Atomic structure and dynamics of grain boundaries

Y. Mishin

Department of Physics and Astronomy

Co-authors and collaborators:

J. W. Cahn (NIST & Univ. of Washington)

V. Ivanov (GMU)

Supported by the US Department of Energy
(Office of Basic Energy Sciences)

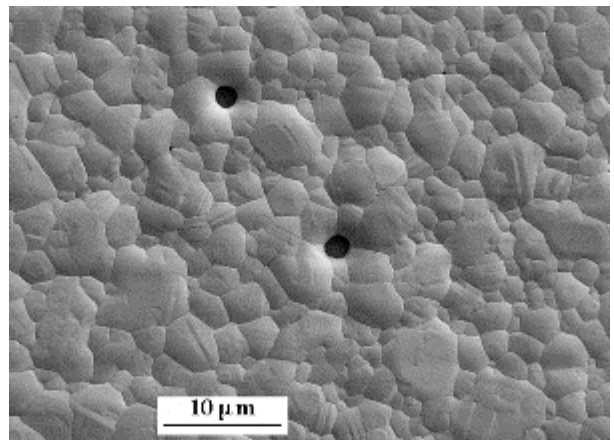
Applied and Computational Mathematics Seminar (October 5, 2007)

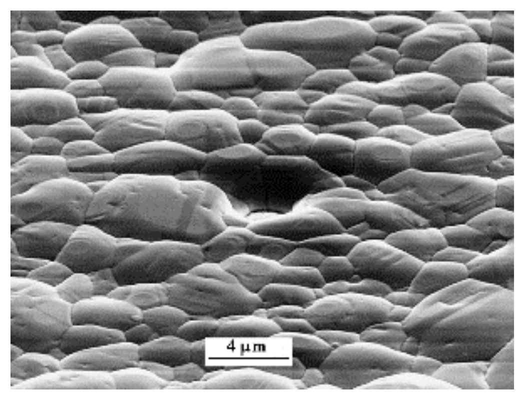
Contents:

- What are GBs and why should we worry about them?
- Geometric description of GBs
- Atomic structure of GBs at low and high temperatures
- GB motion: why do they move and how?
- GB motion coupled to shear deformation
  - Phenomenological description
  - Experimental evidence
  - Importance for materials science
  - Theory of modeling
  - **Dynamics of coupled GB motion**
- Conclusions

What are grain boundaries (GBs) and why should we study them?

- Most materials are polycrystalline, i.e. composed of crystallites (grains) separated by interfaces called **grain boundaries**
- GBs exist in metals, semiconductors, ionic crystals and even polymers
- GBs affect or even control many properties of materials, such as
  - GB diffusion
  - GB sliding
  - Mechanical strength
  - Fracture
  - Electric conductivity
  - Phase transformations
  - Nano-structured materials





