

Atomistic Simulations of Interfaces: Does the Emperor have any Clothes?

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Some vignettes demonstrating challenges for atomistic simulations of interfaces

- Thin Films of Ag on Ru
 - Don't know density of film a priori
- Determination of grain boundary structure and defect properties
 - Ideal boundaries
 - General boundaries
- Impurities at interfaces
 - Segregation profiles and location of impurities
 - Determination of energetics
- Finite-size effects on interfaces
 - Can we take our understanding of bulk interfaces to nanoscale
- Interfacial Dynamics
 - Needed to predict structural stability
- Finite temperature continuum/thermodynamic properties of interfaces
 - What are the driving forces

Heterophase interfaces have complex structures: Ag(111)/Ru(0001)

- One cannot simply assume that the two bulk crystal structures continue up to an interface plane!
- Ag/Ru(0001)
 - 7% lattice mismatch
 - For coverages $\geq 2\text{ML}$, surface Ag atoms are in hexagonal layers
 - Experimental observations show a periodic complex reconstruction at the interface
 - Atomic-resolution scanning tunnelling microscopy (STM)

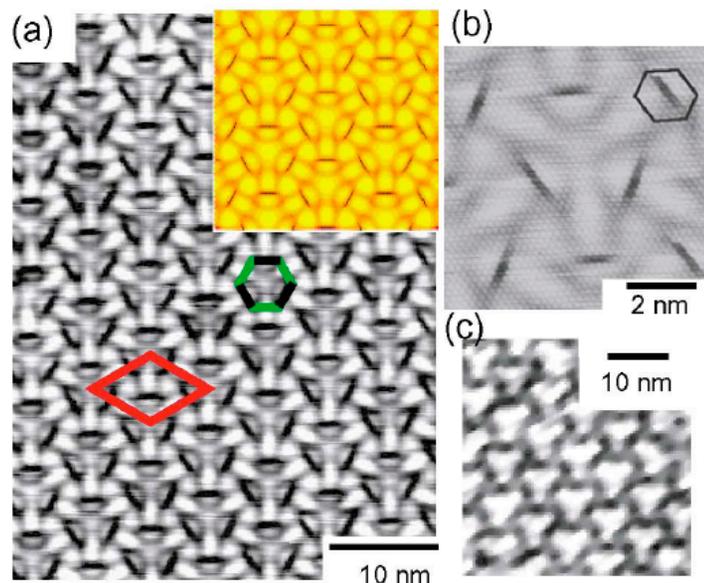
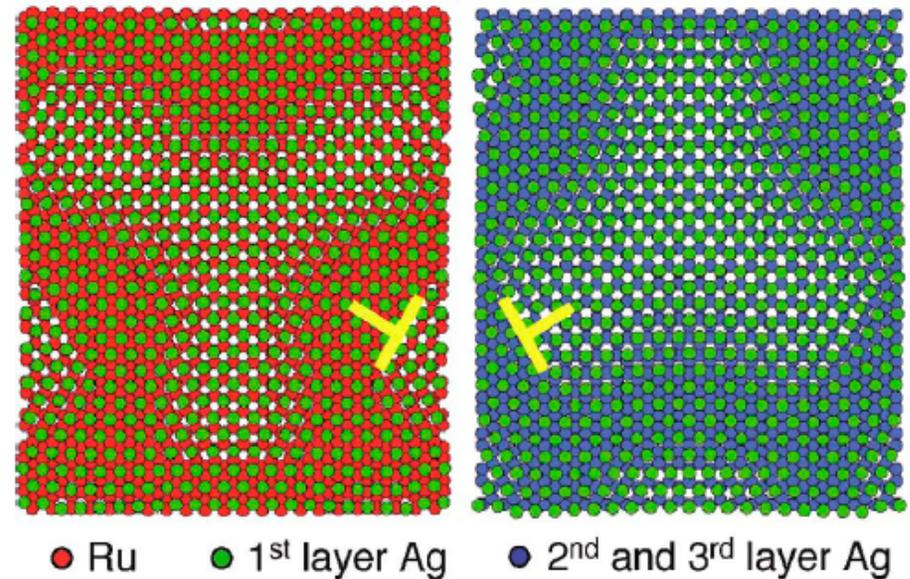


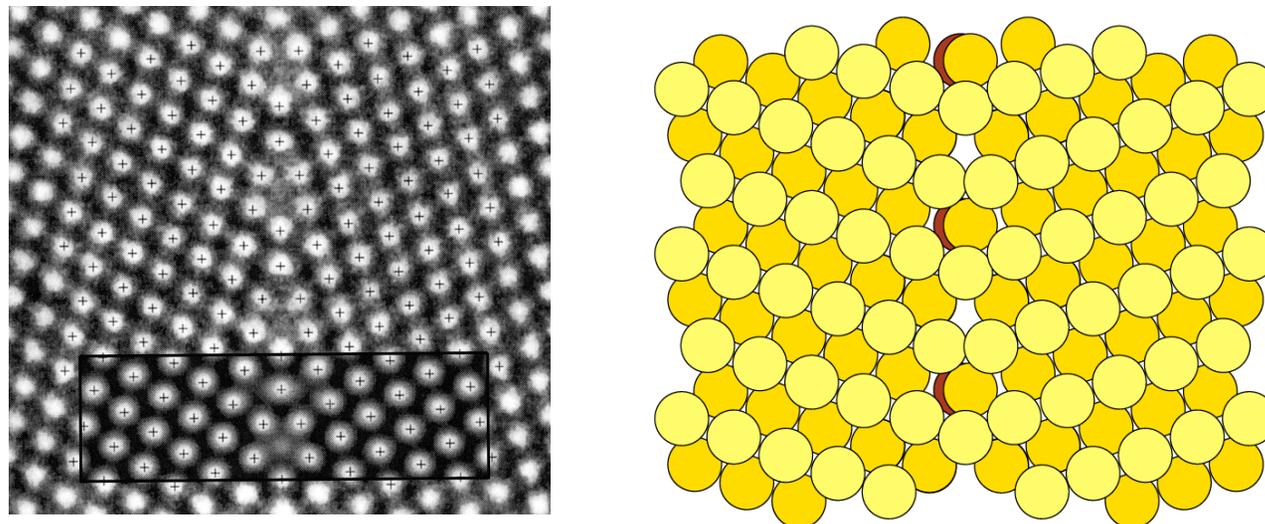
FIG. 1 (color). (a) STM image of a 2 ML film of Ag/Ru(0001). The entire area is covered by a single domain of the dislocation network. The primitive unit cell is indicated in red. A threefold symmetric feature is indicated in green. The color inset shows the height modulation of the EAM calculations. (b) Atomic resolution image with a closed Burger's circuit around black line feature in image, showing the absence of an edge dislocation at the surface layer. (c) STM image of a 6 ML area of Ag/Ru(0001). The structure appears identical to the 2 ML structure except that contrast is reduced.

