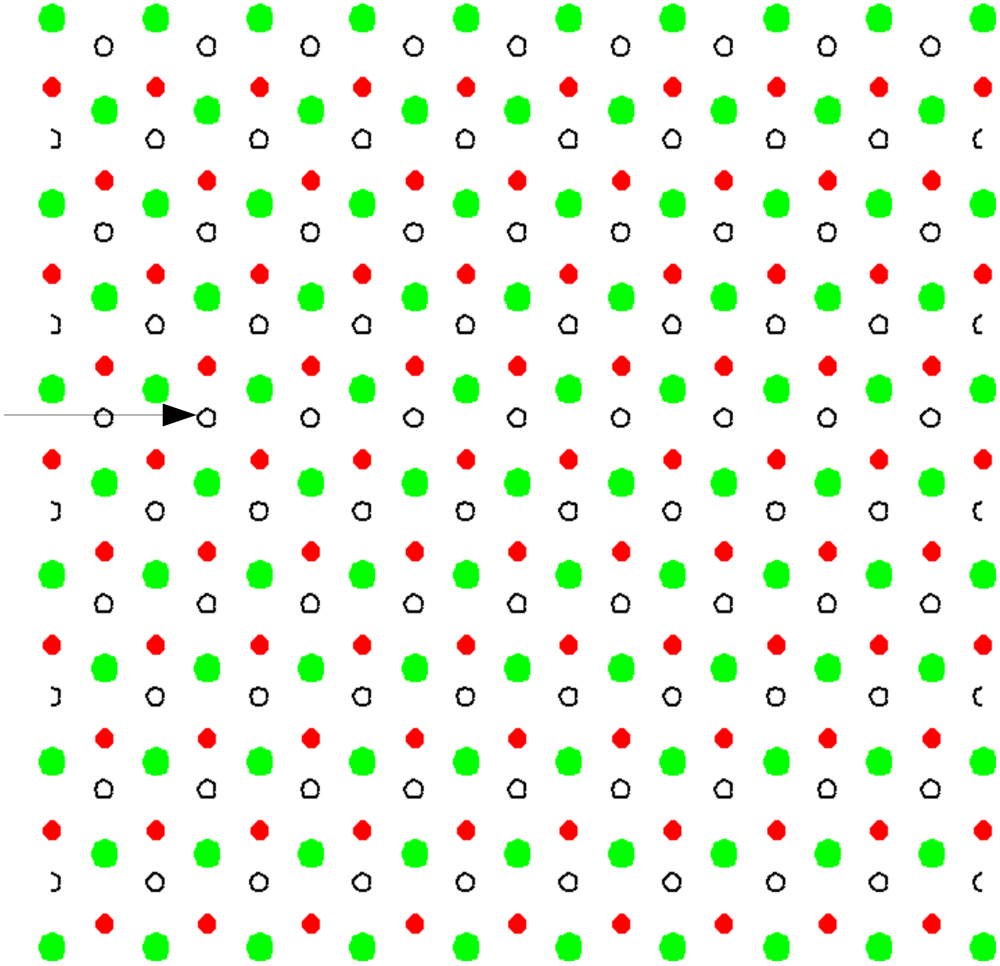
Monolayer ordering

Cu triangular sublattice 1



Monolayer ordering

Cu triangular sublattice 2



two sublattices

strain
a^{Ru} = 2.70 Å
a^{Cu} = 2.55 Å
ε = 5.6 %

Monolayer ordering

Approximate: substrate = **fixed potential** of the form

$$\boldsymbol{V} = \boldsymbol{V_o}\left[\sum_j \boldsymbol{e}^{i\vec{q}_j^{Ru}\cdot\vec{r}} + \boldsymbol{c.c.}\right] \quad \text{add to F, i.e.,} \quad F = \int d\vec{r}\left[\frac{B^l}{2}n^2 + \ldots + \boldsymbol{V}\ \boldsymbol{n}\right]$$

where $\vec{q}_j^{Ru} \equiv$ reciprocal lattice vectors for triangular lattice

If $V_o > 0$ -- honeycomb substrate

- but Cu/Ru lattice mismatch $\left|\vec{q}_j^{Ru}\right| = \alpha\left|\vec{q}_j^{Cu}\right|$

expand n in $\left|\vec{q}_j^{Ru}\right|$, i.e., $n = \sum_{j=1}^{3} \eta_j e^{i\vec{q}_j^{Ru}\cdot\vec{r}} + c.c.$

$$\boxed{\frac{\partial \eta_j}{\partial t} = -\left[\left(\Delta B_o + B^x \Im_j^2 + 3v\left(A^2 - \left|\eta_j\right|^2\right)\right)\eta_j - 2t\prod_{i\neq j}\eta_i^* + \boldsymbol{V_o}\right]}$$

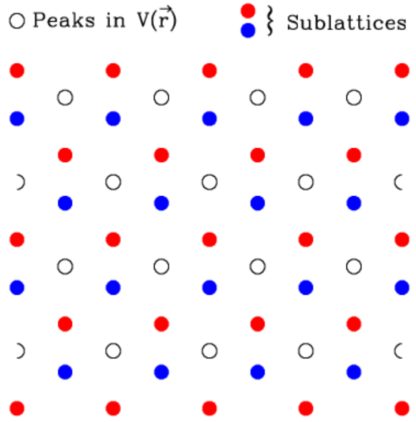
where $\boxed{\Im_j \equiv \nabla^2 + 2i\boldsymbol{\alpha}\,\vec{q}_j^{Cu}\cdot\vec{\nabla} + 1 - \boldsymbol{\alpha}^2}$

misfit strain $\boldsymbol{\varepsilon = 1 - \alpha}$

Monolayer ordering

$$F_{2d} = \int d\vec{r} \left[\frac{\Delta B}{2} A^2 + \frac{3v}{4} A^4 + \sum_{j=1}^{3} \left\{ B^x |\Im_j \eta_j|^2 - \frac{3v}{2} |\eta_j|^4 \right\} - 2t \left\{ \prod_{j=1}^{3} \eta_j + c.c. \right\} + V_o \left(\sum_j \eta_j + c.c. \right) \right]$$

Uniform equilibrium states



Commensurate Phase

$$\eta_j = \phi e^{i\theta}$$

$$F_c = 6\phi V_o \cos(\theta) + 3\left(\Delta B + B^x(1-\alpha^2)^2\right)\phi^2 - 4t\phi^3 \cos(3\theta) + \frac{45v}{2}\phi^4$$

minimize with respect to θ, to obtain,

$$\theta = \pm\left(\pi - \arctan\left(\sqrt{6t\phi^2 - V_o} / \sqrt{2t\phi^2 + V_o}\right)\right) \approx \pm 120^o$$

minimize with respect to ϕ

Incommensurate Phase

$$\eta_j = \phi e^{i\delta\vec{q}_j \cdot \vec{r}} \qquad \delta\vec{q}_j = \vec{q}_j^{Cu} - \vec{q}_j^{Ru} = (1-\alpha)\vec{q}_j^{f}$$

$$F_I = 3\Delta B \phi^2 - 4t\phi^3 + \frac{45v}{2}\phi^4$$

minimize with respect to ϕ $\qquad \phi_{min} = \dfrac{t + \sqrt{t^2 - 15v\Delta B}}{15v}$

Monolayer ordering

$$F_{2d} = \int d\vec{r} \left[\frac{\Delta B}{2} A^2 + \frac{3v}{4} A^4 + \sum_{j=1}^{3} \left\{ B^x |\Im_j \eta_j|^2 - \frac{3v}{2} |\eta_j|^4 \right\} - 2t \left\{ \prod_{j=1}^{3} \eta_j + c.c. \right\} + V_o \left(\sum_j \eta_j + c.c. \right) \right]$$

Uniform equilibrium states

Commensurate Phase $\eta_j = \phi e^{i\theta}$

Incommensurate Phase $\eta_j = \phi e^{i(1-\alpha)\vec{q}_j^f \cdot \vec{r}}$

Energy difference (small V_o limit)

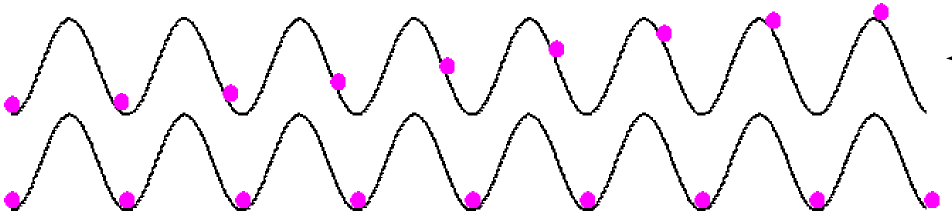
$$F_c - F_I \approx -3\phi V_o + 12\, B^x \varepsilon^2 \phi^2$$

substrate coupling

elastic energy

Equal when

$$V_o^* = 4B^x \varepsilon^2 \phi$$



incommensurate

commensurate

Ru: substrate potential ~ V_o

Cu: monolayer atoms

Cu(a): surface energy E_{111} ≈ 0.6 ev/Atom

Cu/Ru(b) : adhesion E_{adh} ≈ 3.4 eV/atom

$$\frac{E_{adh}}{E_{111}} \approx 5.7 \qquad V_o^{Cu} \approx 5.7\, V_o^*$$

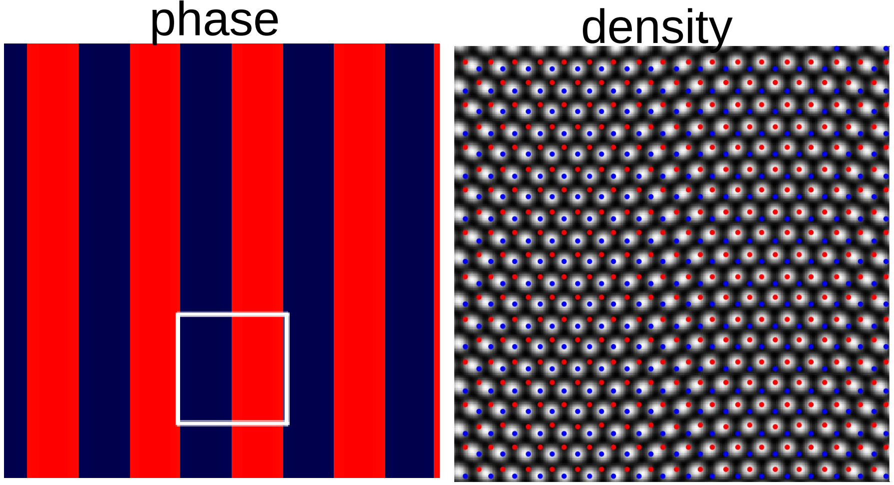
(a) Schimka, Harl, Stroppa, Gruneis, Marsman, Mittendorfer, Kresse, Nat. Mat. Lett (2010)

