# Grain Boundary Structure and Dynamics: a tutorial

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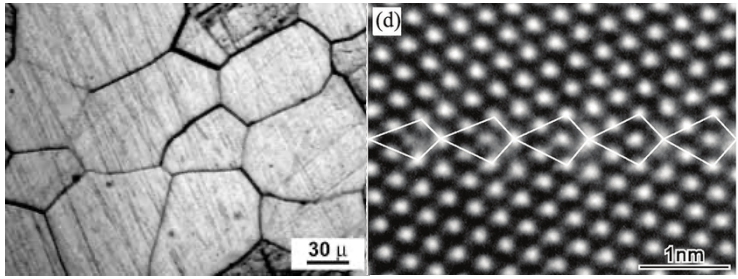
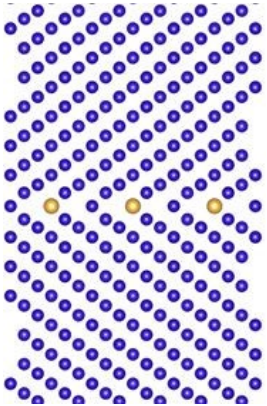
# About This Tutorial

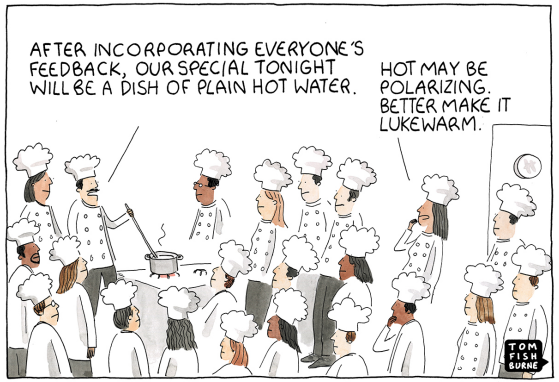
- **A "modern" view of grain boundaries**
  - The study of GBs is ~1 century old
  - Like most fields, it advanced irregularly
    1920s, 1960s, 1980s, 2000s
  - The past decade is another one of these times

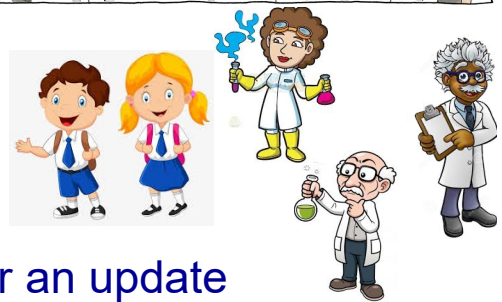



- **What this tutorial is about**
  - GB structure, thermodynamic properties, and dynamics
  - How they are related
  - More ideas and concepts, than details
  - Focus on pure materials



- **What this tutorial is NOT about**
  - A survey or review of the field
  - A discussion of GB chemistry effects



- **Who is this for?**
  - Students new to the field
  - Scientists/engineers from peripheral areas or those looking for an update

# About This Tutorial

## Four lectures

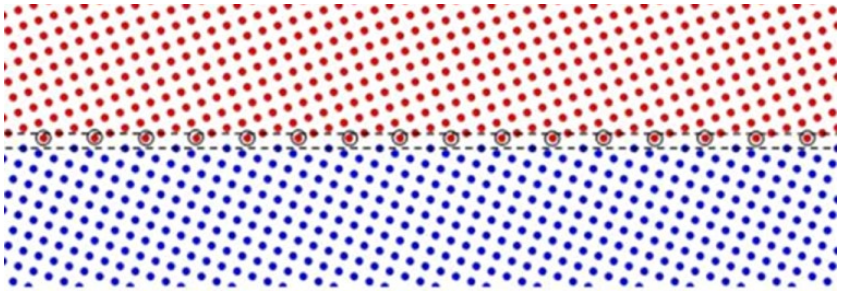
1. GB basics, low angle GBs, structural unit model
2. GB thermodynamics, metastability, defects
3. GB dynamics
4. Continuum, microstructure issues

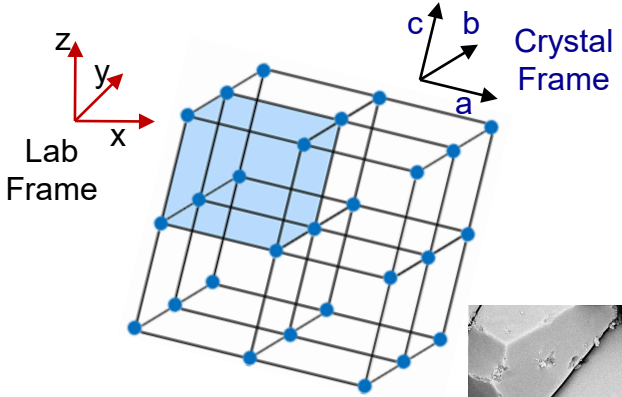
## Lecture 4

- references and reading material
- collaborators, acknowledgements

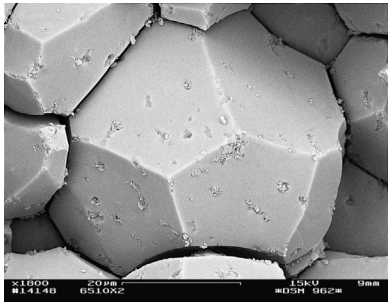
# What is a Grain Boundary?