Calculations reproduced structure through *insight from experiment and physical intuition*

- Solution required consideration of structures with varying numbers of atoms
 - Climb of the edge dislocations in the interface structure
- Experiment provided several key clues to the desired structure
 - Second and above layers of Ag are hexagonal
 - Unit cell dimensions
 - Presence of three-fold structures
- Could calculations get this right in the absence of the experiments?!?
- First Ag layer has a transitional structure
 - Moire pattern between that layer and material above and below
- $D(\text{Ag}) < D(\text{1st layer Ag}) < D(\text{Ru})$



For ideal boundaries we can get structure right and validate it!
Combination of HRTEM and atomistic simulations reveals structural details

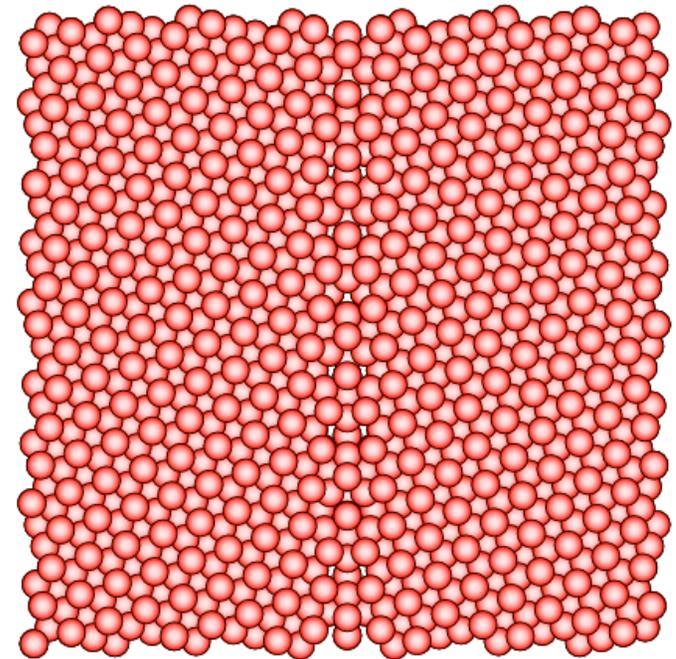


$\Sigma 9$ (2 -2 1)/[1 1 0] symmetric tilt in Al

- Inset is HRTEM image based on image simulation of computed structure
 - +’s indicate the position of intensity maximums for the simulated image
- Agreement between experimental and simulated image requires the alternation of atoms in the boundary
- The correct identification of the structure required the synergistic application of simulation and experiment

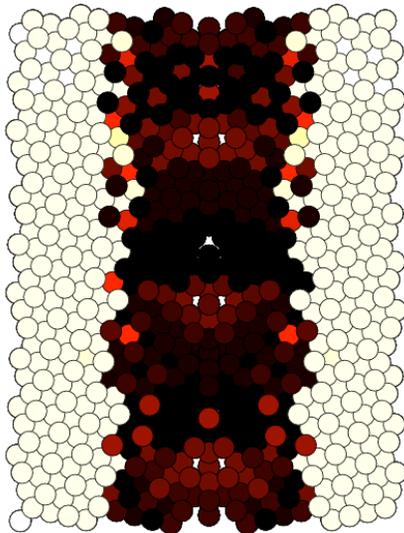
Determination of structure of a reasonably general boundary is fraught with uncertainty

- What is the relative shift of the two grains?
 - Are we stuck in a metastable local minima?
- How do we come up with the initial structure for structural optimization?
 - Shifts?
 - How many atoms?
 - Global optimization?
- We do not have robust ways to do this do this!
 - We cannot rely on experiment to help us get it right

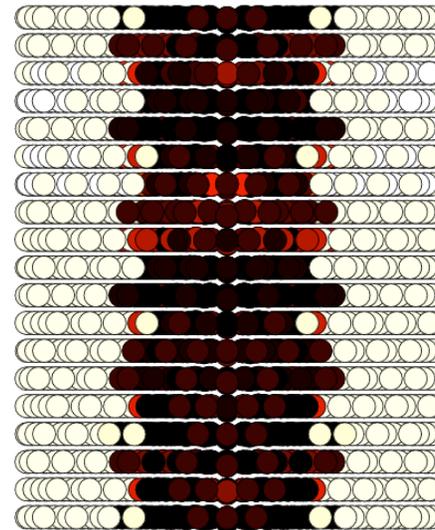


$\Sigma 79$ symmetric tilt in Ni

Interstitial formation energy near a grain boundary: Confirmation that boundaries can be source/sink



View along tilt axis

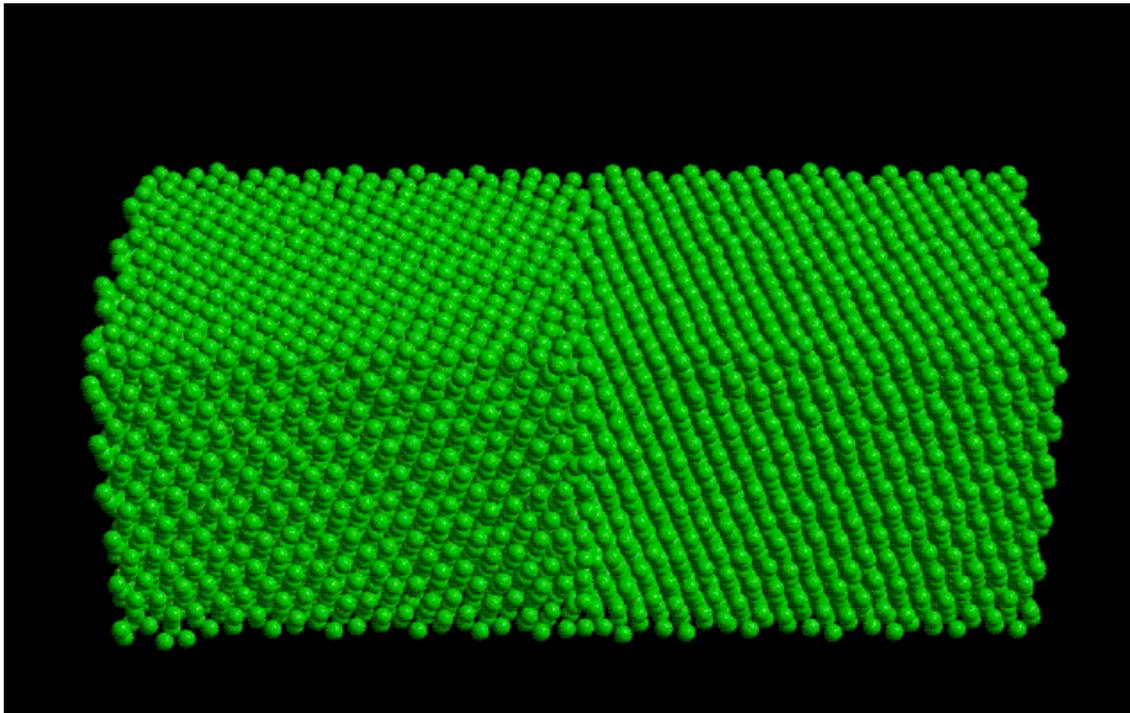


View normal to the tilt axis

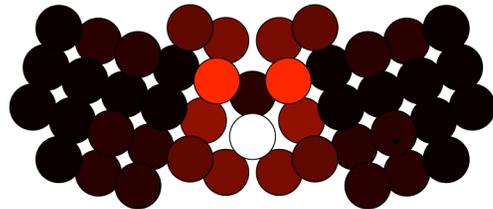
- Shading of atom is the formation energy when that atom is replaced by a [1 0 0] dumbbell
 - Black: 0 eV
 - White: 4 eV
- Interstitial ‘configurations’ near the boundary are highly delocalized