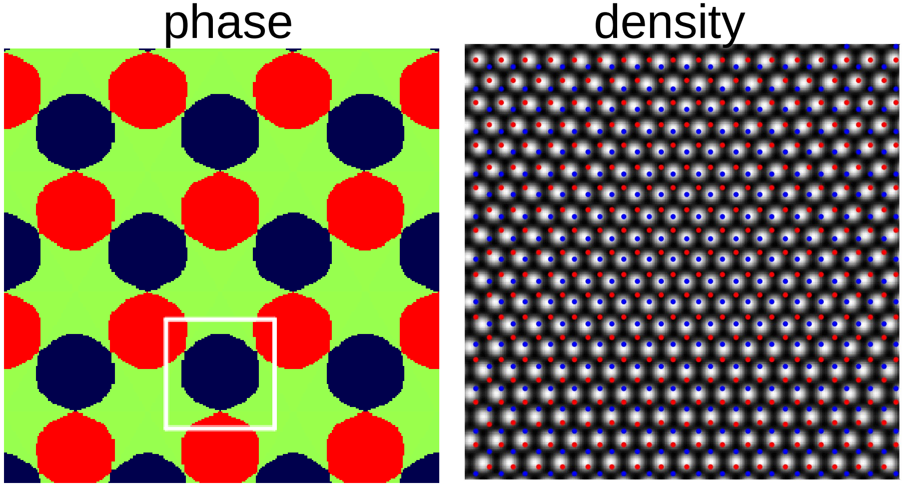
(b) Ding, Deng, Lu, Jiang, Ru, Zhang, Qu, J. Appl. Phys. (2010)

Periodic equilibrium states

Stripe superlattice

Honeycomb superlattice

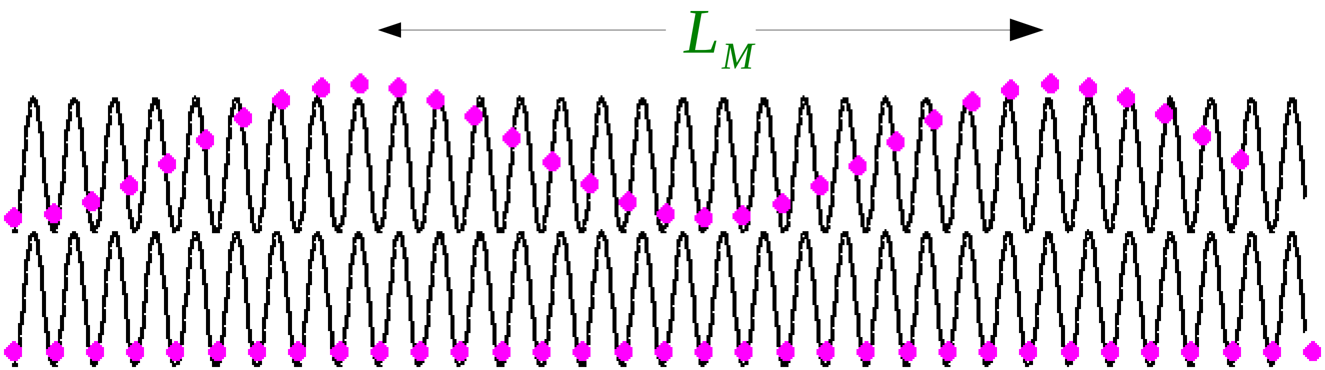




Length scale?