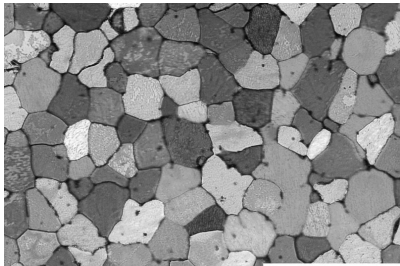
- **An interface across which grain <u>orientation</u> is discontinuous**





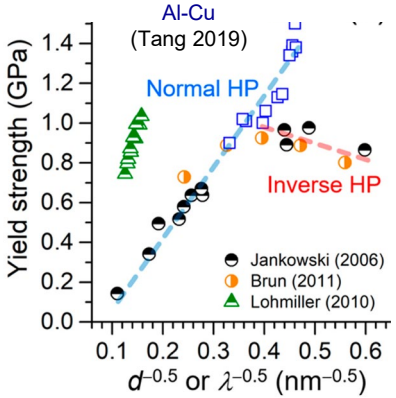

- **Grain boundaries in the "wild"** (rather than domesticated, lab GBs)
  - Grains are finite-size domains of ~fixed crystal orientation
  - GBs are rarely flat
  - Microstructure:
    - Spatial arrangement of grains / crystal orientations
    - GB and GB triple-line networks
  - Manipulate microstructure through thermomechanical processing
  - Grain boundary engineering

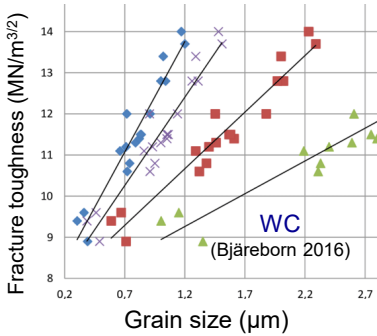




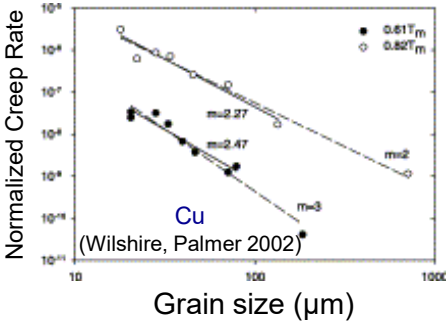
# How Do GBs Affect Material Properties?

- **GBs and mechanical deformation**
  - Yield strength:
    - GBs block dislocations (smaller is stronger) – Hall-Petch
    - GBs slide (smaller is weaker) – inverse Hall-Petch
  - Fracture toughness
  - Creep
  - Fatigue (crack nucleation vs growth)
  - …



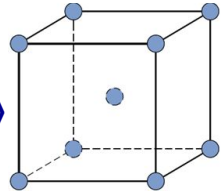



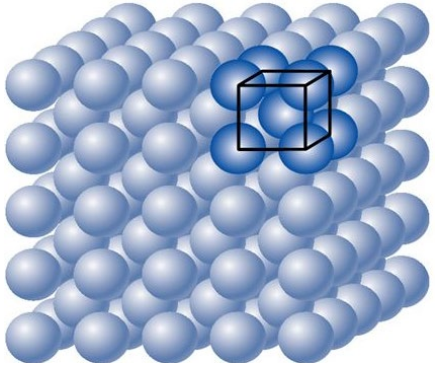

- **GBs and electrical/optical behavior**
  - Metals: resistance ⇧ as grain size ⇩
  - Semiconductors: GBs are recombination sites
  - Polycrystalline ceramic varistors: electrical breakdown at GBs
  - Conductivity of superionic ceramics ⇧ as grain size ⇩
  - In some semiconducting 2d materials, GBs are metallic
  - Optical transparency: diffuse scattering ⇧ as grain size ⇩
  - Solar cells: photoluminescence quantum yield/conversion efficiency ⇧ as grain size ⇧



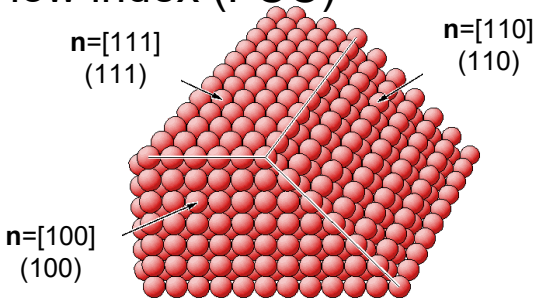
# Macroscopic Degrees of Freedom

- **Surface**
  - Consider a body centered cubic (BCC) lattice
  - Cleave it to create surfaces; choose normal **n**=⟨*pqr*⟩
  - Different surfaces {*pqr*} have different structures

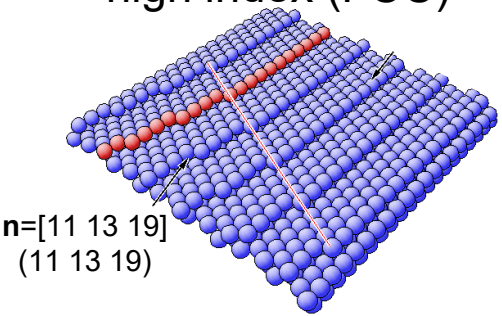




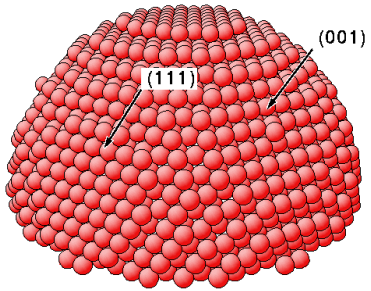
low index (FCC)




high index (FCC)



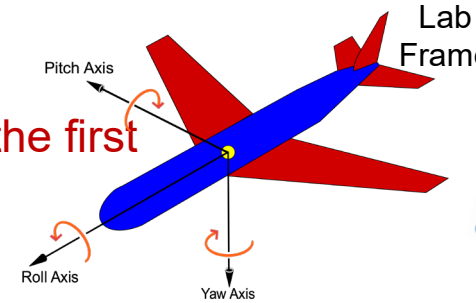

curved surface **n** = f($\theta_1$,$\theta_2$)