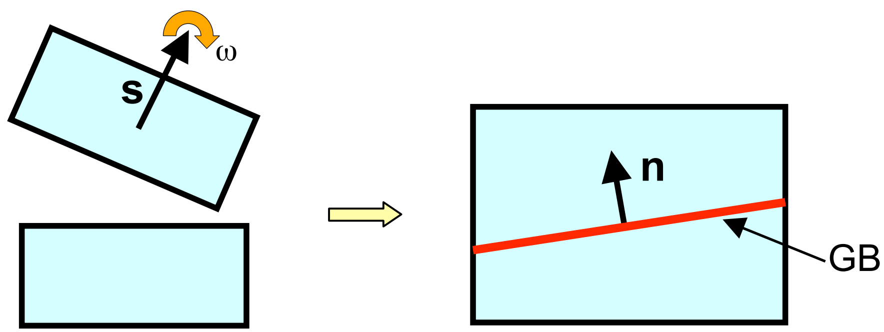
NiO thin film

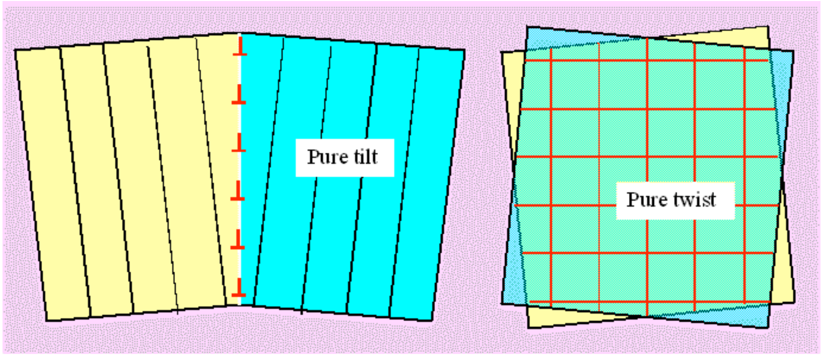
H. De Monestrol et al., *Interface Science* **11**, 379 (2003)

Geometric description of GBs

A GB is defined by 5 geometric parameters, called **macroscopic degrees of freedom**. One possible choice of the parameters:

- Rotate one grain relative to the other around an axis **s** by an angle ω
- Join the grains along a plane defined by a normal unit vector **n**





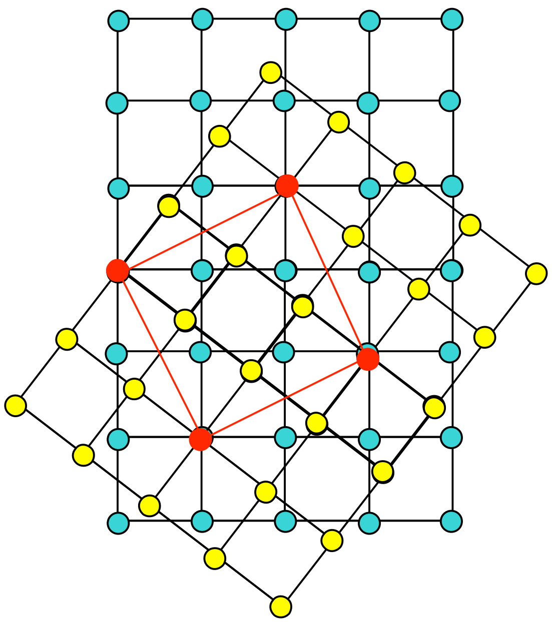
- GBs with **s**||**n** are called **twist** GBs
- GBs with **s**⊥**n** are called **tilt** GBs
- Most GBs **mixed** (have both tilt and twist components)
- **Low-angle** (ω <10°) versus **high-angle** GBs

Atomic structure of GBs: ordered or disordered?

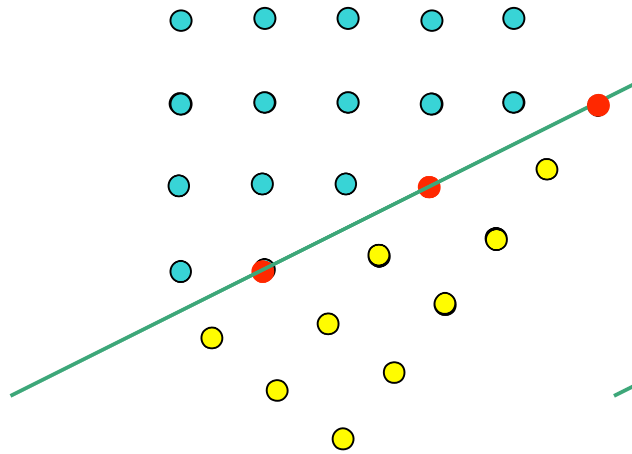
- Before late 1930s: “Amorphous-cement” model [Rosenhain & Archblutt, 1919]
- 1930s-1940s – observations of “special” GBs
- Coincident site lattice (CSL) model [Kronberg and Wilson, 1947]
- Starting 1950s-1960s – Experimental evidence of atomically ordered GB structure
- Starting 1970s-1980s – Computer simulations of GB structures

Current status: ordered at low temperatures, disordered at very high temperatures