Natural length scale

$$L_M = \frac{2\pi}{q^{Ru} - q^{Cu}}$$



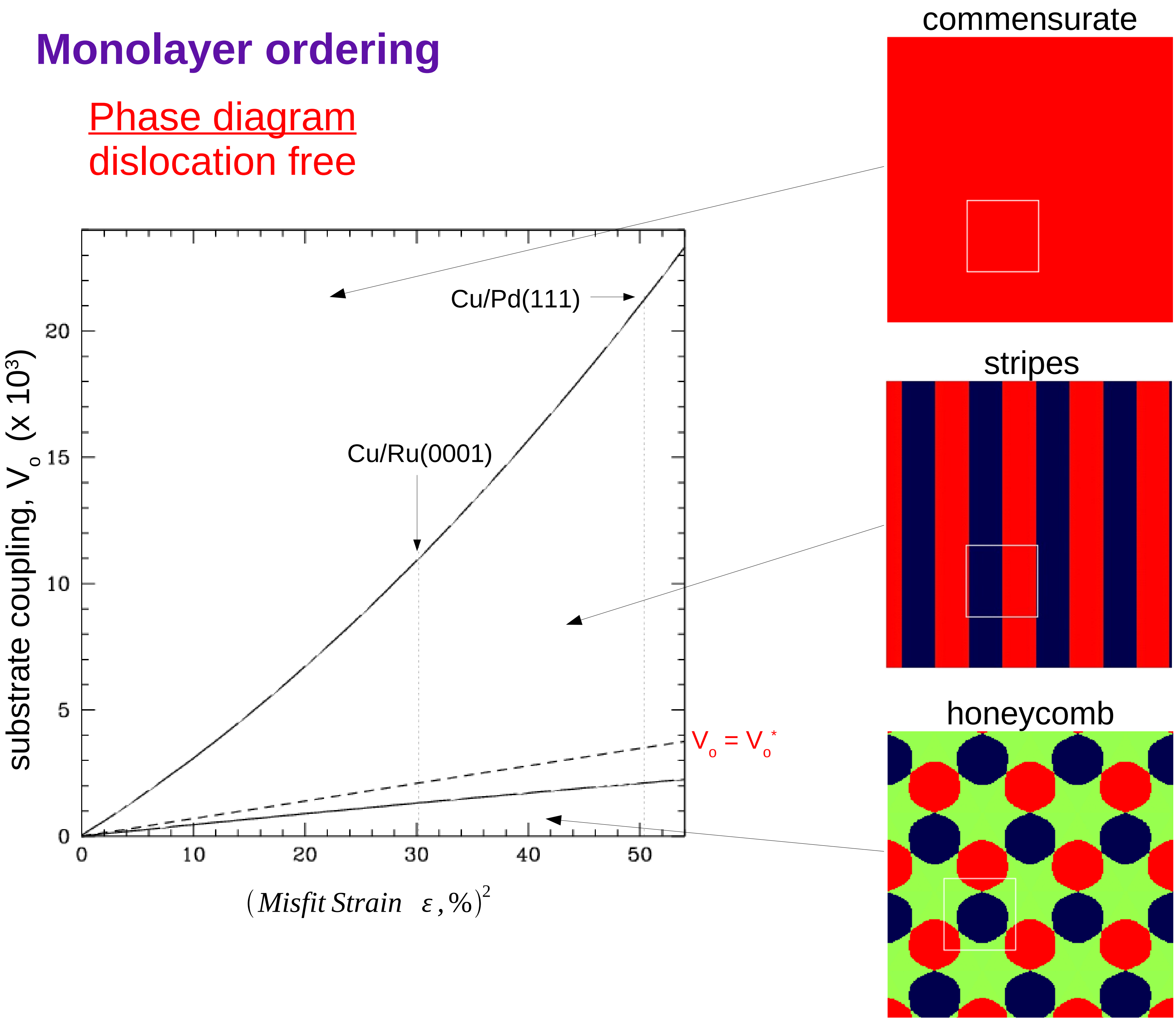
incommensurate

commensurate

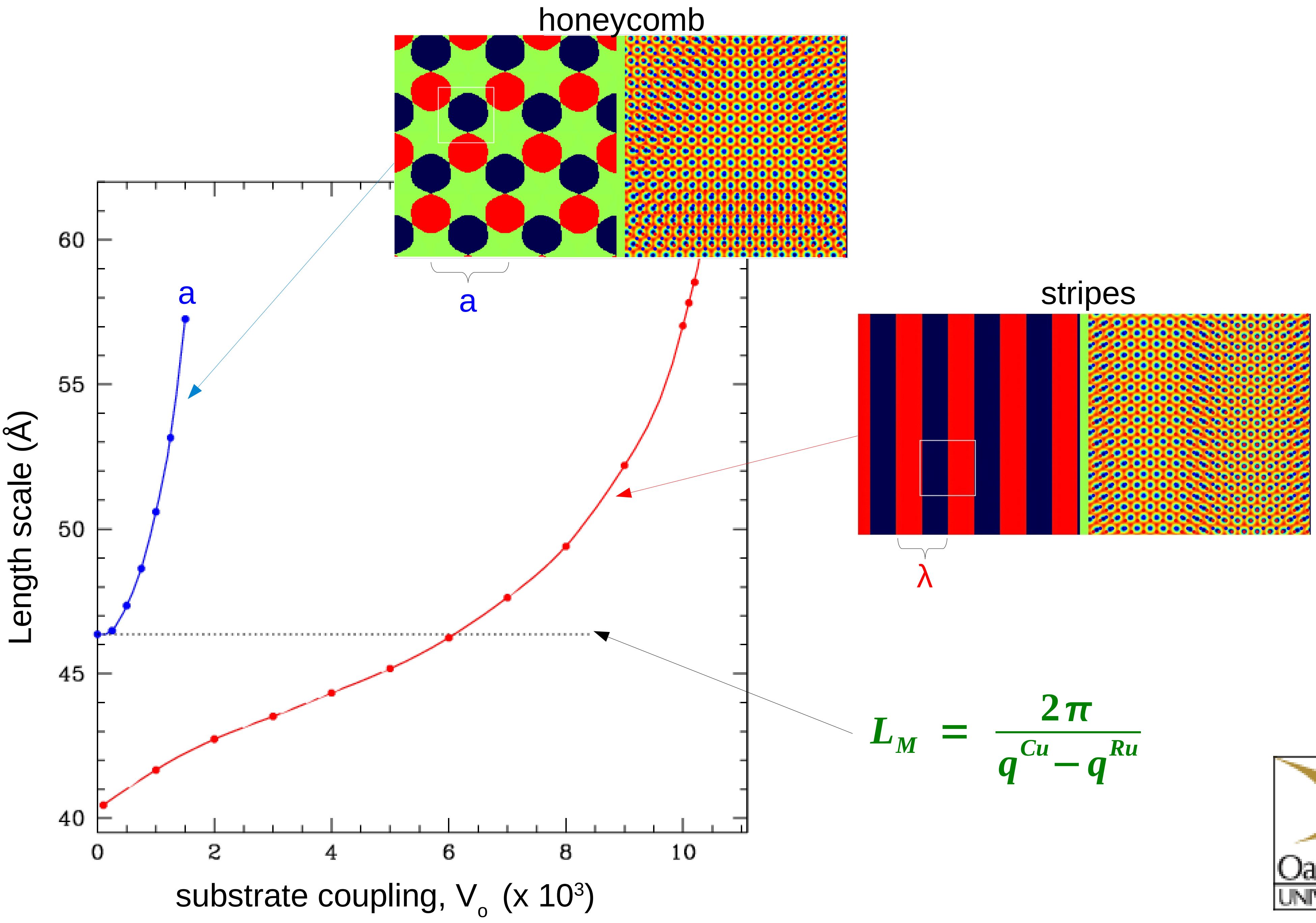
Monolayer ordering

Phase diagram

dislocation free



Monolayer ordering, Length scales, Cu



$$L_M = \frac{2\pi}{q^{Cu} - q^{Ru}}$$

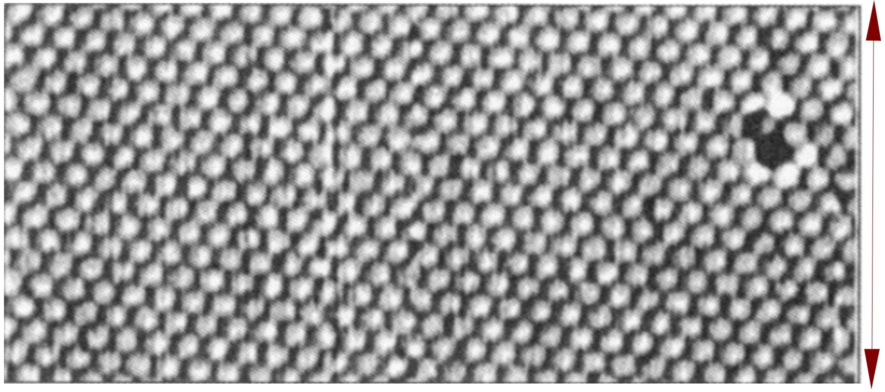
Oakland
UNIVERSITY

Monolayer ordering, Comparison with experiment

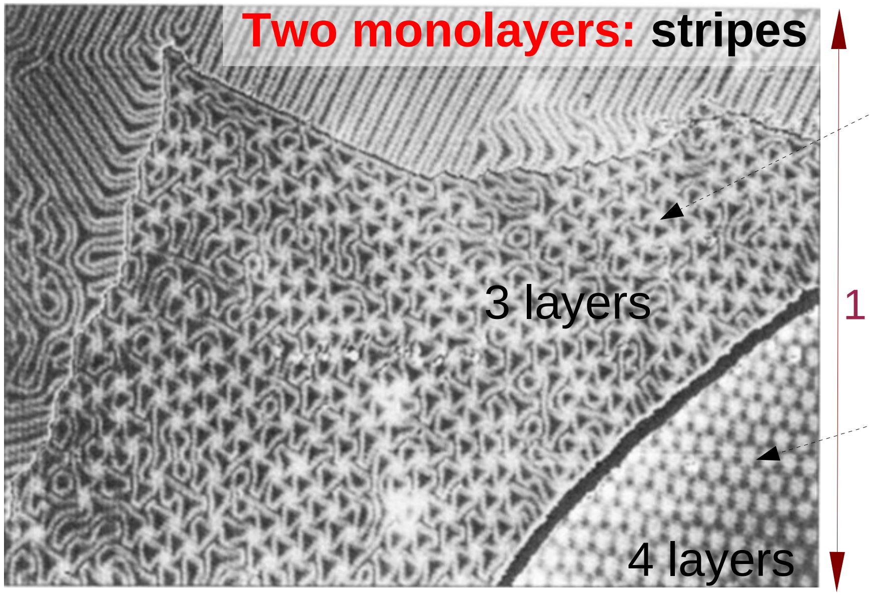
Günther, Vrijmoeth, Hwang and Behm, PRL **74**, 754 (1995): Cu/Ru(0001)

STM images

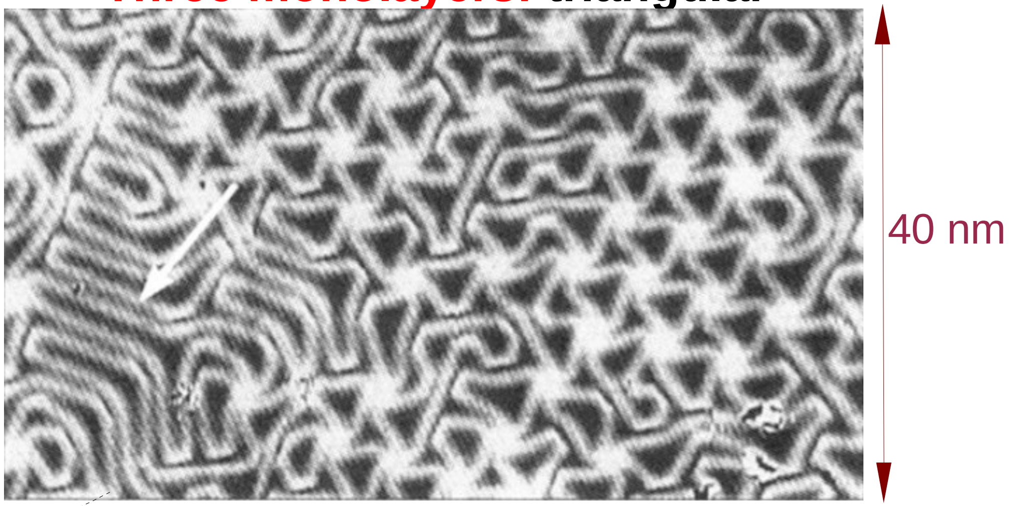
One monolayer: fully commensurate



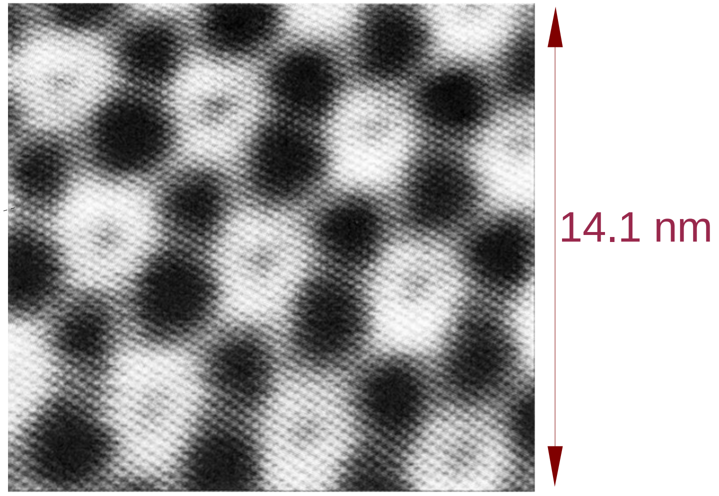
Two monolayers: stripes



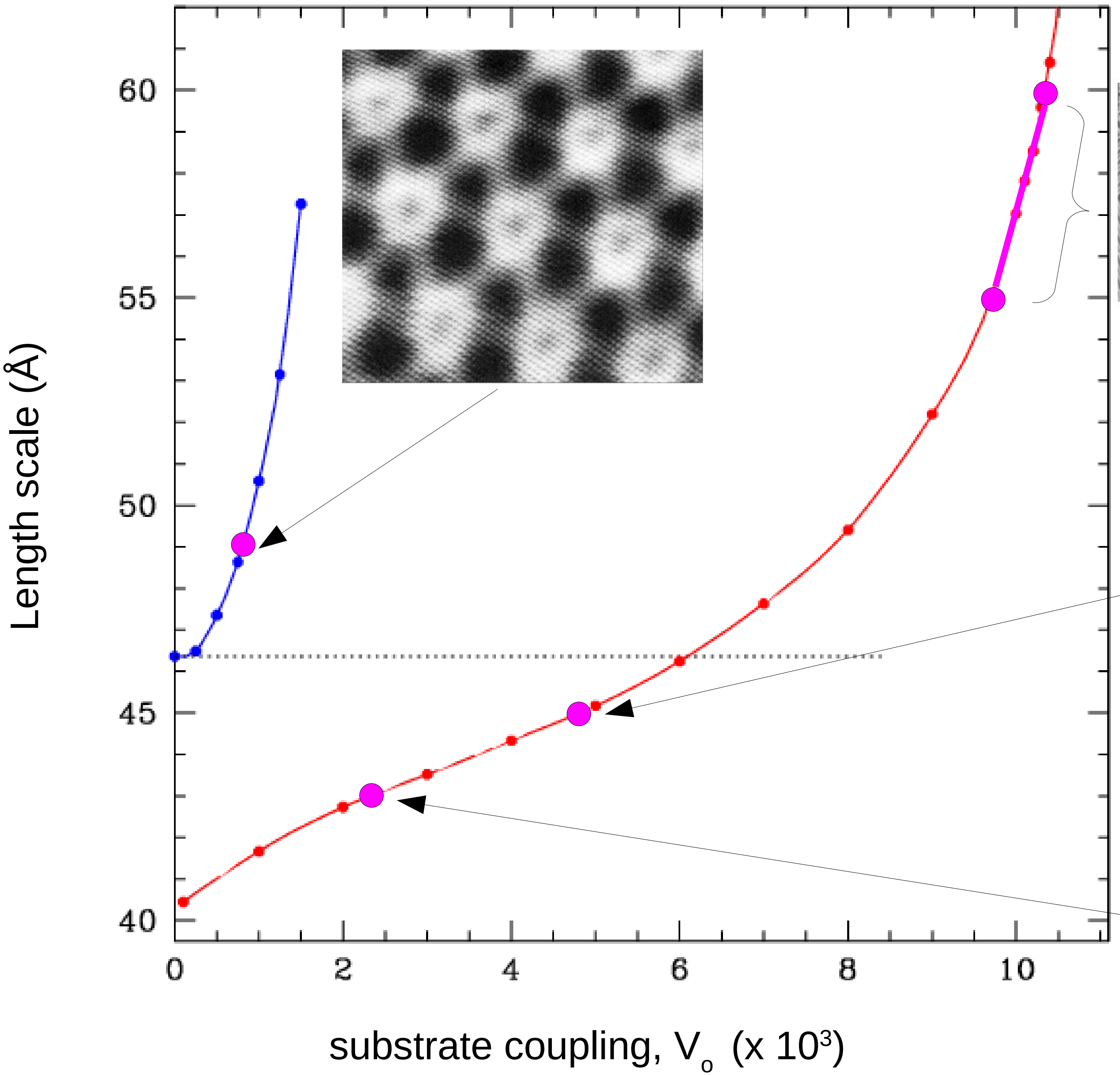
Three monolayers: triangular



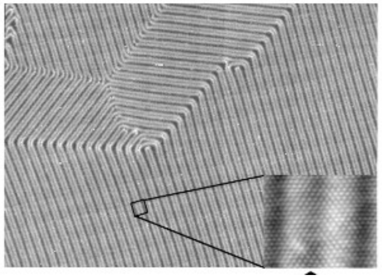
Four monolayers: honeycomb



Monolayer ordering, Length scales, Cu

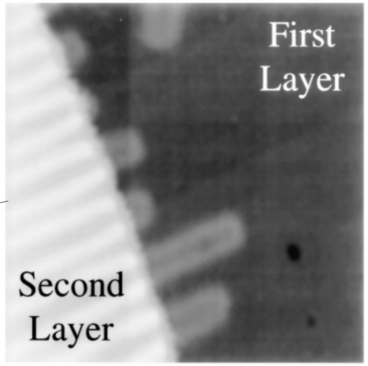


Figuera, Schmid, Bartelt, Pohl, Hwan
PRB **63**, 165431 (2001)