Energetics of Interstitials and Adatoms plays a role in thin film stress formation

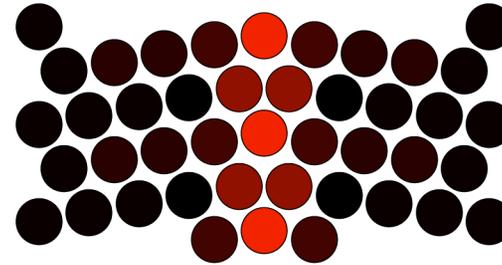
- Desposition of Ni adatoms onto Ni substrate with an intersecting grain boundary
 - $T/T_m = 0.5$
- Incorporation of adatoms into boundary creates compressive stress in the thin film



Variation of Ag energies near grain boundary in Cu



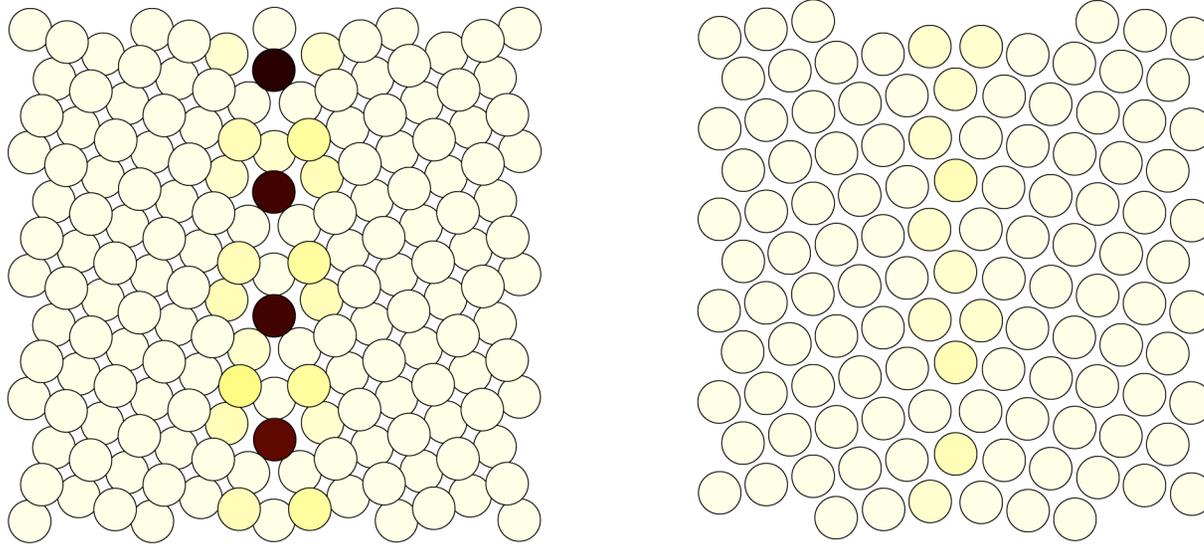
$\Sigma 5$



$\Sigma 11$

- Energies of Ag substitutional atoms computed with the EAM
 - Shading represents the substitutional energy
 - black: 0.04 eV above bulk value
 - white: 0.67 eV below bulk value
 - Maximum energies: -0.67 eV ($\Sigma 5$) and -0.18 eV ($\Sigma 11$)
- The preferred site is consistent with size effect considerations
- General enhancement of Ag near the boundary consistent with modulus interaction
 - Ag has smaller moduli than Cu
 - Preliminary LDA results indicate Ag impurities reduce the elastic moduli
- Strength of the segregation driving force depends strongly on the particular interface chosen

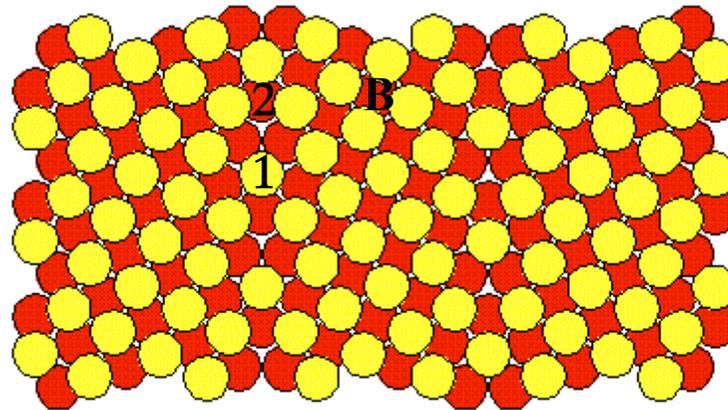
MC simulations can determine equilibrium concentrations assuming substitutional occupation



- Simulations conditions:
 - 750 K; $c_{\text{Ag}}(\text{bulk}) = 0.5\%$
- Shading represents Ag content
 - white = 0% Ag and black = 100% Ag
- $\Sigma 5$ boundary has strong Ag segregation to one site in the boundary with modest enhancement near the boundary
- $\Sigma 11$ boundary shows modest Ag segregation near the boundary

Benchmark of EAM results for Ag segregation energies

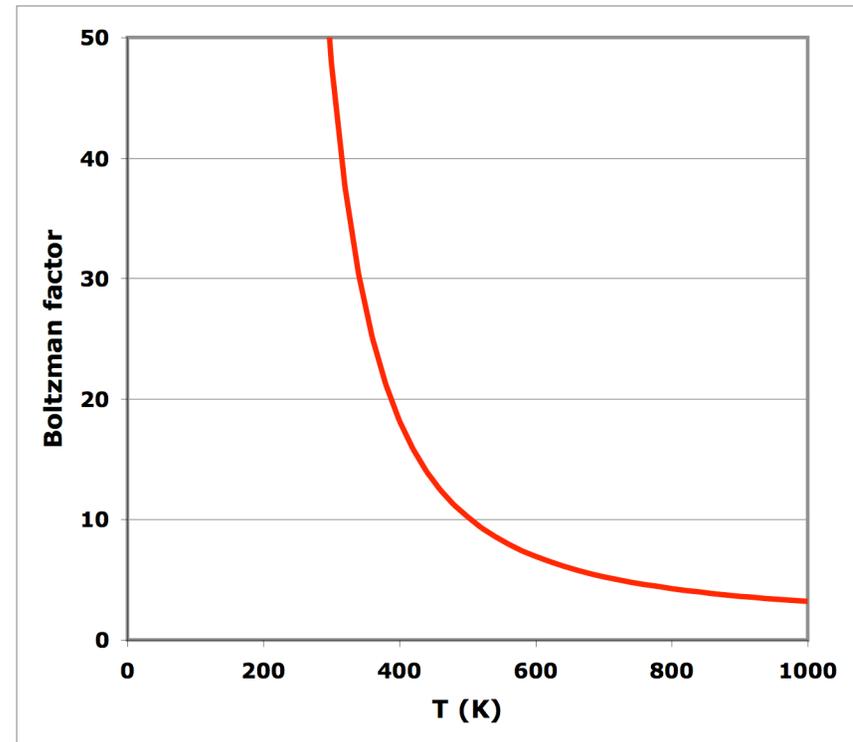
Comparison with LDA predictions



- Energies of Ag impurities at the Cu $\Sigma 5$ boundary calculated both with the EAM potentials and with LDA
 - LDA calculations performed using the Vienna Ab initio Simulation Package (VASP)
- Reasonable agreement between EAM and LDA results for the Cu-Ag potentials
 - $E_1 - E_B$
 - LDA: -0.75 eV; EAM: -0.64 eV
 - $E_2 - E_B$
 - LDA: -0.16 eV; EAM: -0.06 eV