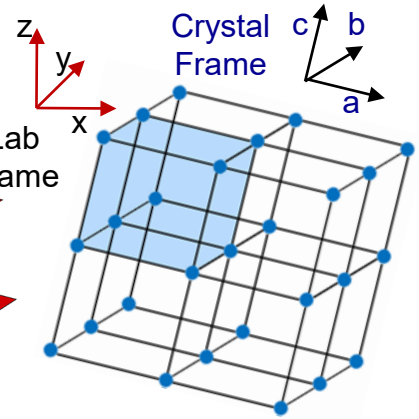


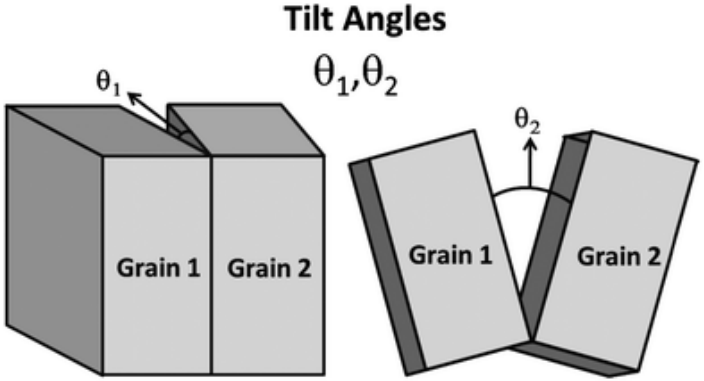

  - Surface normal – 2 degrees of freedom **n** = ⟨*pqr*⟩ = f($\theta_1$,$\theta_2$)
    because the normal is a unit vector (just direction): $p^2 + q^2 + r^2 = 1$

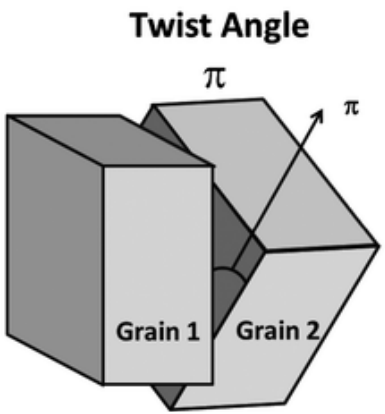
# Macroscopic Degrees of Freedom

- **Grain/crystal orientation**
  - 3 angles/parameters set crystal orientation w.r.t. lab frame
  - GB → 2 crystals:
    - Fix the orientation of the 1st : arbitrary
    - Fix the orientation of the 2nd relative to the first
  - 3 parameters/angles define misorientation
  - Many ways to do this
  - Here's a common one



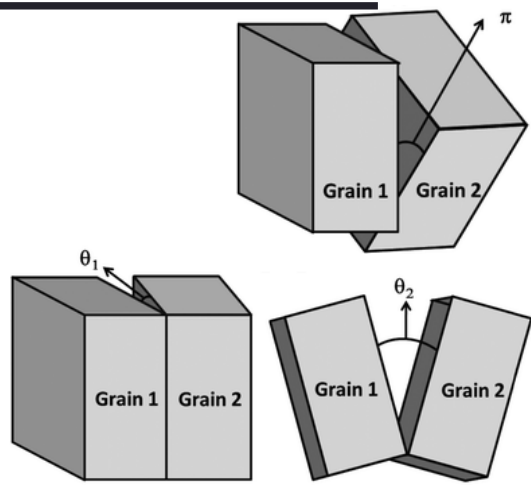




  - Another is to specify a rotation axis (2 parameters) and a rotation angle (1 parameter)

# Common Terminology

- **Twist Grain Boundary**
  - Rotation axis is perpendicular to GB plane
- **Tilt Grain Boundary**
  - Rotation axis lies within the GB plane
  - Symmetric tilt GB: GB is a mirror plane
- **Mixed (tilt/twist) and Asymmetric Grain Boundary**
  - Asymmetric: not symmetric/rotation axis in the GB plane
  - Mixed: rotation axis does lie within the GB plane
- **Faceted Grain Boundary**
  - Decomposition of GB into *flat* planes of other (more symmetric) GBs



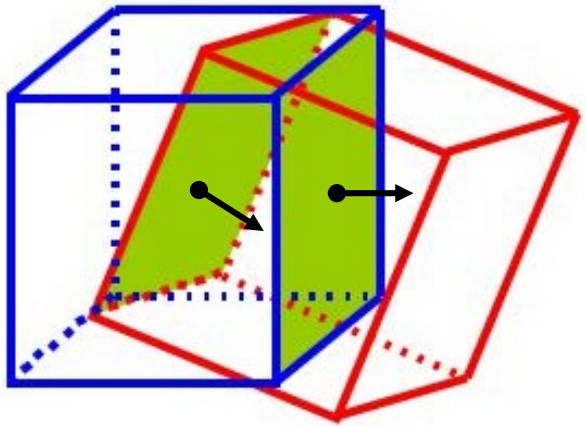

Twist GB Symmetric Tilt GB Asymmetric Tilt GB Mixed GB Faceted GB

Faceted GB

**O**: rotation axis, $\Theta_o$: asymmetry (inclination) angle , $\Theta_p$: mixed (inclination) angle

# Macroscopic Degrees of Freedom

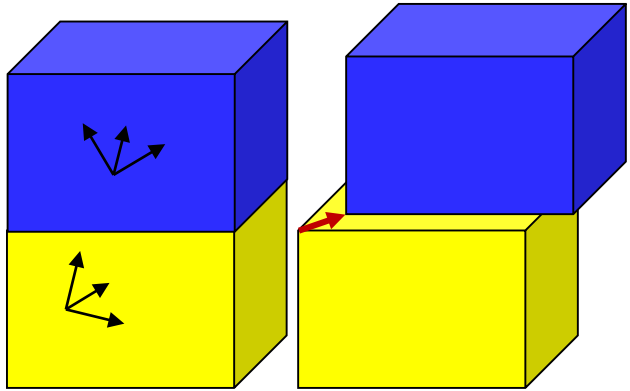
- **Grain boundary bicrystallography variables**
  - Once the misorientation between the grains is fixed (3 angles/parameters), choose the GB inclination – like for a surface (2 angles/parameters)