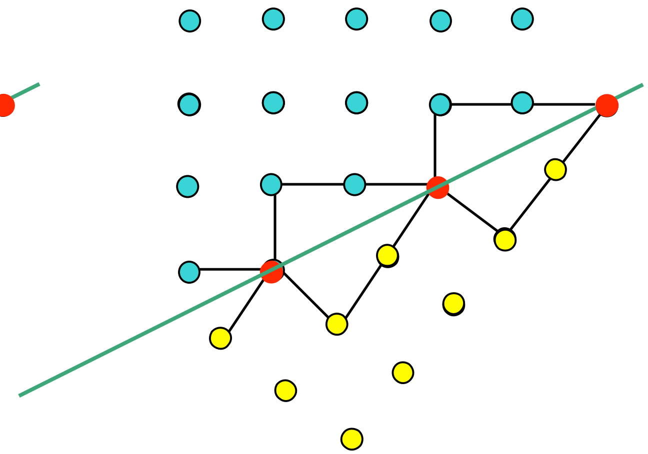
Coincidence site lattice (CSL) model



Σ5 CSL



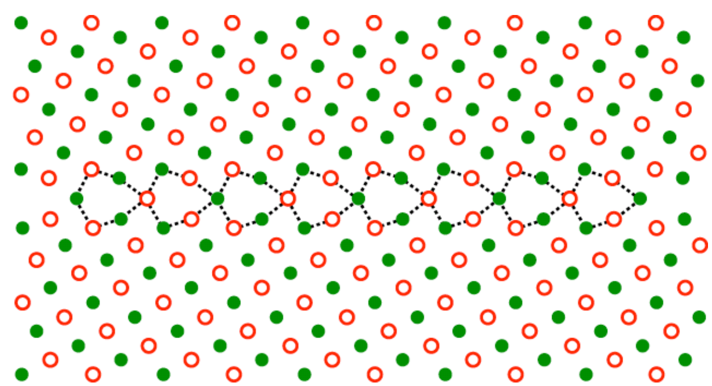
Σ5 GB



Σ5 structural units

Σ - reciprocal density of coincident sites

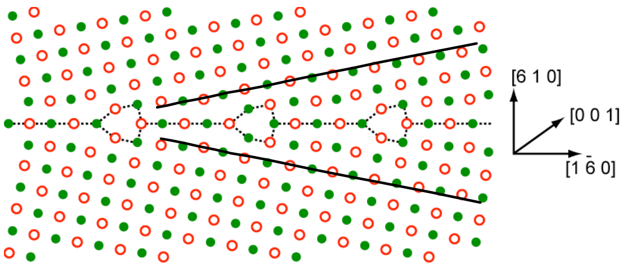
Relaxed structure



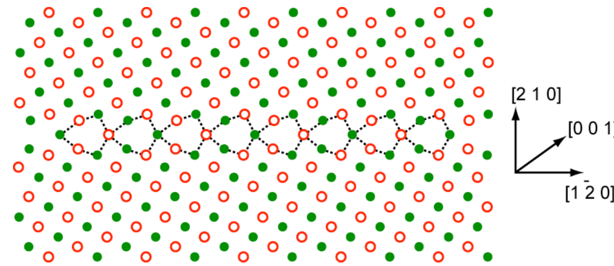
GBs with small Σ are believed to be "special"