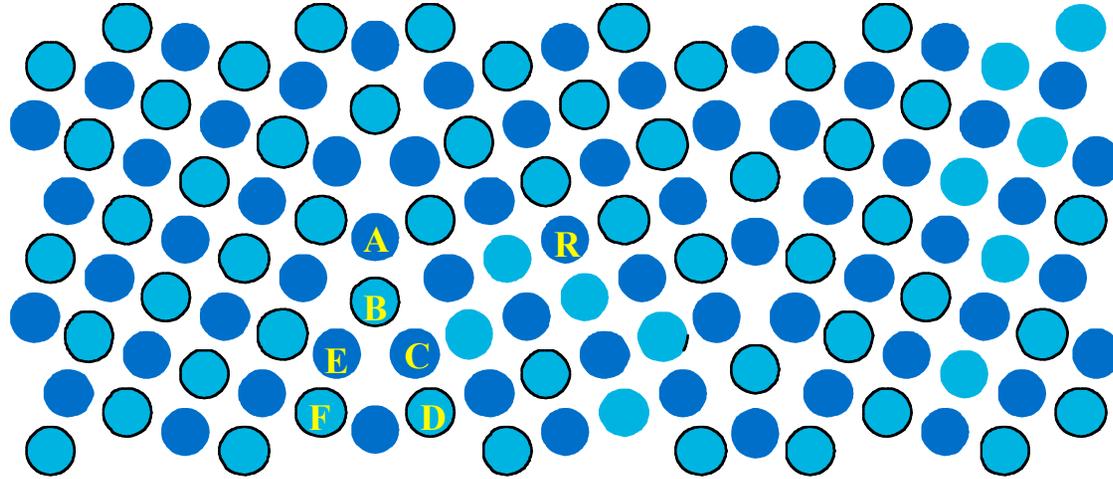
What's 0.1 eV between friends?!?

- That level of error is 'good' for empirical potentials especially in alloy systems for currently available potentials
 - Ag/Cu would be expected to be an 'easy' alloy system
- An error of 0.1 eV in a segregation energy can easily translate into an order of magnitude error!
- More rigorous energy calculations (eg. DFT) do not lend themselves to *direct* application of statistical methods
 - Introduce simplified models (eg Ising-like models) to treat statistical aspects
 - Limited exploration of possible structures



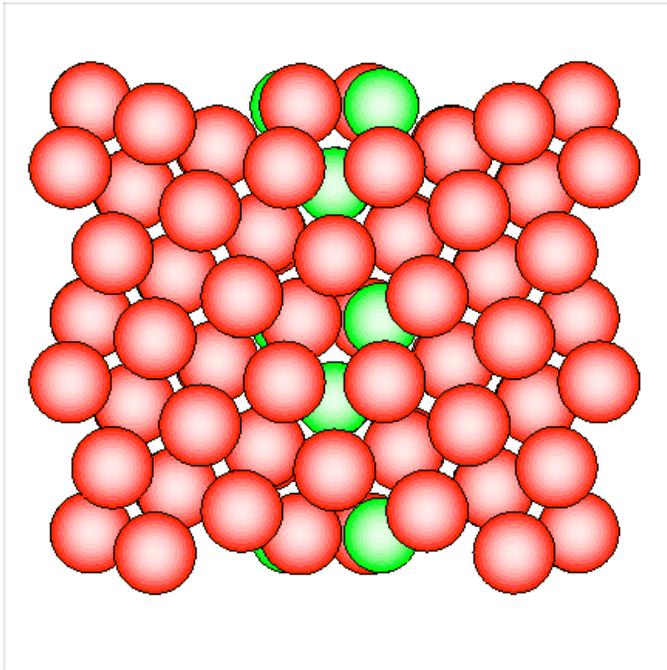
$$\frac{c_i}{1 - c_i} = \frac{c_B}{1 - c_B} \text{Exp}\left(\frac{-\Delta F_i}{k_B T}\right)$$

Cu segregates to multiple sites within the Σ 5(310) grain boundary in Al



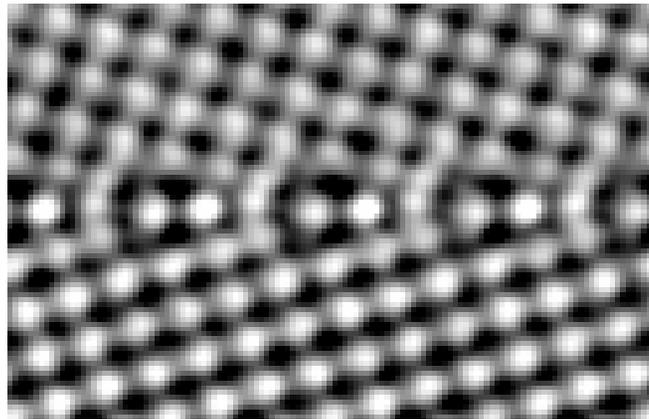
- First Cu atom per CSL cell goes primarily to site A
 - segregation energy = 0.46 eV
 - segregation energy to site C or E = 0.38 eV
 - repelled from sites B (0.65 eV) and sites D or F (0.04 eV)
- Second Cu atom per CSL cell alternate between sites C and E
 - segregation energy = 0.46 eV
- Third Cu atom per CSL cell fills in the other sites at C and E
 - segregation energy = 0.09 eV

2 Cu atoms per CSL unit cell should segregate to the $\Sigma 5(310)$ boundary

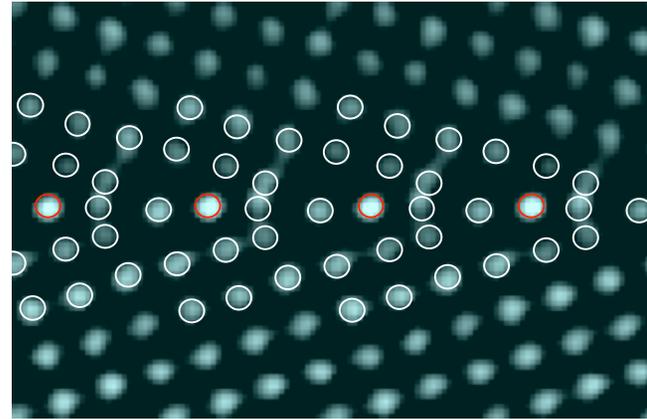


- Small energy difference between various arrangements of Cu on the second layer sites
 - expect compositional disorder on those sites
- Segregation saturates after about 2 Cu atoms per CSL cell for concentrations below solubility limit.
 - Segregation energy for third Cu does not overcome bulk configurational entropy
 - $TS_c \sim 0.2 \text{ eV}$
 - Confirmed by simple analytical segregation model