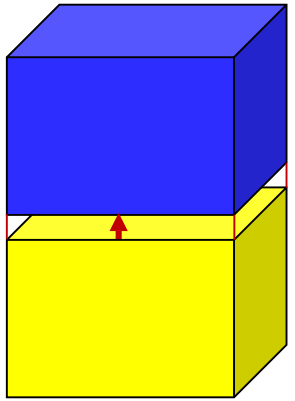
- GBs have **3+2=5** macroscopic, bicrystallographic degrees of freedom
  - These degrees of freedom are for *continuum* (structureless) grains
  - Does not depend on crystal structure or atomic structure of the GB

# Microscopic Degrees of Freedom

- In-plane translations of one structureless grain with respect to another do not change anything
- But, when the grains have an atomic structure, in-plane translations change GB structure & energy
- These lateral translations create 2 additional *conservative* degrees of freedom

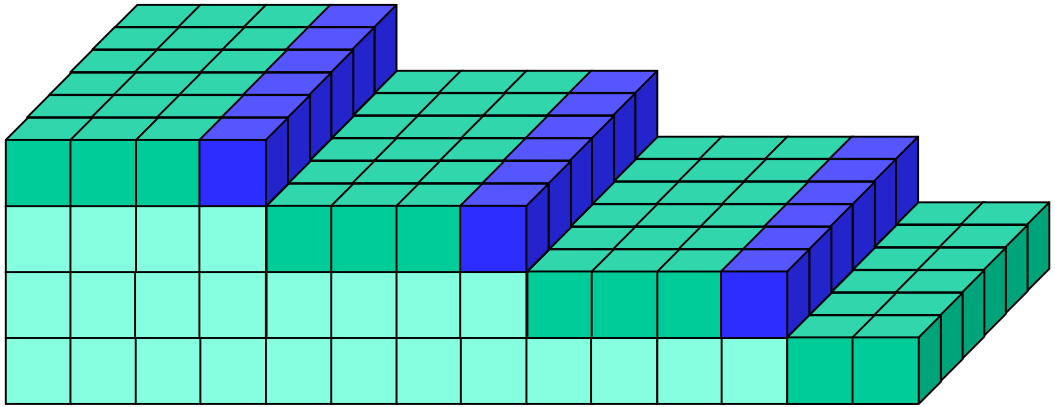


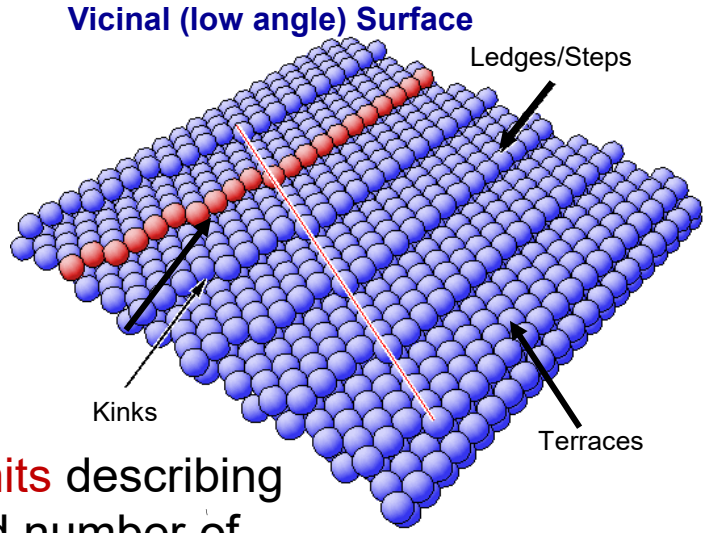
- We can also translate one grain with respect to the other in the direction normal to the GB plane
- This is a single, *non-conservative*, *microscopic* degree of freedom
- Requires the addition or removal of “extra atoms” at the GB plane



# **Surface Structure:** a brief digression

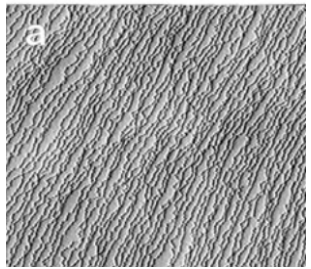
- A surface (at least at low T) can be viewed as an ensemble of terraces, ledges (or steps), kinks and adatoms






- Can think of the surface as made up of structural units describing *terrace units* and *step units*, each with a fixed number of broken bonds/atomic bonding arrangement (topology)