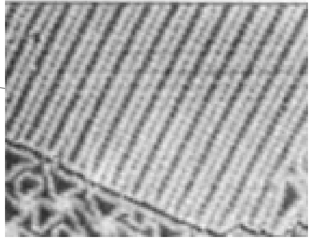
$\lambda \approx 55-60$ Å

Schmid, Bartelt, Hamilton, Carter, Hwang,
PRB **78**, 3507 (1997)



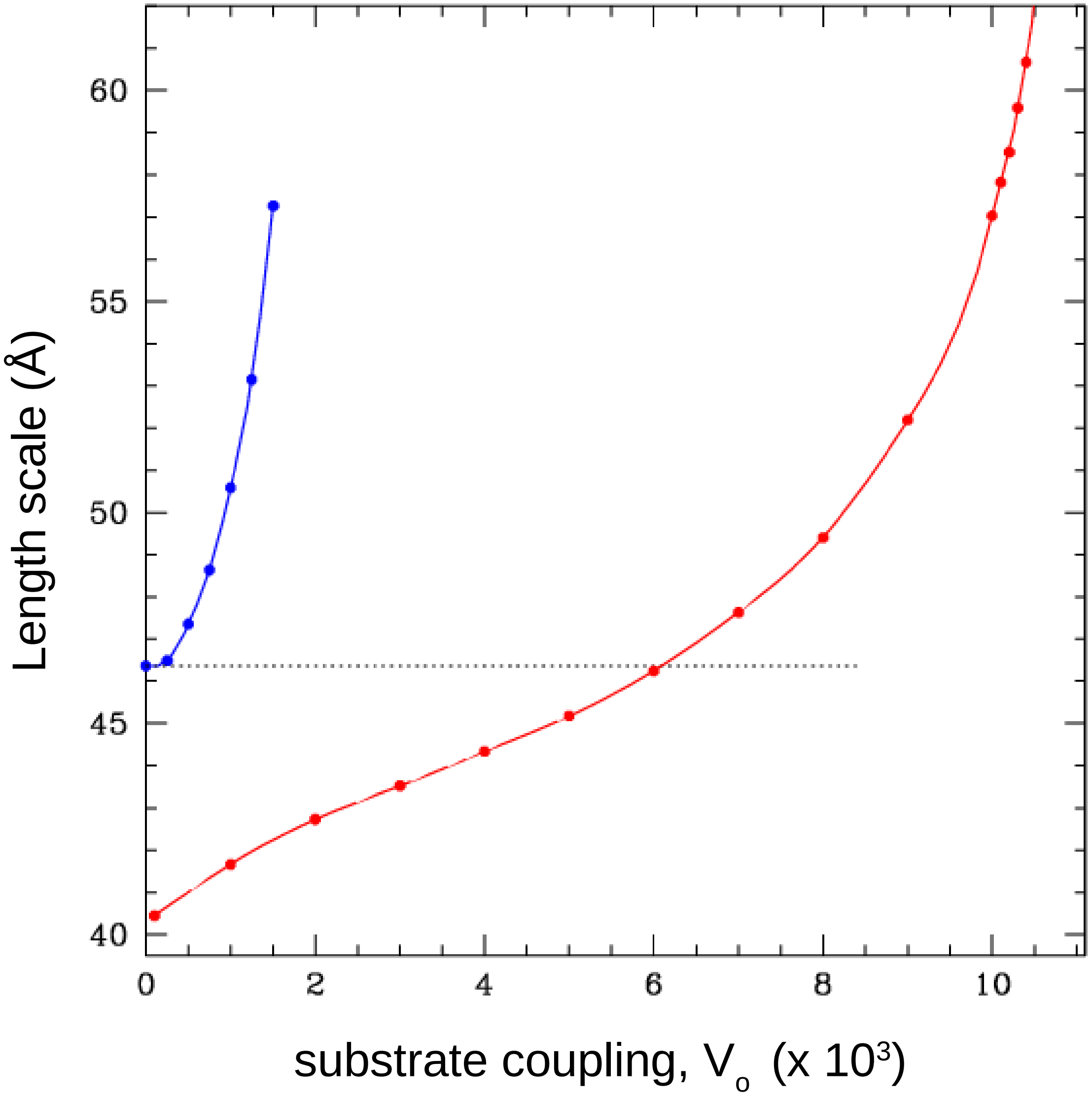
$\lambda \approx 45$ Å

Günther, Vrijmoeth, Hwang ,Behm,
PRL **74**, 754 (1995)