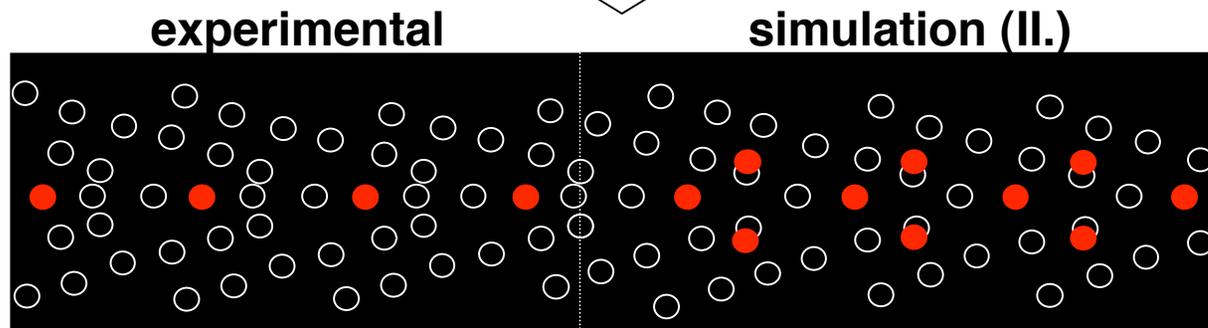
HRTEM observations are clearly at odds with this predicted structure



Reconstructed phase image



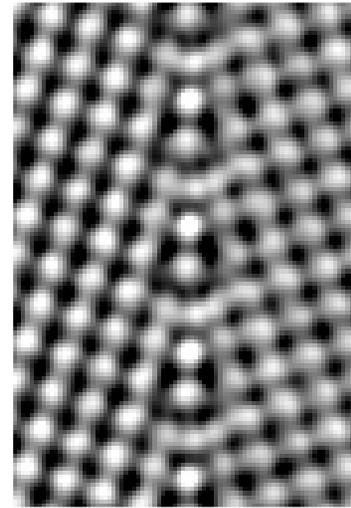
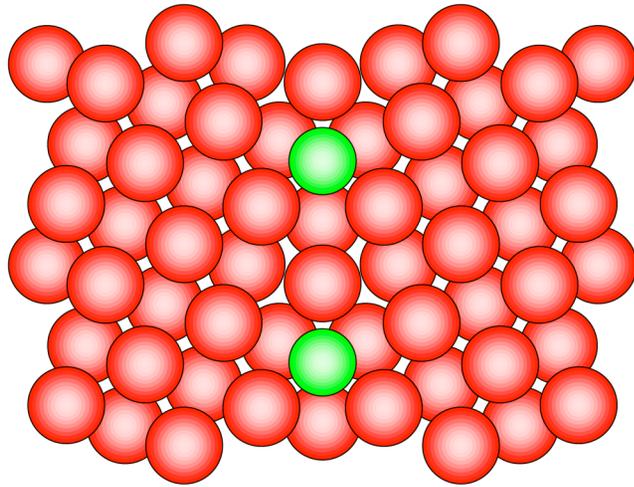
Extracted structure



experimental

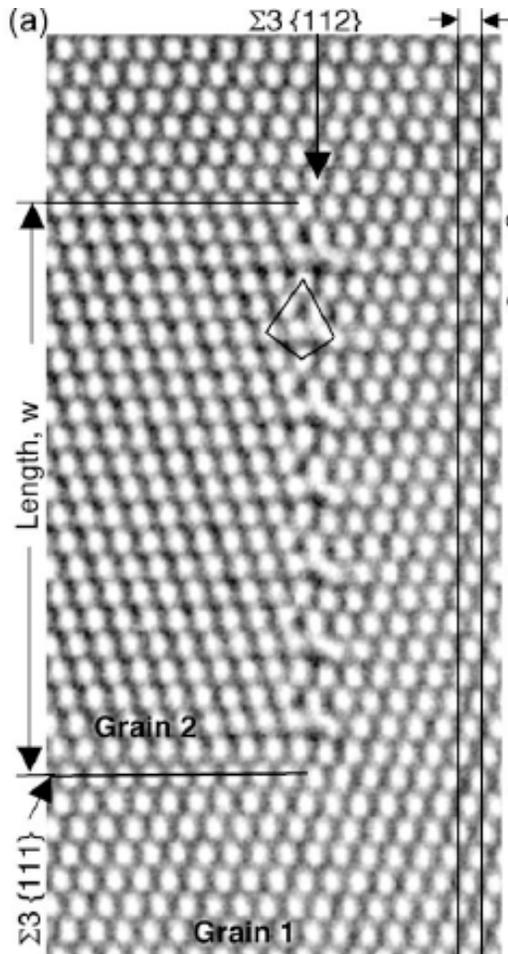
simulation (II.)

Interstitial Cu is energetically very favorable at Al $\Sigma 5(310)$ grain boundary



- Cu strongly segregated to the interstitial site
 - Segregation energy ~ 0.65 eV
 - larger than to any of the substitutional sites
- Three-atom repeat in the central plane in agreement with the experimental observation
- Enhanced contrast in experimental image does *not* correspond to the interstitial site
- *Bulk substitutional impurity is interstitial at the interface!*

Finite-size effect in Grain Boundary: Nanoscale interfaces \neq Bulk interfaces?



- Shift along $\Sigma 3 \{112\}$ grain boundary depends on the boundary length
 - Planar boundaries are assumed to be shifted
- Transition between shifted and unshifted depending on length
 - Calculated and observed experimentally

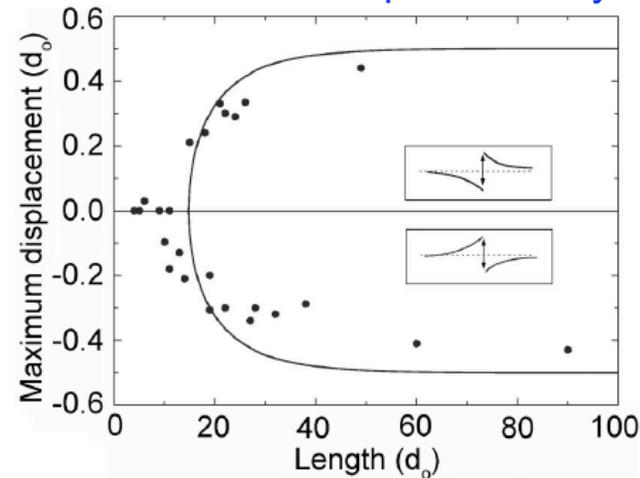
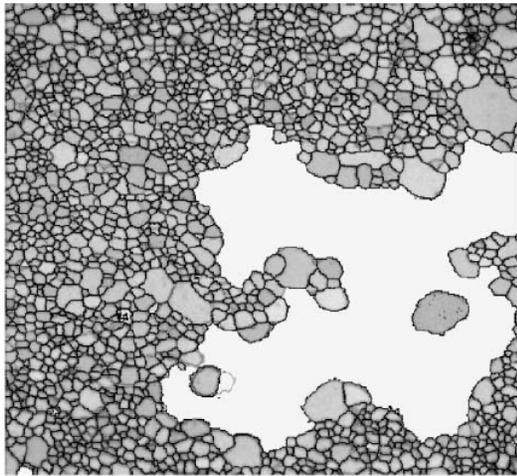


FIG. 4. Maximum local displacement versus grain boundary length. The solid line is obtained from Eq. (8) and $\lambda = 870$; see text for details.