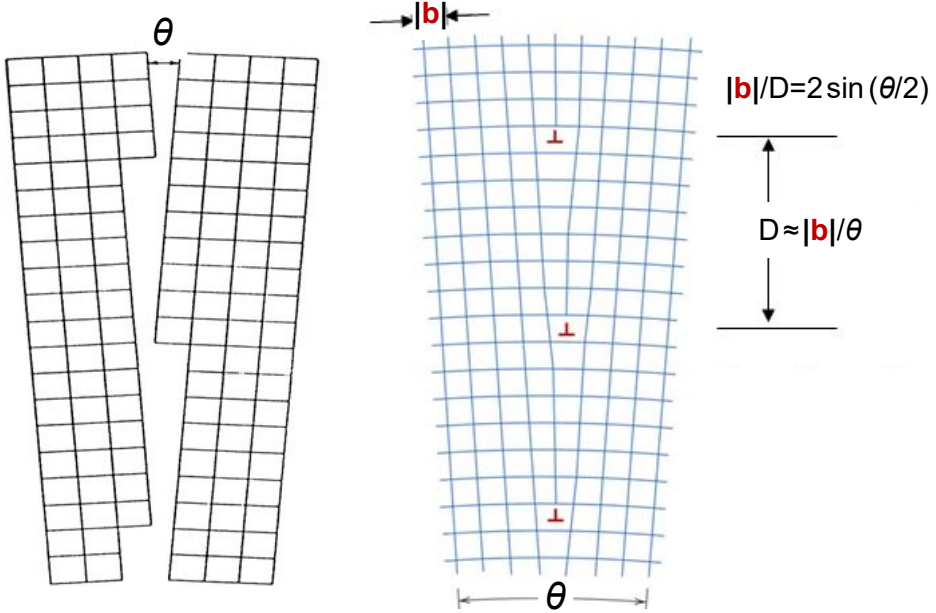
- Small changes in miscut angle (deviation from terrace normal) simply changes the relative number of *terrace units* and *step units* per unit length/area

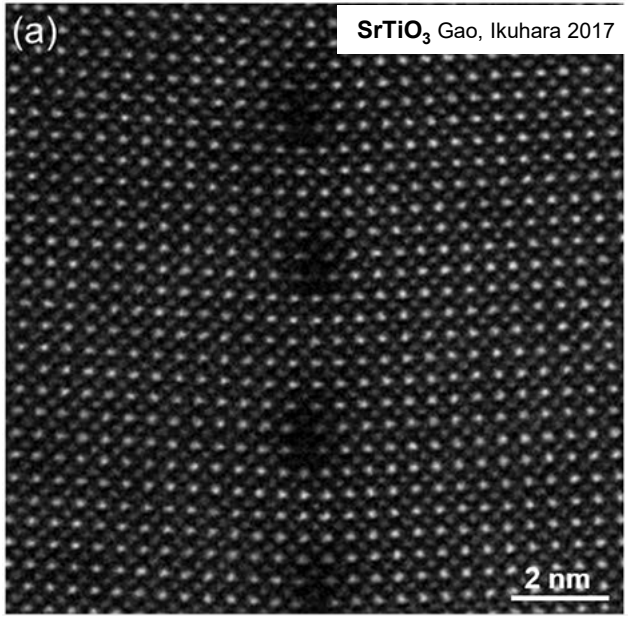



Vicinal (001) Si
Patella, 2004

# Low Angle Grain Boundaries

- Create a low angle grain boundary by joining two vicinal surfaces, each w/normal $\theta/2$ from the singular orientation: **surface steps → edge dislocations**



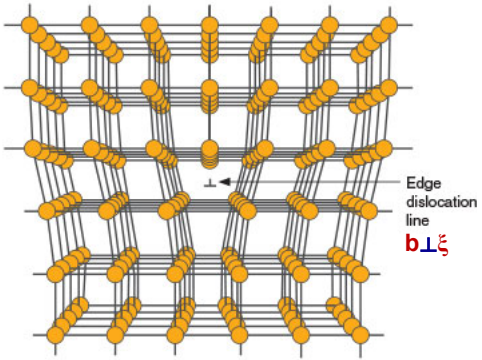



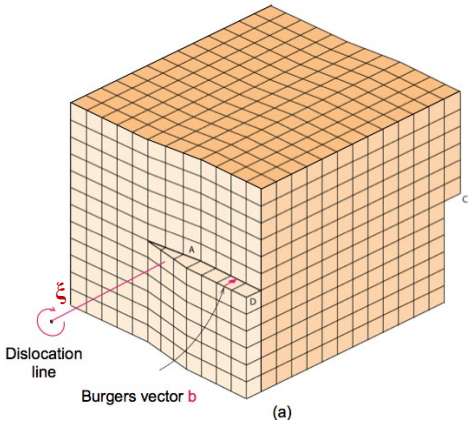

- A low angle GBs can be thought of as a combination of two structural units:
  an edge *dislocation core unit* + a *perfect crystal unit*
- *Perfect crystal units* have the same bonding topology as the crystal but may be distorted
- Far from the GB, the crystals are perfect (undistorted)

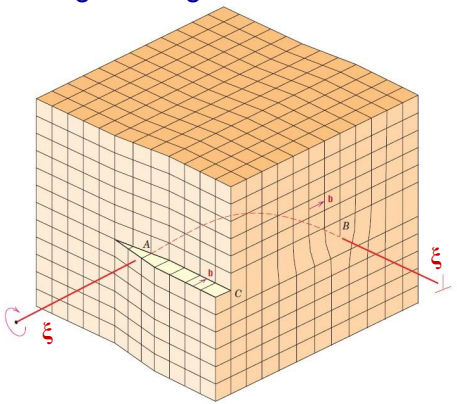
# Dislocations & Dislocation Arrays

- Dislocations are characterized by a Burgers vector **b** and line direction ξ: edge **b⊥ξ**, screw **b||ξ**

Burgers vector – constant along dislocation
Line direction – changes along curved dislocation




All (non-zero) components of the dislocation stress field:

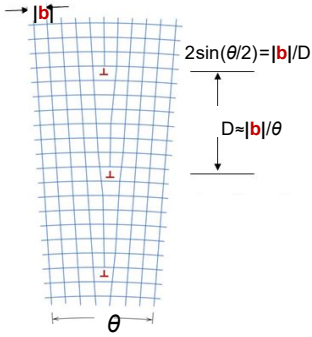
$$\sigma \sim \frac{\mu b f(\theta)}{r}$$

Elastic energy per unit length:

$$\frac{E}{l} \sim \mu b^2 \ln\left(\frac{R}{r_c}\right) + e_c$$

where $r_c$ and $e_c$ are the dislocation core size and core energy (per unit length) – determined self-consistently