$\lambda \approx 43$ Å

Monolayer ordering, Comparison with experiment



Implication

Decrease V_o

~~~ Increase # Layers (N)~~

~ decrease R

Why?

Consider Ratio

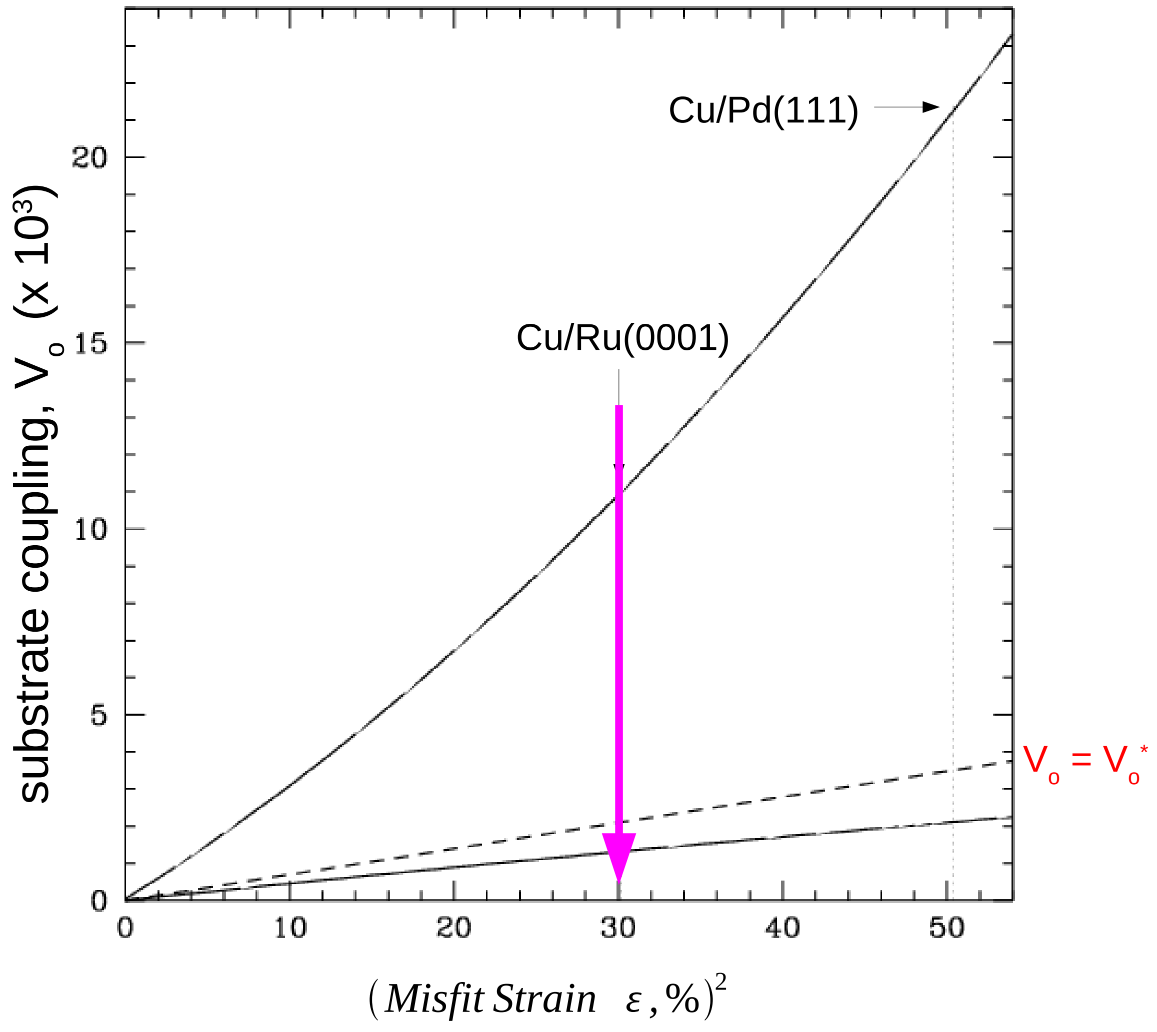
$$R = \frac{\text{Adhesion Energy, } E_{Ad}}{\text{Elastic Energy, } E_{El}}$$

Increase N,
Decrease effective E_{Ad}
Increase effective E_{El}

N increases → R decreases

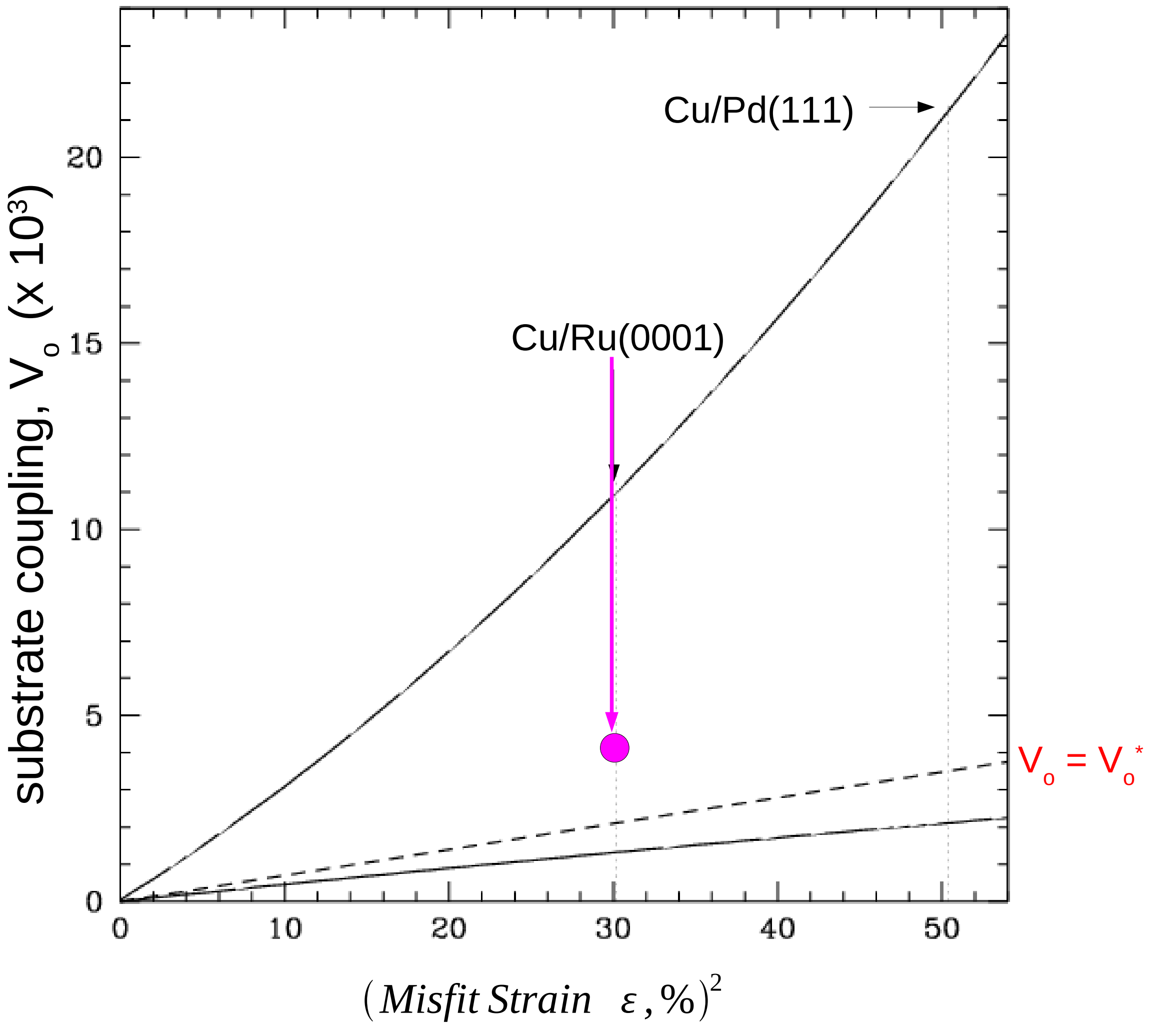
Model, $E_{Ad} \sim V_o$
E_{El} fixed

Monolayer ordering, Dynamics: Adding Layers



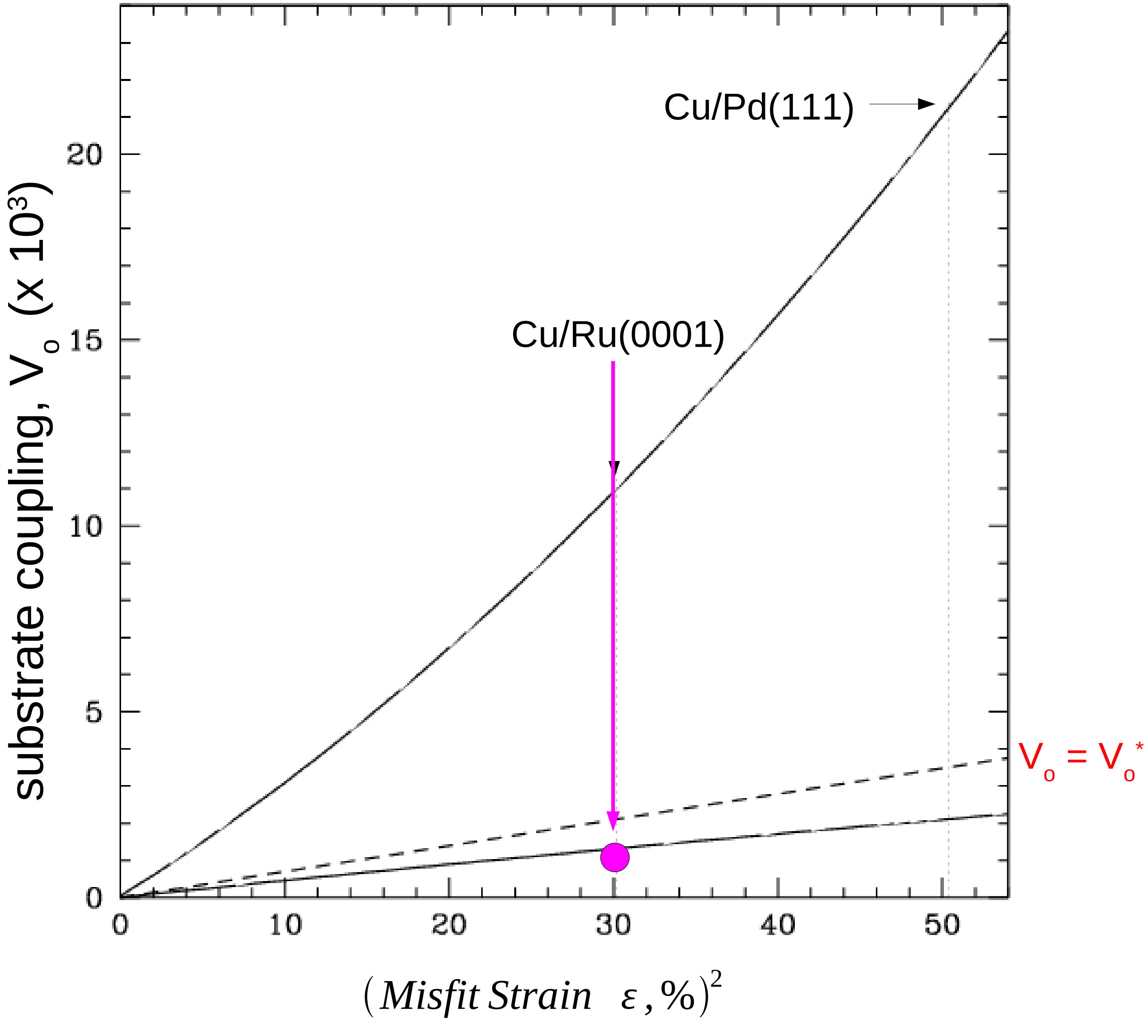
Monolayer ordering, Dynamics, annealing - stripes

$V_o = 3.25 \times 10^{-3}$



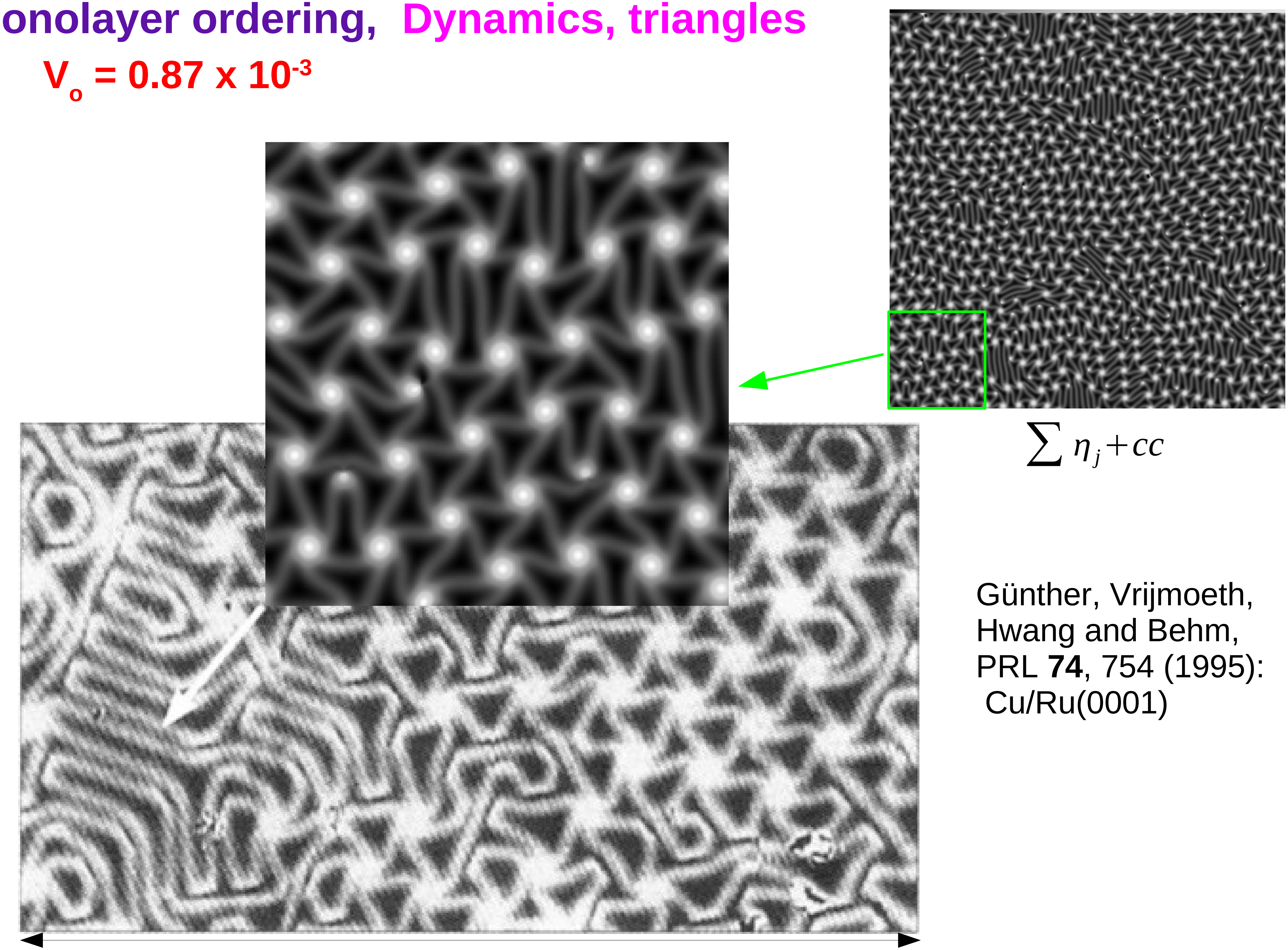
Monolayer ordering, Dynamics, annealing - triangles

$V_o = 0.87 \times 10^{-3}$



Monolayer ordering, Dynamics, triangles