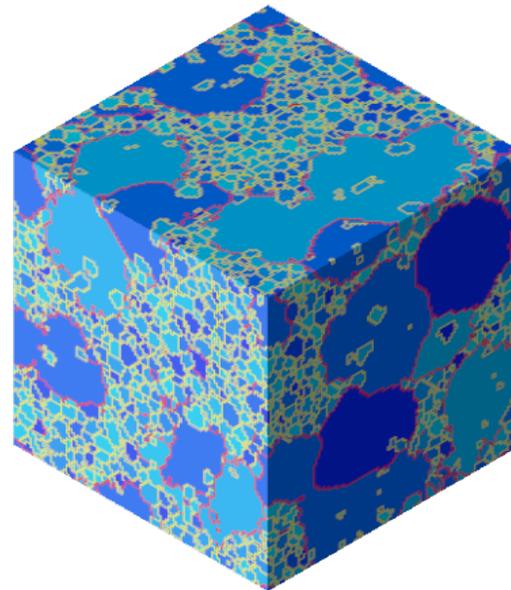
Why do we need to know the grain boundary mobility?

- In silicon steels, abnormal growth of Goss texture grains gives favorable electrical properties



(b) 240.0 μm = 80 s

Goss grain (white) in Fe-3%Si steel
A. L. Etter *et al.*, *Scripta Mater.* **47** 725 (2002)

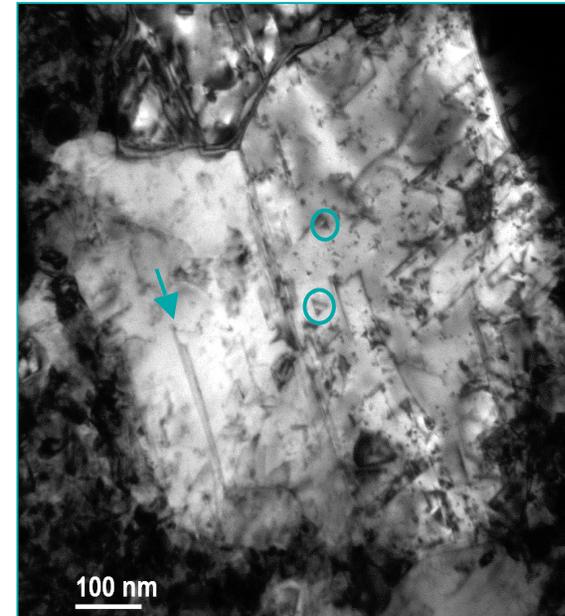


simulation captures abnormal growth phenomenology

- The only simulation input (beyond normal grain growth physics) is a grain boundary mobility function that depends on crystallography.
- What is the crystallographic dependence of grain boundary mobility?

Abnormal grain growth in nanograined metals leaves defects in growing grains

- In conventional metals, recrystallization and/or abnormal grain growth results in largely defect-free grains
- Abnormal grain growth in nanograined metals leaves stacking fault tetrahedra and twin boundaries in the growing grain
 - SFT related to the excess volume associated with the grain boundary?



Abnormal grain growth in nanograined Ni
D. Follsteadt, SNL/NM

Is there a faster, better, cheaper way to measure mobility?

Goal: Measure **mobility** of **flat** boundaries of **arbitrary crystallography** using **small system** size and **short run** times.

Idea: Use a mesoscale paradigm

- When we want a boundary to move, we just give it a driving force
- Why not do the same on the atomic scale?

For an atom in the favored/growing grain:

$$\varphi = \varphi_{EAM}$$

For an atom in the unfavored/shrinking grain:

$$\varphi = \varphi_{EAM} + u$$

Additional free energy per atom drives the unfavored grain to shrink; thus the boundary moves. This energy is of undetermined, arbitrary origin.

Constructing the artificial potential

- Define an order parameter:

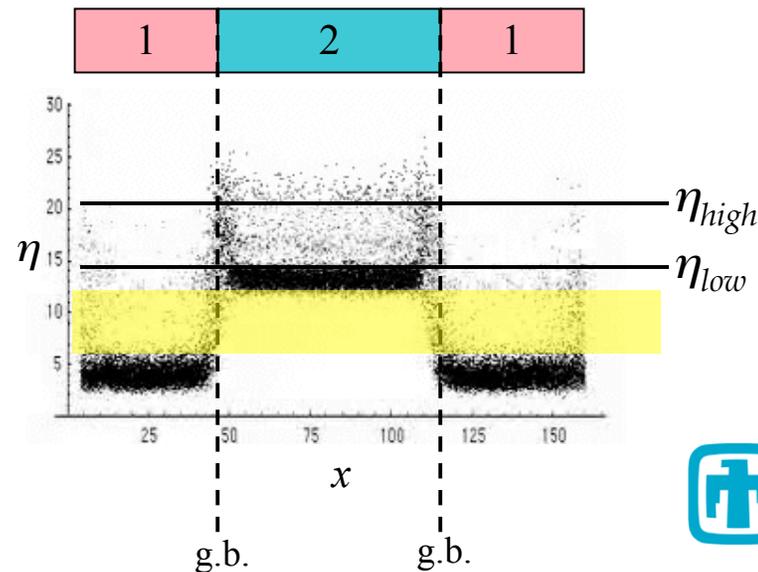
$$\eta_i = \sum_{j=1}^{nn} |r_j - r_j^*|$$

ideal position in orientation 1

$\eta_i = 0$ for perfect atoms in grain 1
 $\eta_i \equiv \eta_{12} > 0$ for perfect atoms in grain 2

- At finite temperatures, atoms in grain 1 have a spread of non-zero η 's \Rightarrow We define atoms with $\eta_i \leq \eta_{low} = f \eta_{12}$ to be "perfect" grain 1 atoms. Likewise, atoms with $\eta_i \leq \eta_{high} = (1-f) \eta_{12}$ are "perfect" grain 2 atoms.