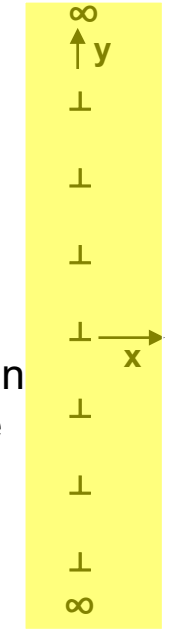
# Dislocations & Dislocation Arrays




- Consider an array of edge dislocations as in the tilt GB
- The stress field of this array $\sigma_{xy} \cong \frac{2\pi\mu b x}{(1-\upsilon)} e^{-2\pi x/D} \cos\frac{2\pi y}{D}$
- The stress field decays exponentially with $|x|$ and is periodic in $y$
- The low angle GB (Read-Shockley) energy associated with the dislocation array is

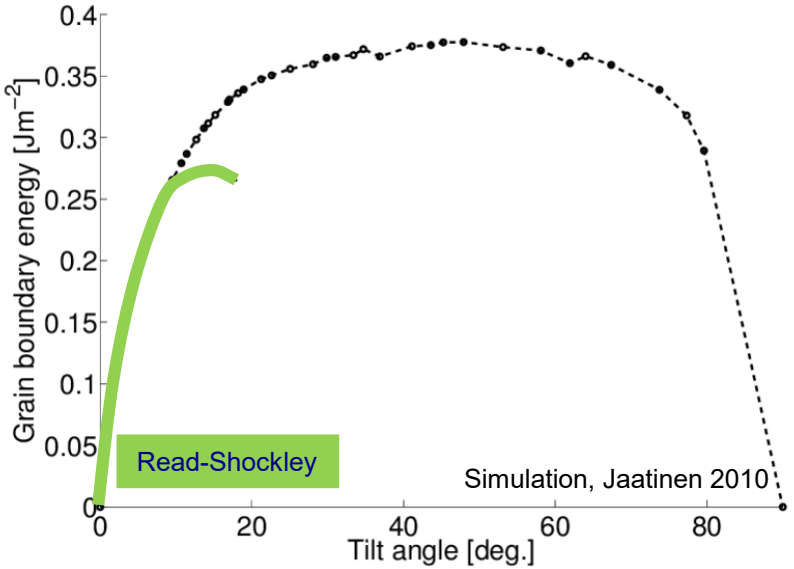
$$\gamma \cong \frac{\mu b^2}{4\pi(1-\upsilon)D} \ln\left(\frac{e\alpha D}{2\pi b}\right) = \gamma_0 \theta \ln\left(\frac{e\theta_m}{\theta}\right)$$

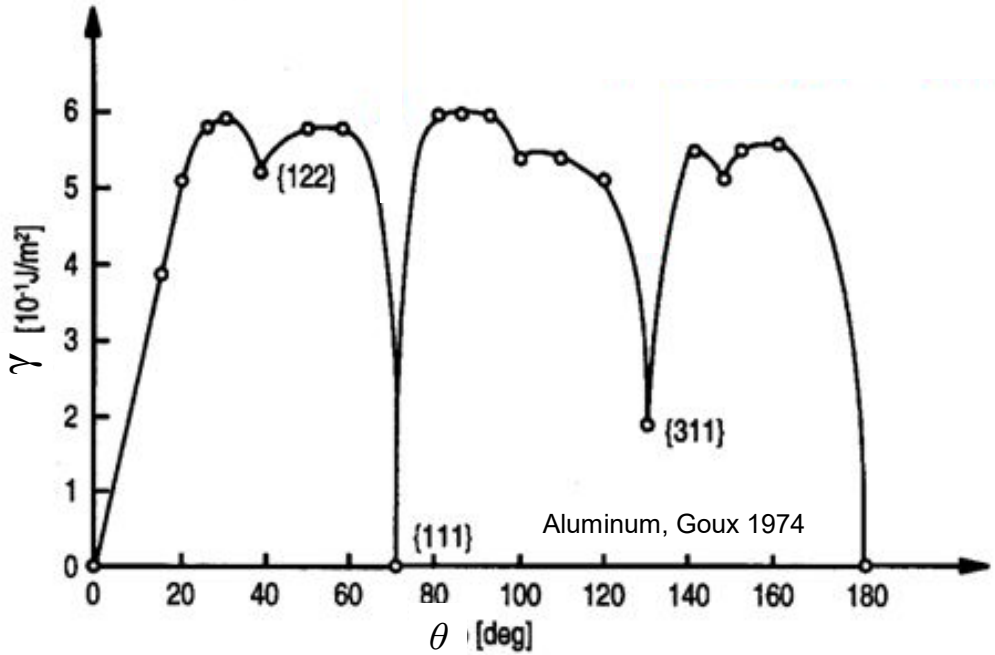
where $\alpha = r_c/b$, $\theta_m = \alpha/2\pi$ and $\gamma_0 = \mu b/4\pi(1-\upsilon)$ – note that the dislocation core energies are buried in this expression by the appropriate choice of $r_c$ and $\theta_m$



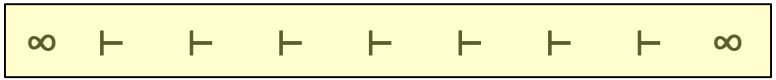

- This energy is finite although the strain energy associated with a single dislocation is infinite – this is because the array of dislocations screens the stress field of the individual dislocation (an infinite order multi-pole)