Typical grain boundary structures

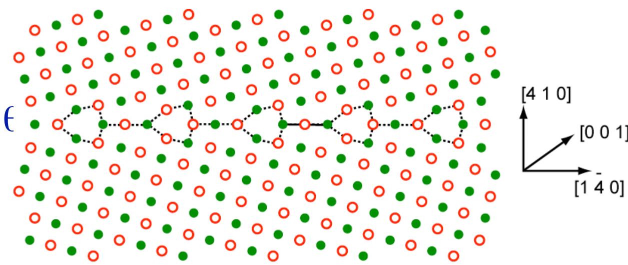
Σ37(610) θ =18.92°



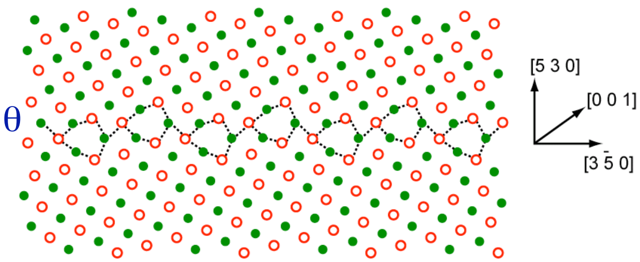
Σ5(210) θ =53.13°



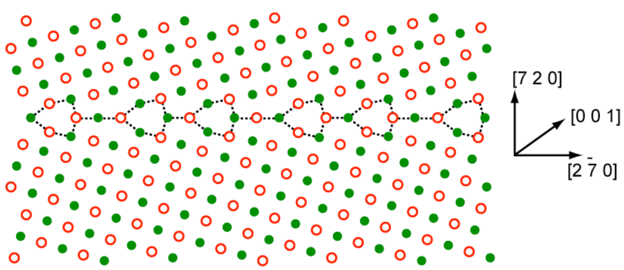
Σ17(410) θ =28.07°



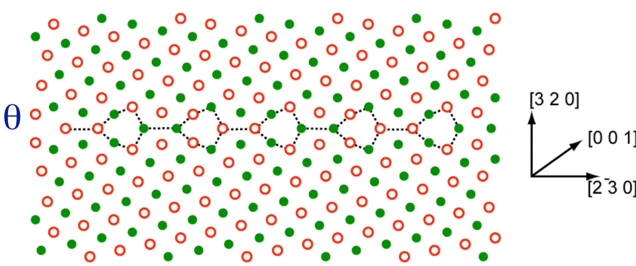