- Thus, only atoms with $\eta_{low} < \eta_i < \eta_{high}$ are grain boundary atoms:

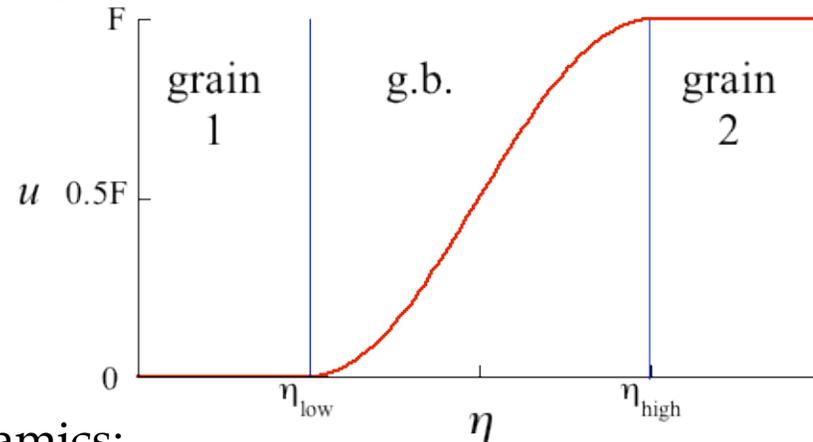


Adding the excess free energy

- Define the excess free energy function as:

$$u(r_i) = \begin{cases} 0 & \eta_i \leq \eta_{low} & \text{grain 1 atoms} \\ \frac{F}{2}(1 - \cos 2\omega_i) & \eta_{low} < \eta_i < \eta_{high} & \text{g.b. atoms} \\ F & \eta_{high} \leq \eta_i & \text{grain 2 atoms} \end{cases}$$

where $\omega_i = \frac{\pi}{2} \frac{\eta_i - \eta_{low}}{\eta_{high} - \eta_{low}}$



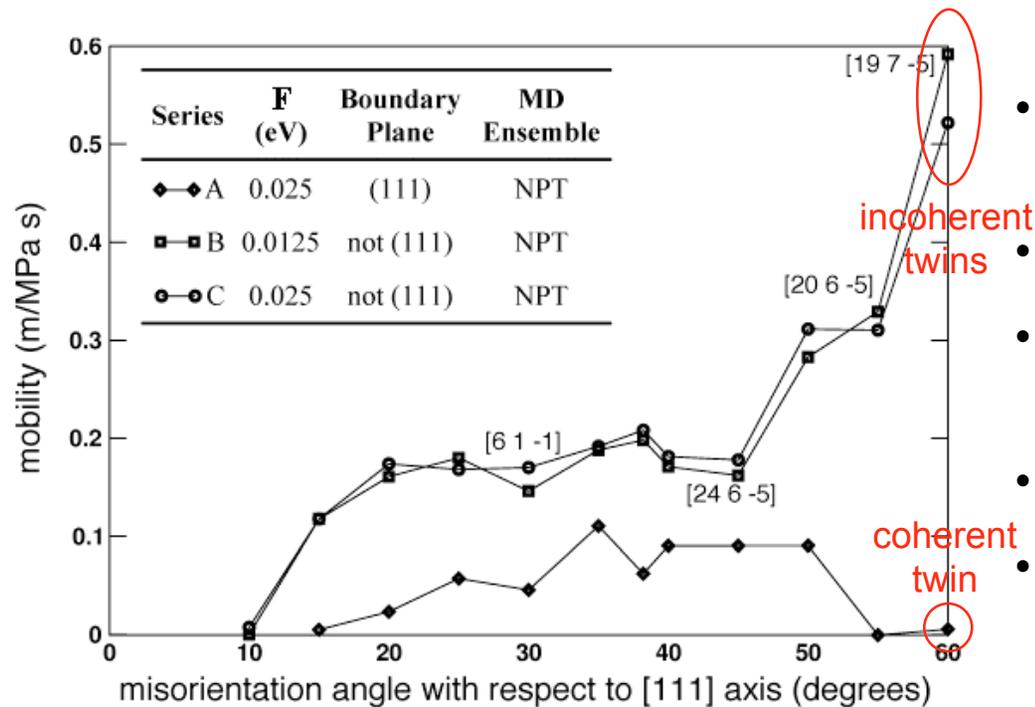
- Now, we just run molecular dynamics:

Our potential: $\varphi(r_i) = \varphi_{EAM}(r_i) + u(r_i)$ and force: $f(r_i) = -\frac{\partial \varphi(r_i)}{\partial r_i}$

We implement these in Sandia's LLAMPS code for MP MD.

Crystallographic dependence of mobility

For pure and mixed (111) twist boundaries in Al:



- M is comparable in form and magnitude with other simulations and experiments
- Low angle boundaries are low mobility
- $\Sigma 7$ 38° [111] is a cusp; $\Sigma 3$ 60° [111] is a well
- Mixed-type boundaries have higher M
- The mixed $\Sigma 3$ boundary is the highest yet measured; the pure $\Sigma 3$ is the lowest

⇒ It is clear that grain boundary plane is critical.

Grain Boundary Stiffness has been almost unstudied to date

- The boundary stiffness is the driving force for curvature driven boundary migration
 - $\Gamma = \gamma + \gamma''$
- The grain boundary energy ($T=0$) has been computed by a variety of authors
- The finite temperature grain boundary free energy has received some attention
 - The temperature dependence is significant!
- Finite temperature stiffness difficult to address through simple computation of γ for various orientations
 - Numerical issues
- 2D studies of boundary stiffness
 - Lobkovsky, A.E., A. Karma, M. I. Mendeleev, M. Haataja, and D.J. Srolovitz (2004), *Acta Materialia* **52**, 285-292.
 - Traut, Z.T., M. Upmanyu (2005), *Scripta Materialia* **52**, 1175-1179.

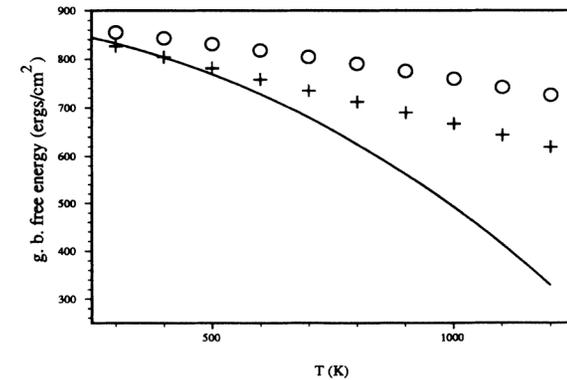
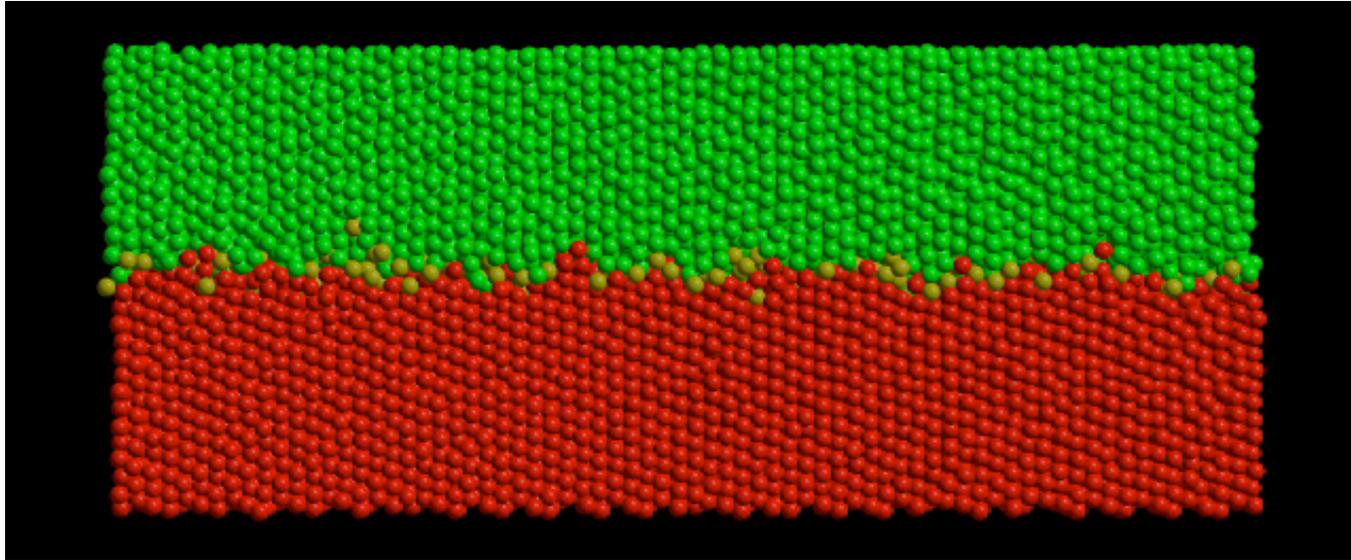