# Dislocations & Dislocation Arrays



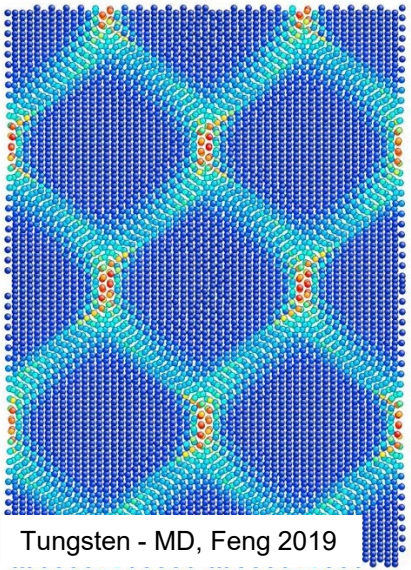




When dislocation spacing becomes comparable with dislocation core size, the dislocation model (Read-Shockley) for low angle GBs **fails** : the energy is dominated by the core NOT elasticity

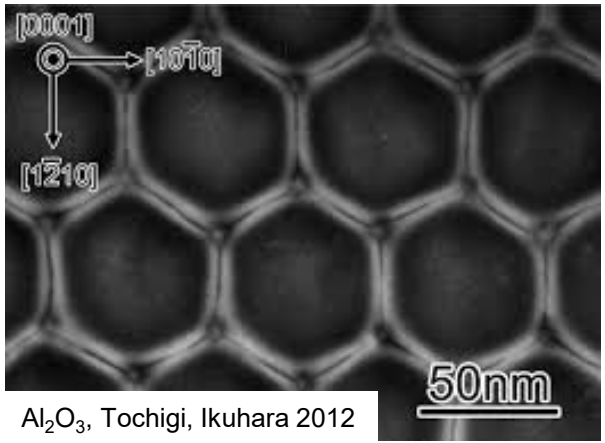


# Low Angle Grain Boundaries

- Previous discussion of low angle GBs focused on pure tilt GBs
- For pure twist GBs, the dislocations must have screw character; to cancel long-range stress field at least 2 sets of dislocations (**b**'s) are required
- For general low angle GBs (mixed, asymmetric) at least 3 sets of dislocations are required



Tungsten - MD, Feng 2019




$Al_2O_3$, Tochigi, Ikuhara 2012

# Low Angle Grain Boundaries: conclusions

**What are the key take away points from consideration of vicinal surfaces and LAGBs that we can generalize?**

1. Planar interfaces can be described as an array of structural units; each with a unique atomic structure and bonding topology
2. The relative abundance of structural units depends on characteristic of the structural units (e.g., step height, Burgers vector) and macroscopic degrees of freedom (e.g., interface inclination, GB misorientation)
3. For vicinal surfaces/low angle GBs, the structural units correspond to terraces/perfect crystal AND steps/dislocations
4. For GBs, inclusion of elasticity for the dislocations is essential
5. Prediction of grain boundary energy requires description of the energy of the ideal structural units **(core structure and bonding)**, long range elastic effects **(elasticity)**, and the relative abundance/type of each structural unit **(bicrystallography)**

**Multi-scale:** bonding, atomic structure, continuum, crystallography

# Structural Unit Model for Large Angle GBs

## The structural unit model is based on the 3 central ideas:

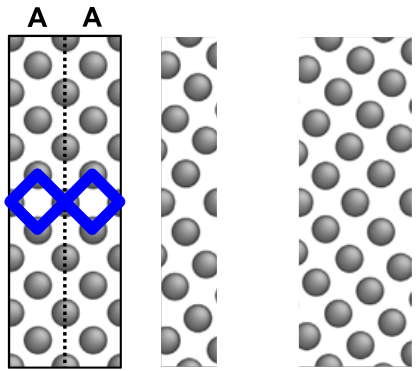
Bishop 1968
Sutton/Vitek 1983

1. **Describe GB structure as a 2D combination of structural units (SU); assign a letter to each** (choice is not fixed, but must be consistent)

**[100] Symmetric Tilt GB in a BCC Bicrystal**

Misorientation: $\theta_A = 0°$ $\theta_C =$ $\theta_B =$

SU sequence:




SU size: $p_A$

2. **SU Combination:**

- GB with only 1 type of unit: delimiting GB
- GBs with misorientation between delimiting GB angles are combinations of the SU from the delimiting GBs: ratio of # of units $f(\theta)$

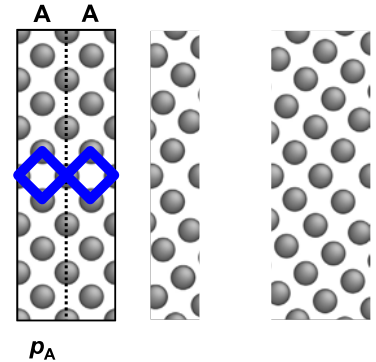
$$\frac{n_A}{n_C} = \frac{p_A}{p_C}\frac{\sin[(\theta_c - \theta)/2]}{\sin[(\theta - \theta_A)/2]}$$

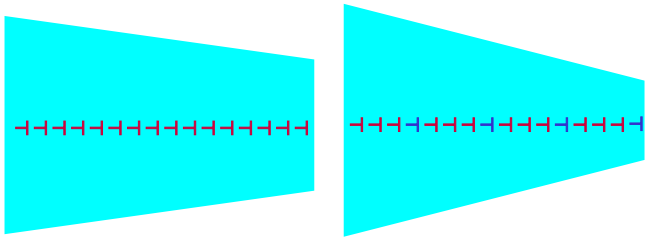
# Structural Unit Model

## 3. SU Sequence:

- Consider the delimitting GB with SU *"C"*: since $\theta$ is finite and there is only one SU, it must have an associated Burgers vector (with a component normal to the GB plane)
- Dislocations of same *b* repel one another, so minimize energy by maximizing their separation
- Consider $\theta = 18.92^{\circ}$: we can view the minority SUs *"C"* as dislocations on the delimiting *"A"* SU GB: these *"C"* SUs are secondary GB dislocations
- If there exists an $n_A$ and $n_C$ for a given $\theta$ that satisfies $n_A p_C \sin[(\theta - \theta_A)/2] = n_C p_A \sin[(\theta_c - \theta)/2]$, this GB is rational or periodic, if not, it is irrational (i.e., aperiodic)
- There is **nothing** physically special about a rational vs irrational (periodic or aperiodic GB)