Σ17(530) θ =61.93°



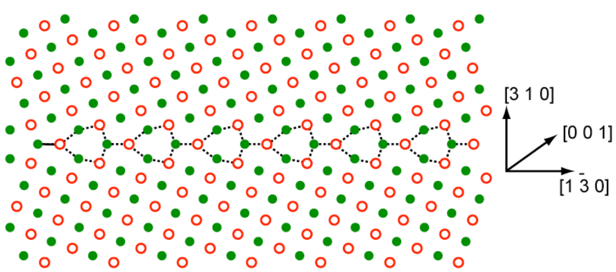
Σ53(720) θ =31.89°



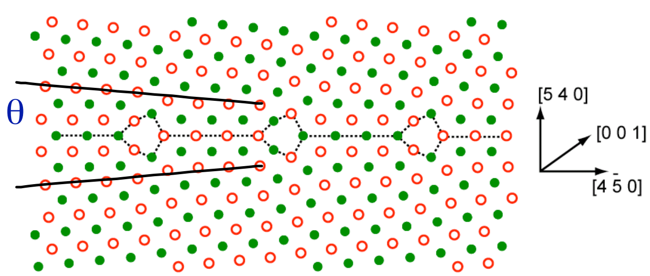
Σ13(320) θ =67.38°



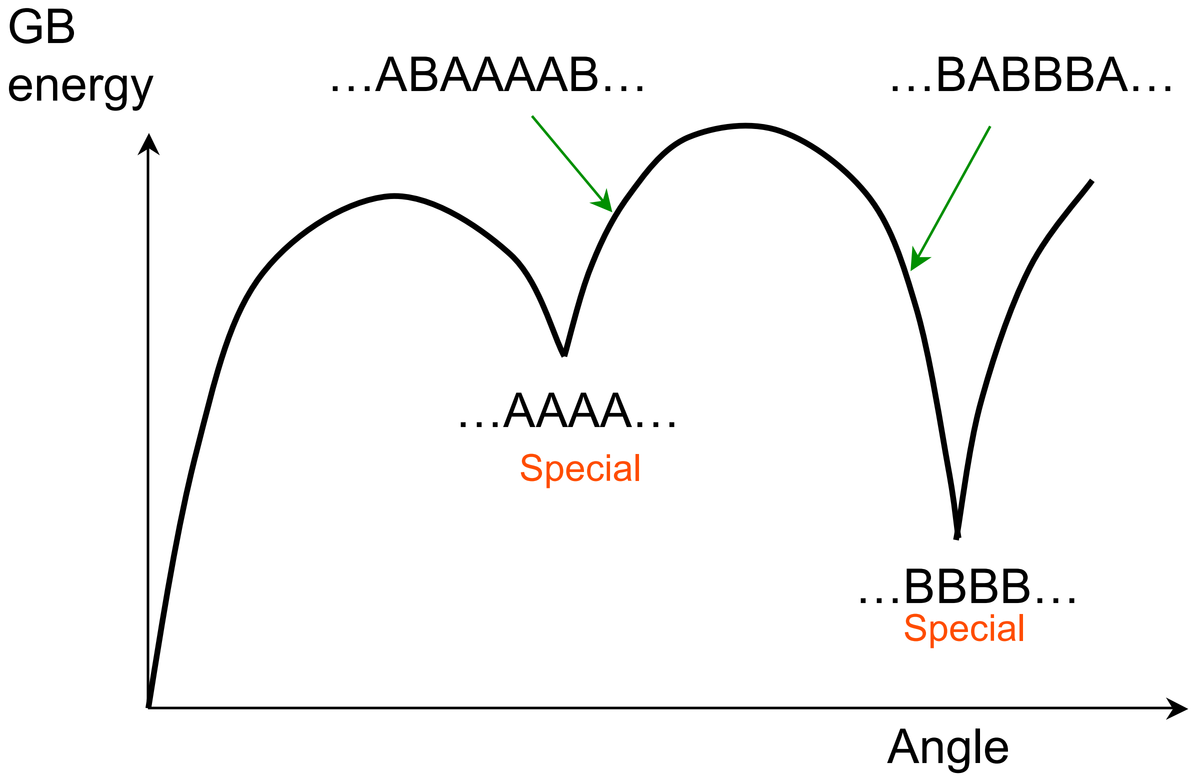
Σ5(310) θ =36.87°



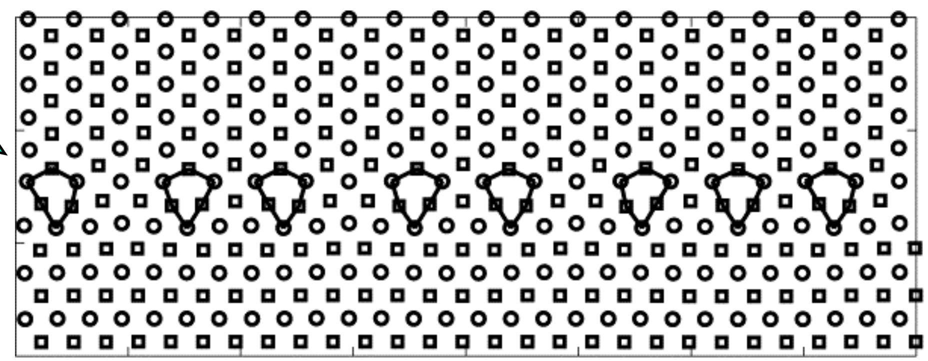
Σ41(540) θ =77.32°