$V_o = 0.87 \times 10^{-3}$

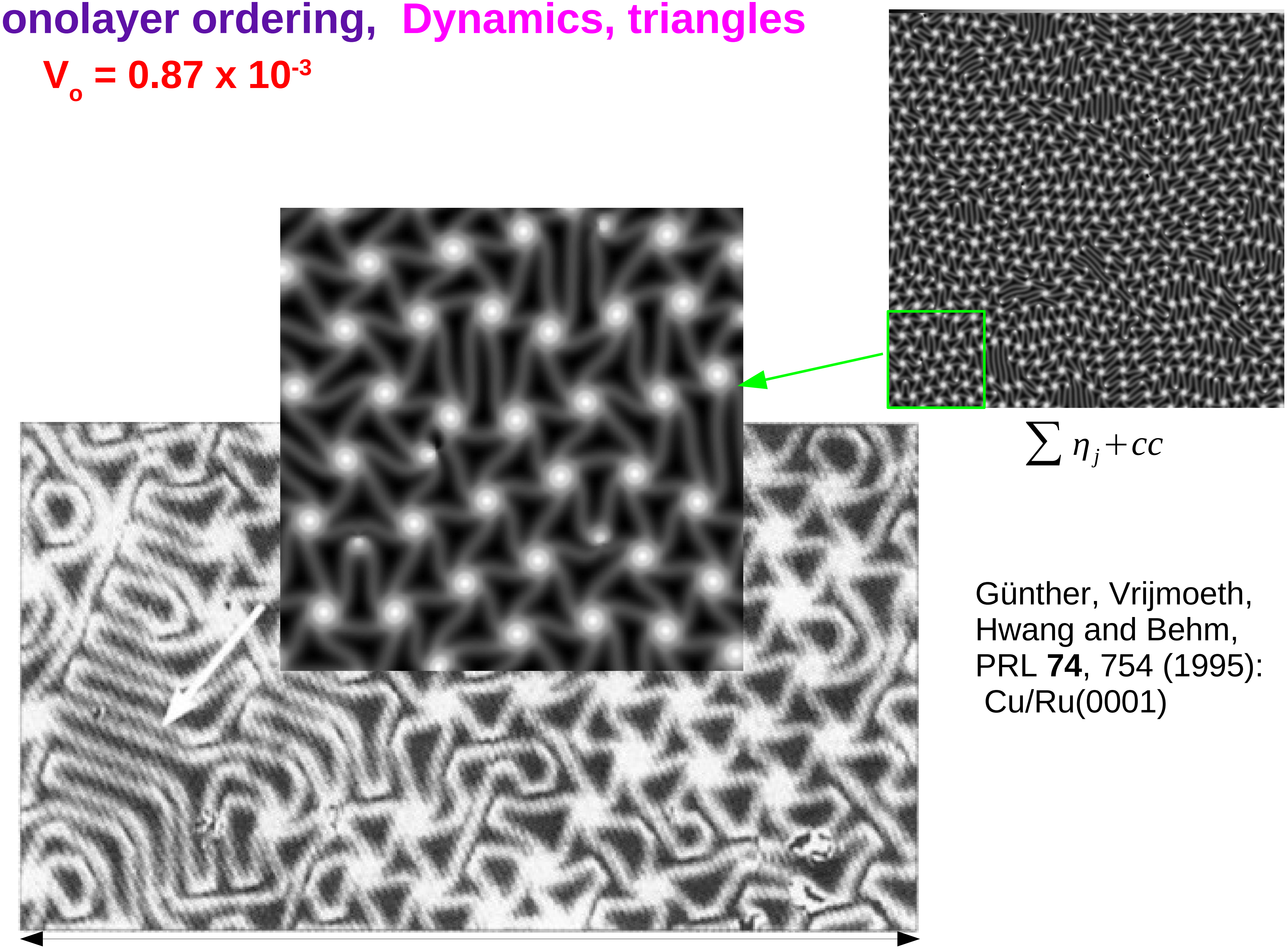


$$\sum \eta_j + cc$$

Günther, Vrijmoeth, Hwang and Behm, PRL **74**, 754 (1995): Cu/Ru(0001)

Monolayer ordering, Dynamics, triangles

$V_o = 0.87 \times 10^{-3}$

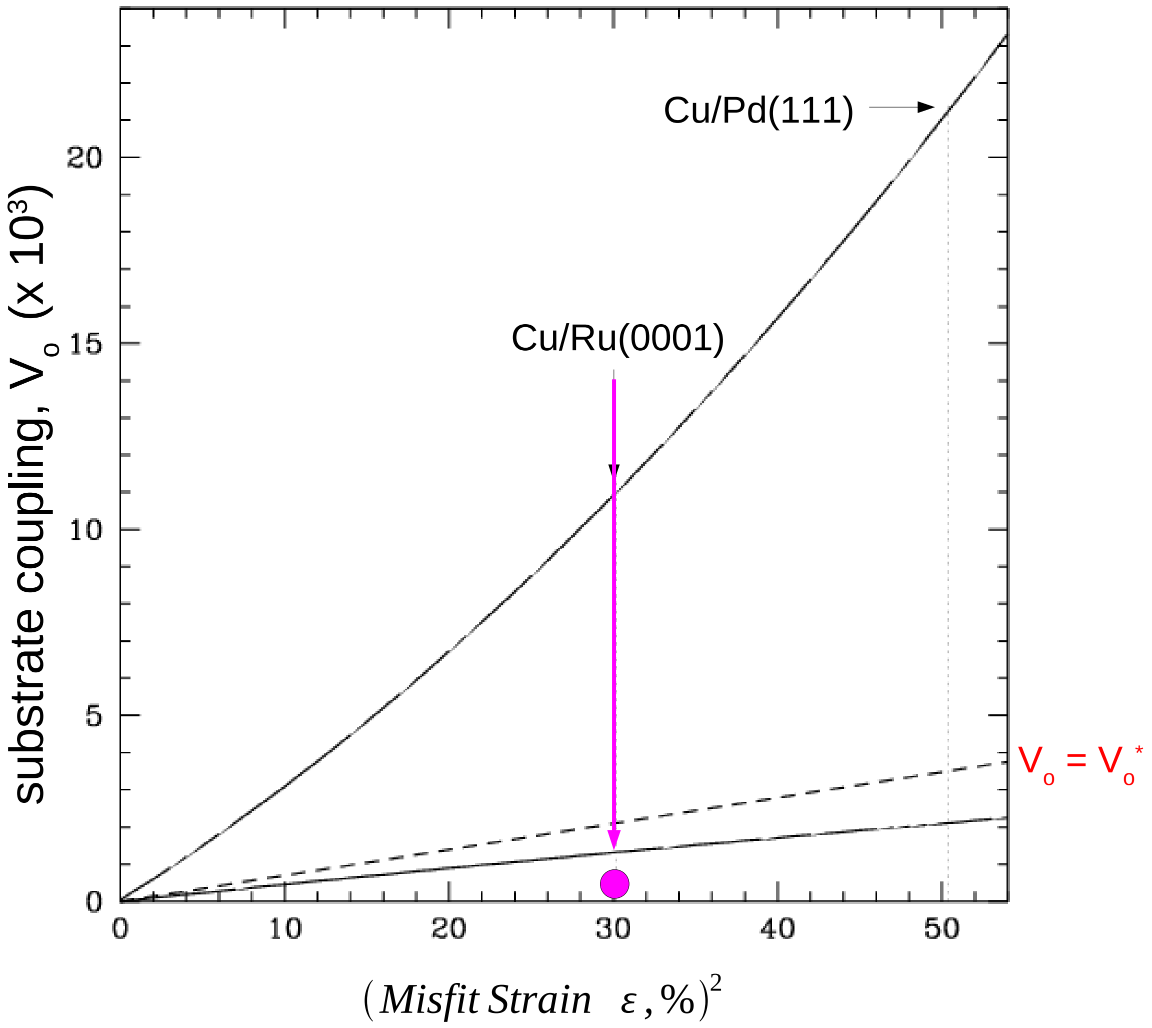


$$\sum \eta_j + cc$$

Günther, Vrijmoeth, Hwang and Behm, PRL **74**, 754 (1995): Cu/Ru(0001)

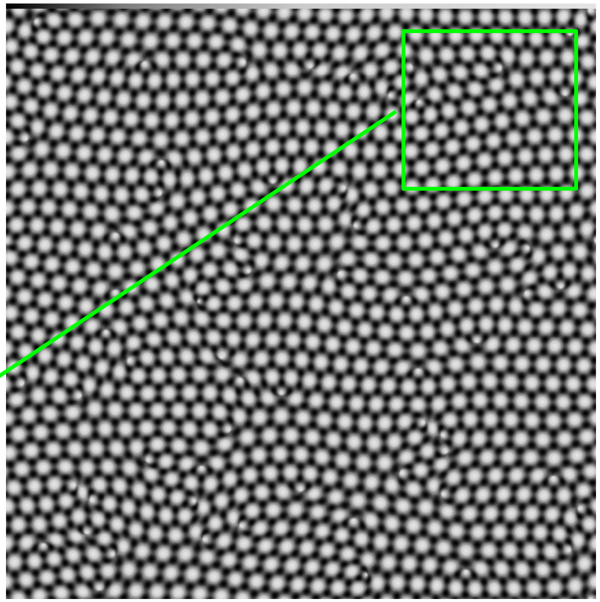
Monolayer ordering, Dynamics: honeycomb

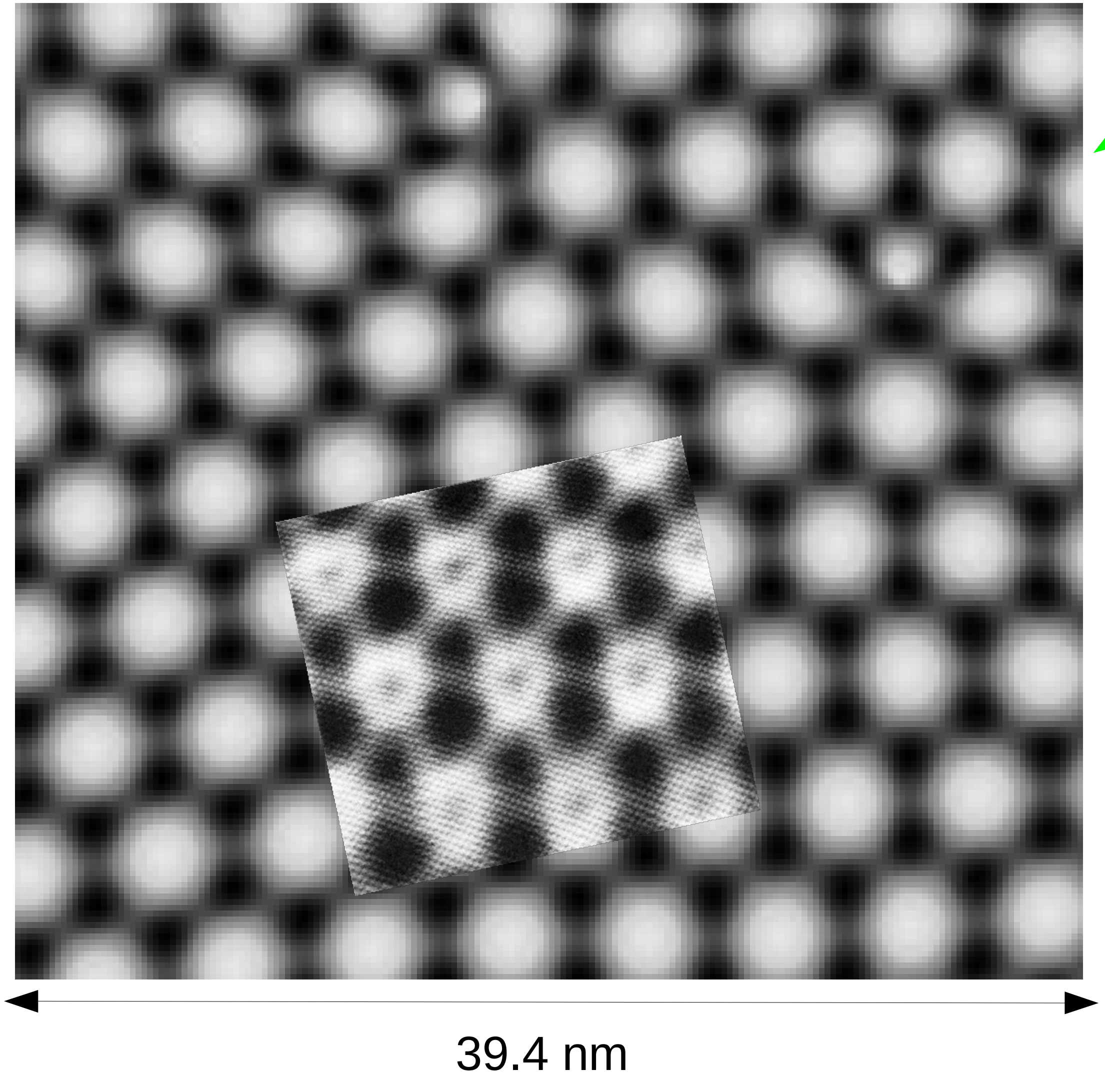
$V_o = 0.43 \times 10^{-3}$



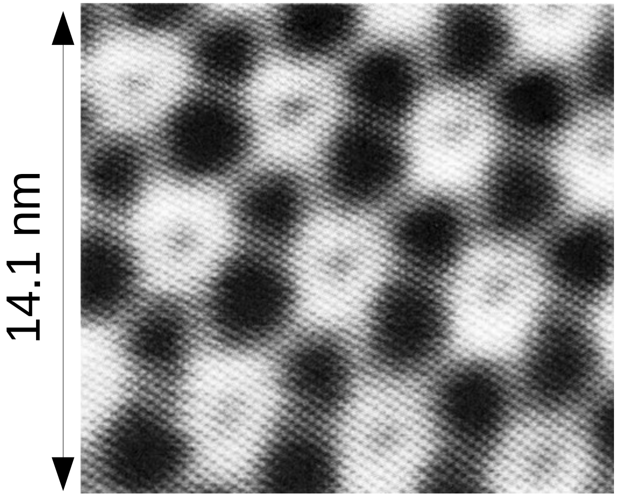
Monolayer ordering, Dynamics, honeycomb

$V_o = 0.43 \times 10^{-3}$



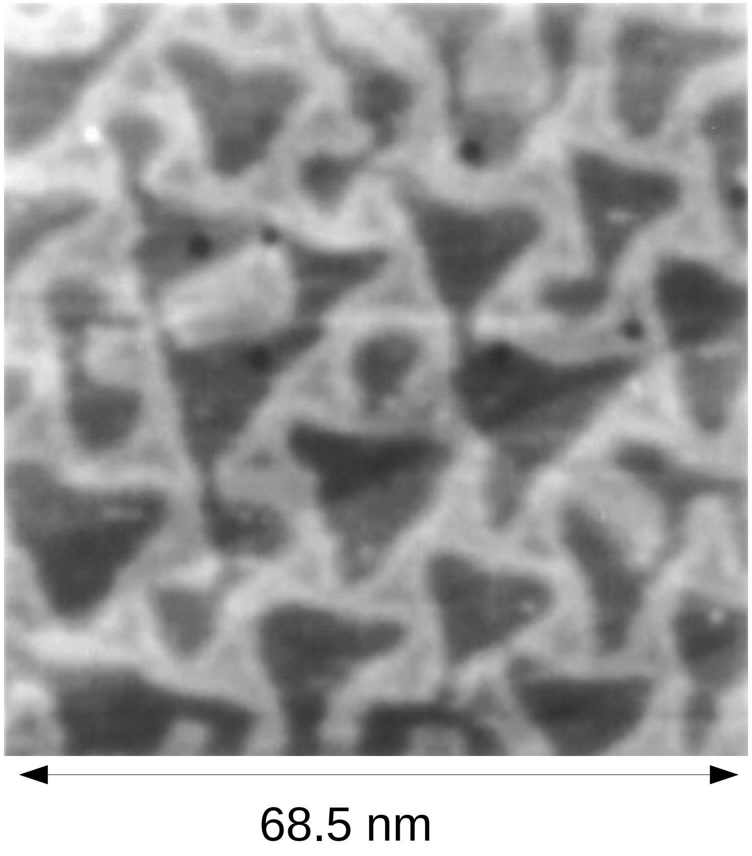


Günther, Vrijmoeth,
Hwang and Behm,
PRL **74**, 754 (1995):
Cu/Ru(0001)

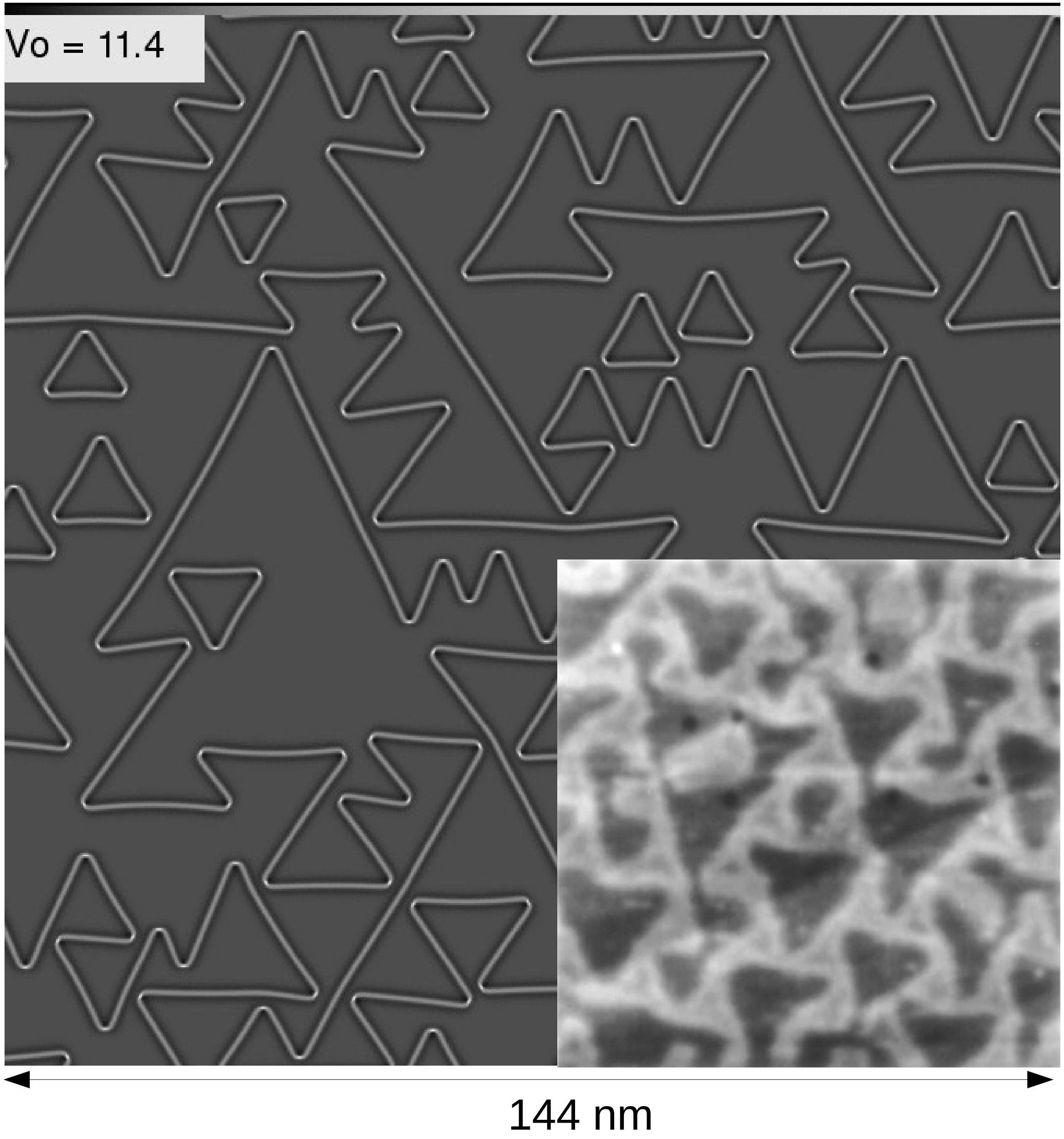