$\theta_A = 0°$ $\theta_C =$ $\theta_B =$



# Grain Boundary Energy vs Misorientation

- Grain boundary energy: GB SU/core energy + elastic energy $\gamma(\theta) = \gamma^c(\theta) + \gamma^{el}(\theta)$
- The core energy depends on the geometry and energy of the delimiting GBs

$$\gamma^c(\theta) = \frac{1}{p}\left[n_x p_x \cos\left(\frac{\theta-\theta_x}{2}\right)\gamma_x + n_y p_y \cos\left(\frac{\theta_y-\theta}{2}\right)\gamma_y\right]$$

where the repeat distance $p$ and number of units of each type are

$$p = n_x p_x \cos\left(\frac{\theta-\theta_x}{2}\right) + n_y p_y \cos\left(\frac{\theta_y-\theta}{2}\right) \qquad \frac{n_x}{n_y} = \frac{p_y}{p_x}\frac{\sin[(\theta_y-\theta)/2]}{\sin[(\theta-\theta_x)/2]}$$

and $\gamma_x$ and $\gamma_y$ are the energies of the delimiting GBs

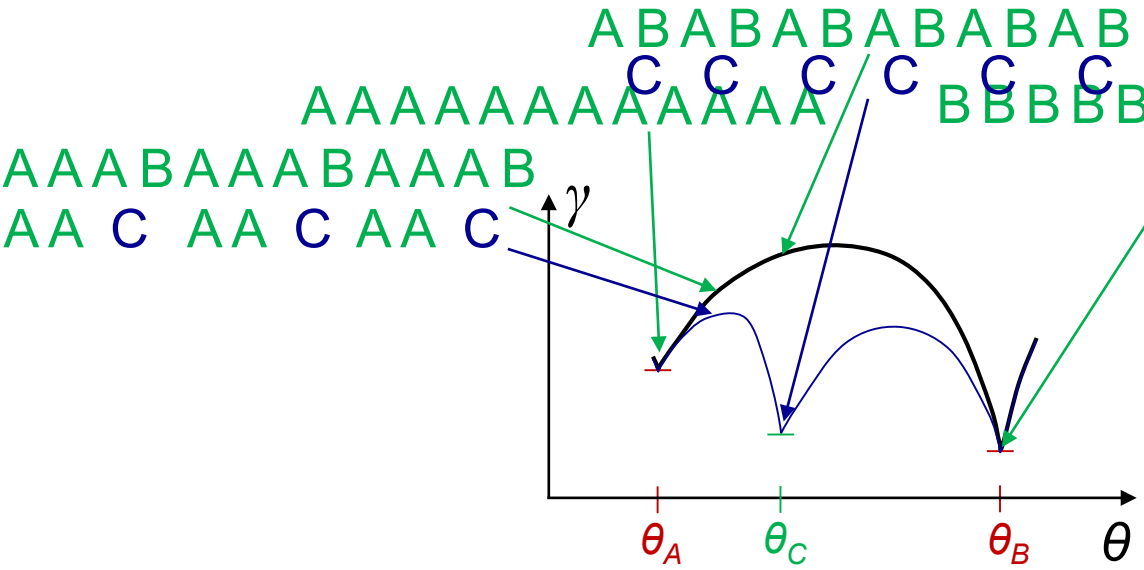
- The elastic energy is that of the secondary GB dislocation array $b_y = 2p_y \sin\left(\frac{\theta_y-\theta_x}{2}\right)$

$$\gamma^{el}(\theta) = \frac{\mu b_y^2}{4\pi(1-\nu)D_y}\ln\frac{eD_y}{2\pi\pi r_y}$$

or, more accurately (Li 1961) $\gamma^{el}(\theta) = \frac{\mu b_y^2}{4\pi(1-\nu)D_y}\left[\eta^* \coth\eta^* - \ln(2\sinh\eta^*) - \frac{\eta_0^2}{2}\mathrm{csch}\ \eta^{*2}\right]$, where $\eta_0 = \pi r_y/D_y$ and $\eta^*$ is the solution to $\eta^* \tanh\eta^* = \eta_0^2$

# Grain Boundary Energy vs Misorientation

- The key question is "where do we get $\gamma_x$ and $\gamma_y$ (the energies of the delimiting GBs)?"
- Since they depend on detailed atomic structure and bonding – resort to atomic-scale simulations



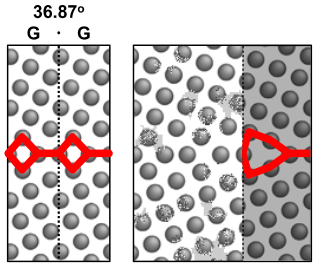

- Just like low angle GBs, this does NOT work when dislocations get too close together
- If minority SU are B, the SU model fails when secondary GB dislocations get too close

**Solution:**

- redefine a "combination" SU as AB→C
- do atomistic simulation for a C delimiting GB
- redo energy for $\theta_A \le \theta \le \theta_C$

**Iterative improvement → desired accuracy w/no or very little additional simulations**

# Grain Boundary Energy vs Misorientation




G=AB  H=CB

Recursive application of SU model by combining AB →C, AAAB→AC,…

solid curve: $\gamma^c$ (013) & (012)
dashed curve: $\gamma^c$ (013), (037), (012)

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solid curve: $\gamma$ (013) & (012) – no recursion

solid curve: $\gamma$ (013) & (012) – 5 recursion steps
dashed curve: $\gamma$ (013), (037), (012)