Structural unit model



Example of an incommensurate GB



90° (110)(100) GB in copper

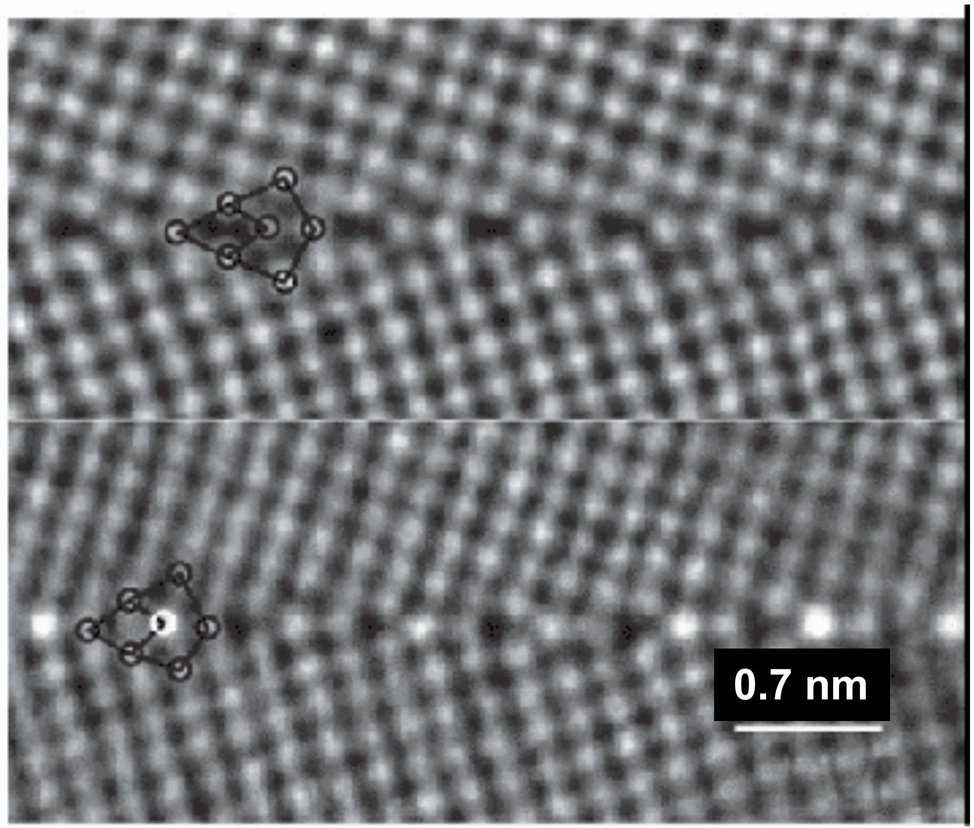
[J.A. Brown, PhD Thesis, GMU, 2006]

Experimental confirmation of the GB structure

High-resolution transmission electron microscopy (HRTEM)