FIG. 9. The interfacial free energy of a Cu $\Sigma 5$ (310)/[001] symmetric tilt boundary as computed from the MC simulations (solid line), QH method (pluses), and LH method (circles).

Interfacial fluctuations observed in molecular dynamics simulations



- Temperature: 1400K
 - $T/T_M = 0.89$
- View along $[-1\ 1\ 0]$ / $[13\ -2\ -11]$ directions
- Color indicates range of value of p_i
 - $p > 0.1$, $p < -0.1$, $-0.1 < p < 0.1$
- Movie shows 75 ps of physical time
 - Frames are separated by 0.5 ps
 - Results are based on 3 ns (40 times length of movie)

The interfacial stiffness can be determined from the fluctuation spectrum

$$A(\vec{k}, t) \approx \sum h(\vec{R}, t) e^{-i\vec{k} \cdot \vec{R}}$$

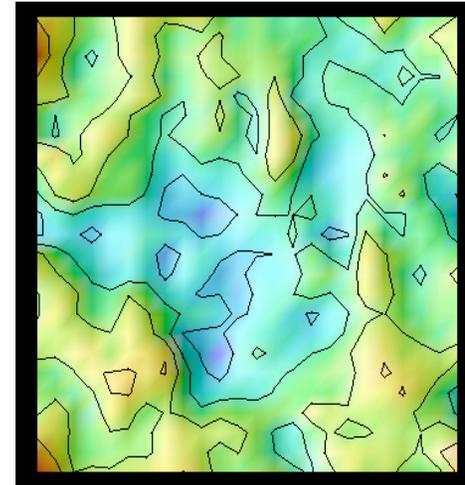
Long wavelength limit
(equipartition theorem)

$$\left\langle \left| A(\vec{k}) \right|^2 \right\rangle = \frac{k_B T}{L_x L_y \Gamma(\hat{k}) k^2}$$

L_x = length of cell in x

$$\Gamma(\hat{k}) = \gamma + \gamma''$$

Snapshot of interfacial height



Height variation $\sim 4\text{\AA}$

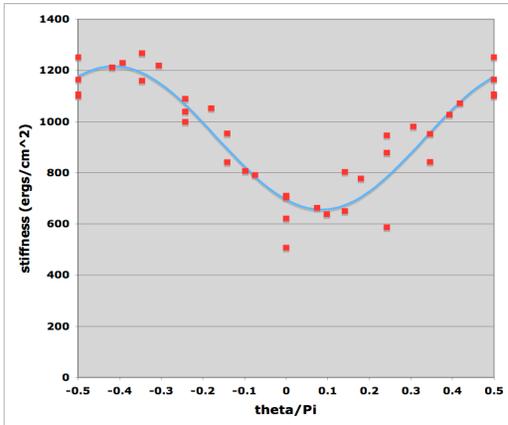
- $A(k, t)$ is computed at intervals of 0.5 ps for a period of 3 ns
- Long-wavelength values do not depend on the details of how the height profile was determined
- All quantities are known except for the stiffness, Γ
- Note that the interfacial stiffness depends on the direction due to the second derivative term

The stiffness, Γ , is not isotropic within the plane

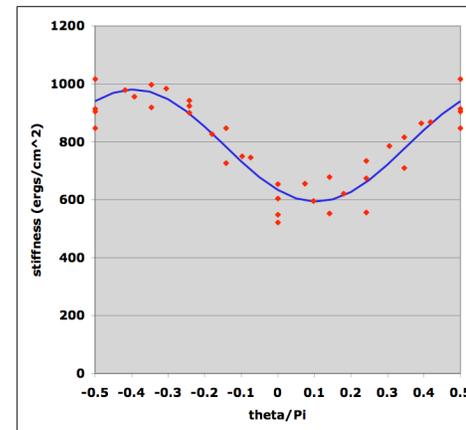
- Compute the stiffness for all k values with $|k| < 0.2 \text{ \AA}^{-1}$
- The average value of Γ decreases with increasing temperature
 - Consistent with finite temperature calculations of γ
- The variation with angle fits a simple cosine behavior
 - Simplest form consistent with symmetry

$$\Gamma(\hat{k}, T) = A(T) + B(T)\cos(2\theta_k + \delta(T))$$

1250 K ($T/T_M = 0.80$)



1400 K ($T/T_M = 0.89$)



Many outstanding challenges for atomistic simulations of interfaces remain

- How to handle the combination of *continuous* and *discrete* variables in determination of interface structure
 - Relaxation of atomic position
 - How many atoms?
 - Where do the different atomic species reside
- Interatomic interactions for interfacial properties determination
 - Empirical potentials are often limiting
 - Insufficiently transferable
 - Simply do not exist in many (most?) interesting cases
 - First principles often too computationally intensive to survey the full range of structures
- Dynamic properties of interfaces have only beginning to be explored
 - Impurity issues are critical!
- Thermodynamics of interfaces have not been thoroughly explored
- Interfaces in confined geometries (eg. Nanoscale systems) can be different from ideal planar interfaces
 - Do we even understand planar interfaces yet?!?

Atomistic Simulation of Interfaces: Does the Emperor have any Clothes?



**We may be ‘scantily clad’,
but we have a great body!**

What do we need from atomistic simulations for simulations to be 'predictive'

- Do we need to get everything quantitatively right?
 - That is a VERY TALL order!
- Is it sufficient for atomistic to identify qualitative and/or semi-quantitative results
 - Insight into mechanisms
 - Order of magnitude of effects
 - How 'right' do the calculations have to be in order to be able have faith in the qualitative results?