Monolayer ordering, partially filled 2nd layer

Schmid, Bartelt, Hamilton Carter, Hwang,
PRL, **78**, 3507 (1997)

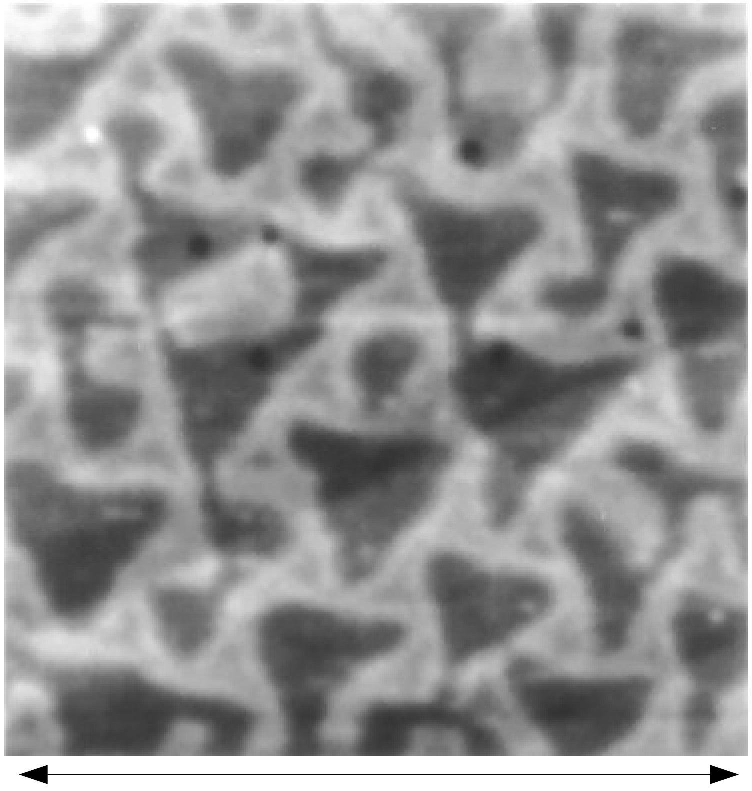


$\sum \eta_j + cc$

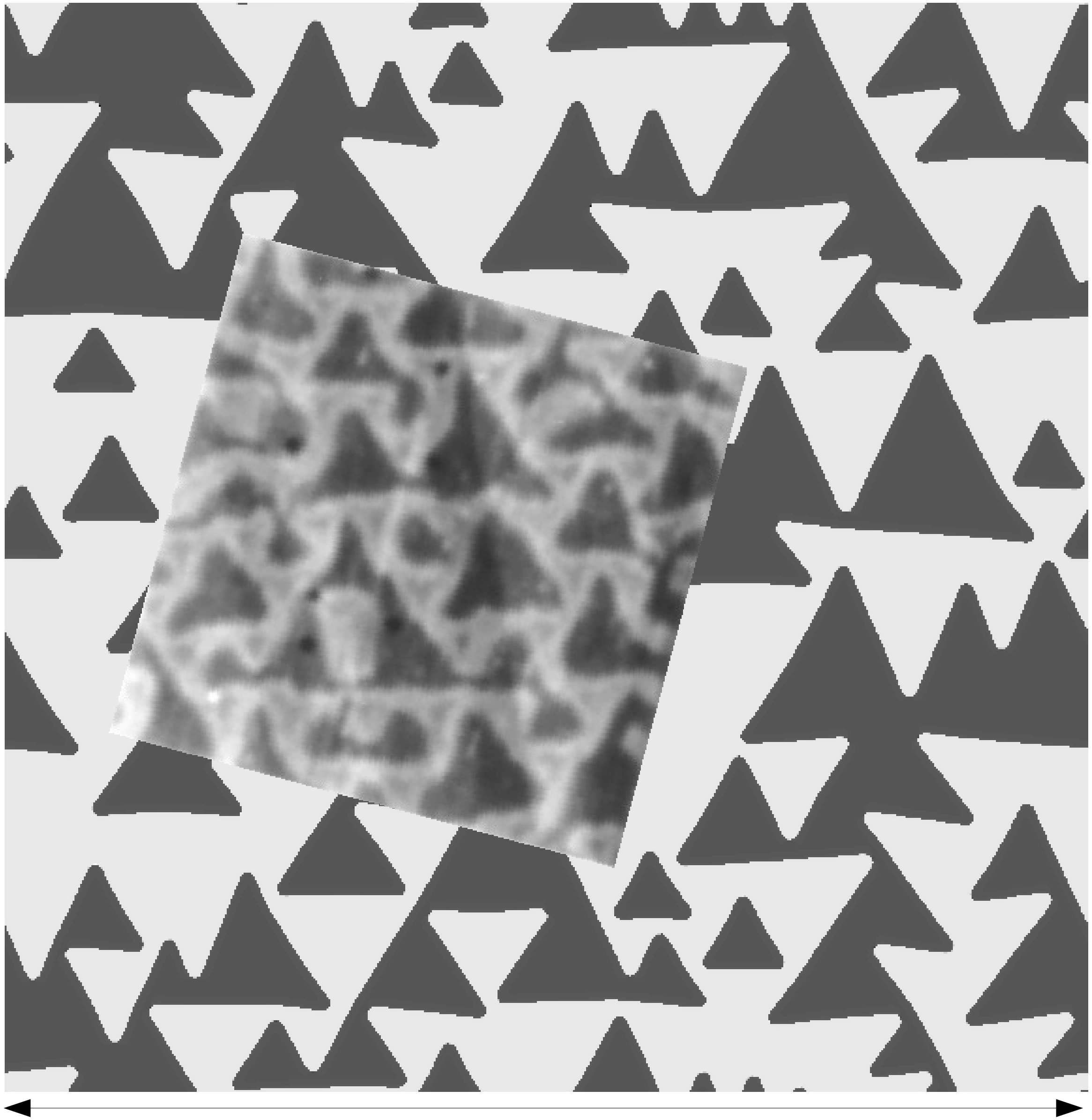


Monolayer ordering, partially filled 2nd layer

Schmid, Bartelt, Hamilton Carter, Hwang,
PRL, **78**, 3507 (1997)

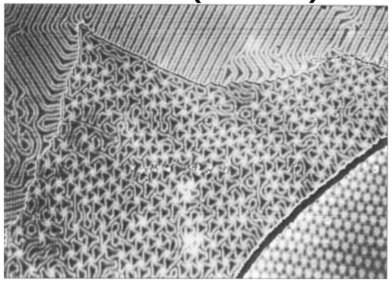


phase



Monolayer ordering: comparison with experiment

Günther, Vrijmoeth, Hwang and Behm, PRL **74**, 754 (1995): Cu/Ru(0001)



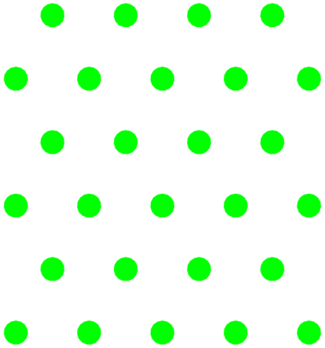
Amplitude model

1) **reproduces** experimental patterns assuming V_o ~ 1/(# layers)

2) implies sample preparation critical

BUT 2D vs 3d missing physics

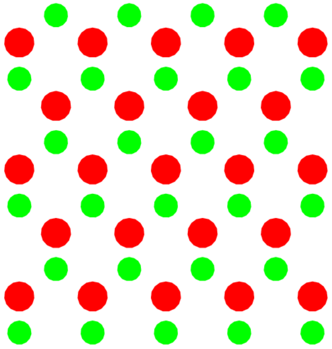
Ru substrate



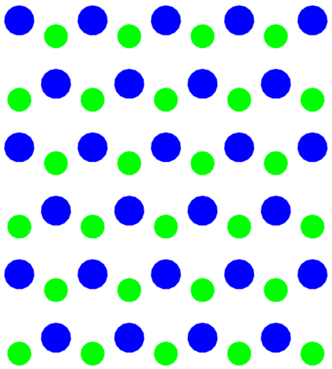
Ru

Cu 1 layer

2 - choices



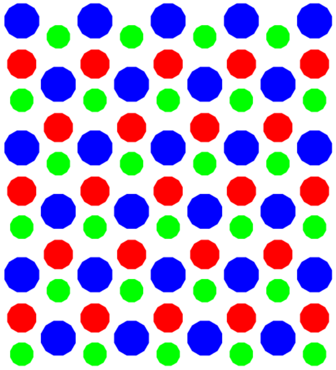
RuCu



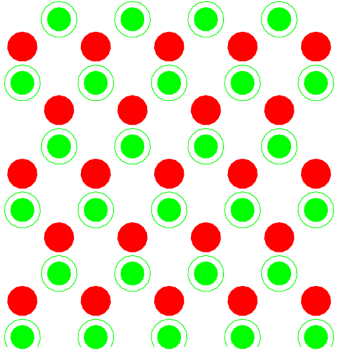
RuCu

Cu 2 layers

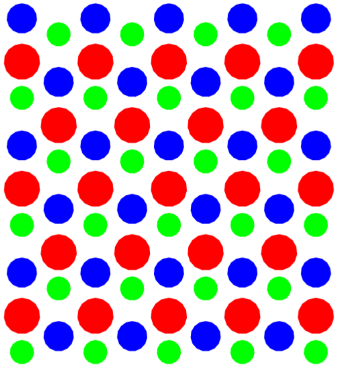
4 - choices



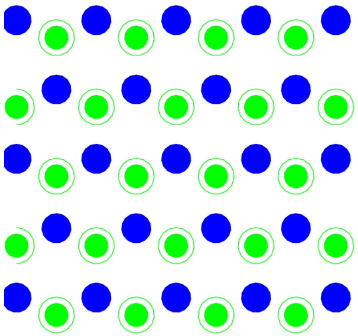
RuCuCu



RuCuCu



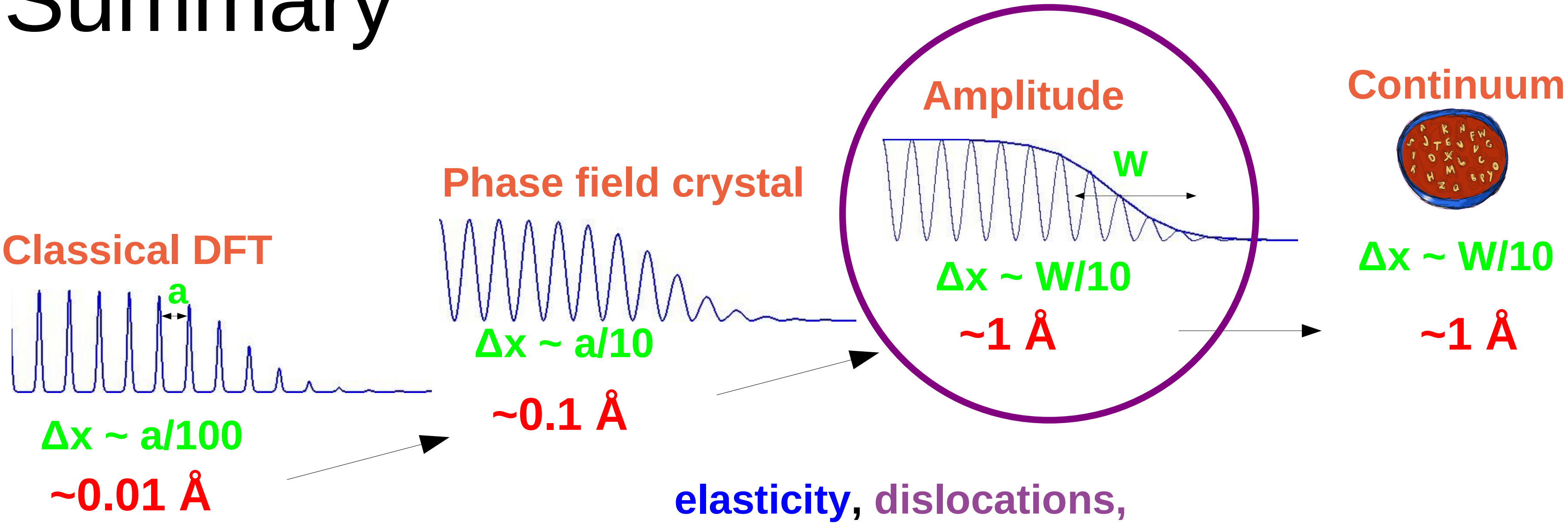
RuCuCu



RuCuCu

- Shockley partial dislocations

Summary



Classical DFT

a

$\Delta x \sim a/100$

~0.01 Å

Phase field crystal

$\Delta x \sim a/10$

~0.1 Å

Amplitude

W

$\Delta x \sim W/10$

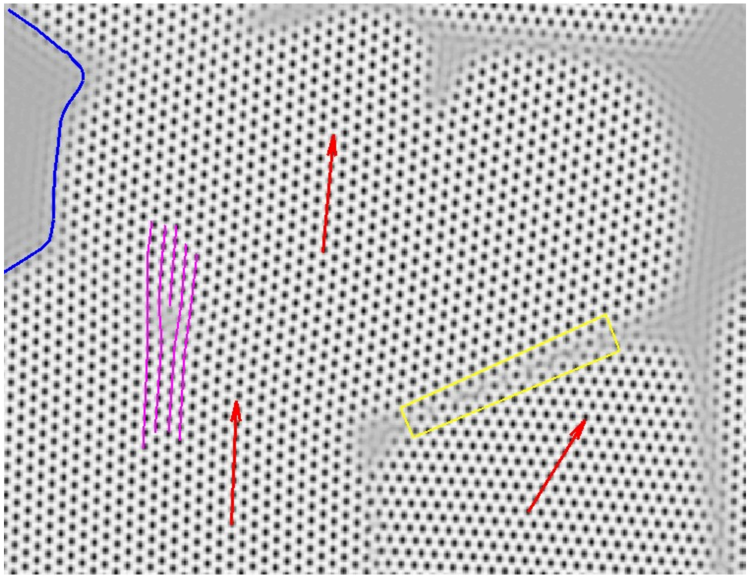
~1 Å

Continuum

$\Delta x \sim W/10$

~1 Å

elasticity, **dislocations,**
multiple xtal orientations



But ....
Multiple Scales approx

W >> lattice constant

No facets
No barriers

True Multiple Scales Model

nm → $\mu\, m$
ms → s