Pure copper

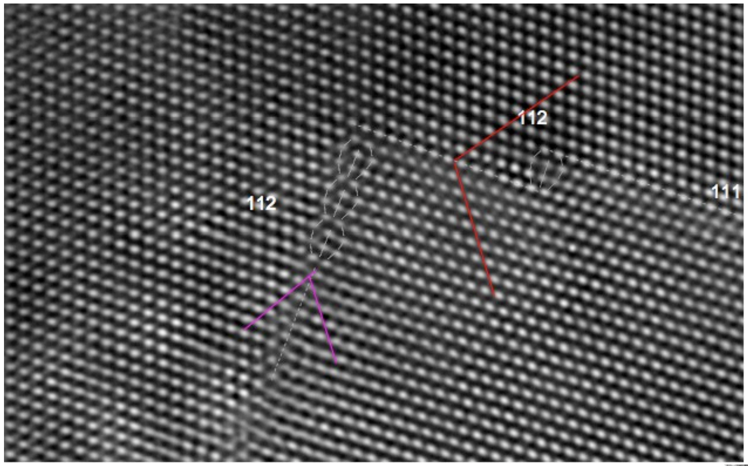
Copper doped with Bi



Σ5 GB in copper

G. Duscher et al, *Nature Materials* **3,** 621 (2004)

Faceting, dissociation and other transformations

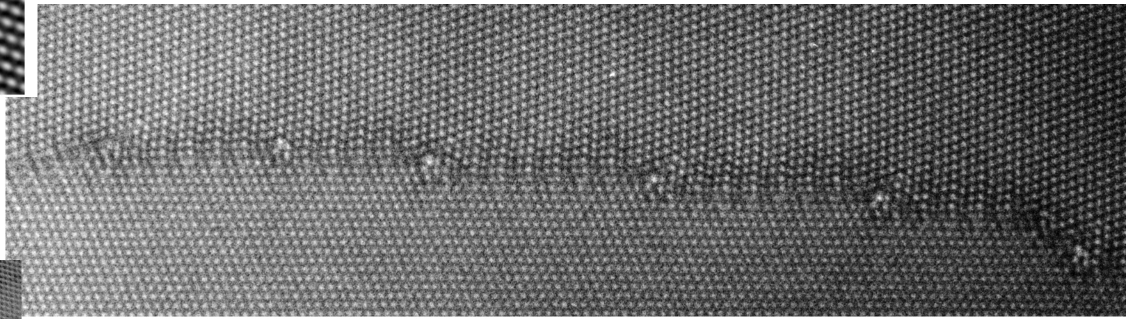


Σ3 GBs in Au

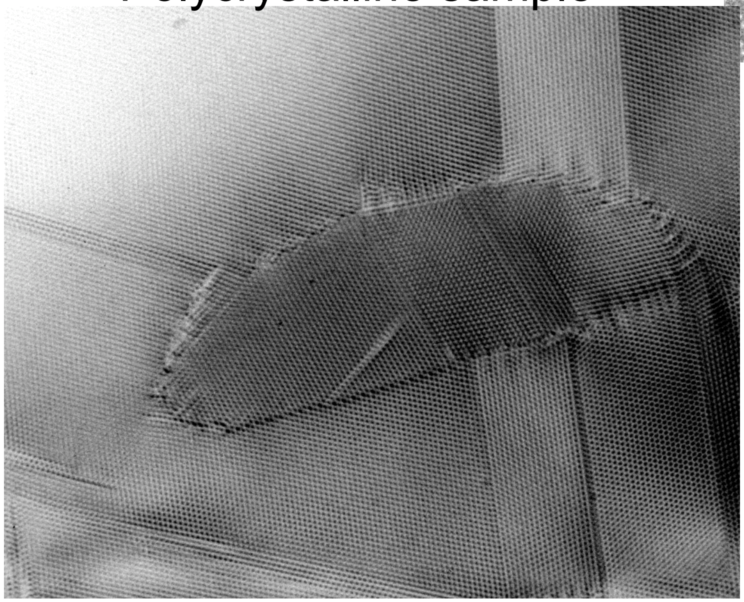
Grain boundaries in gold thin films

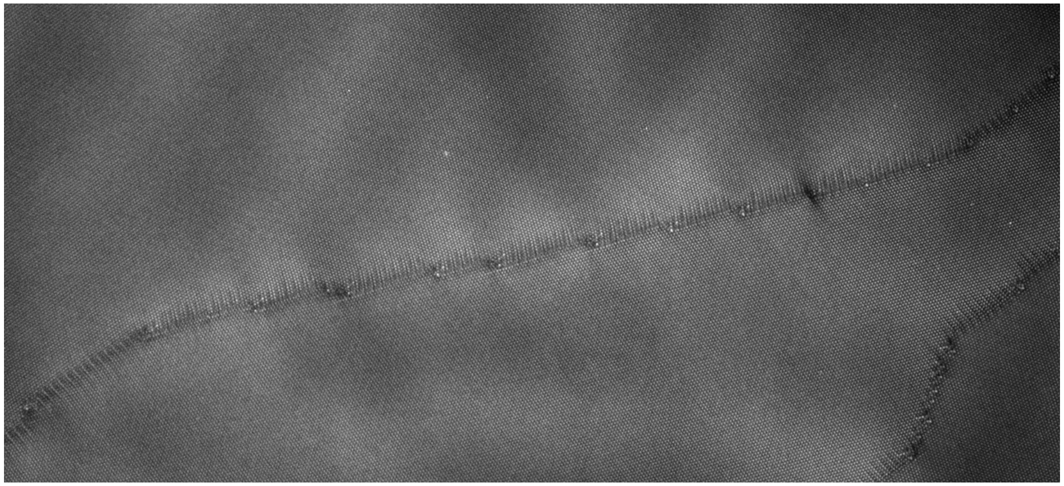
Courtesy D.J. Medlin (Sandia National Labs)

90° (110)(100) GB in Au



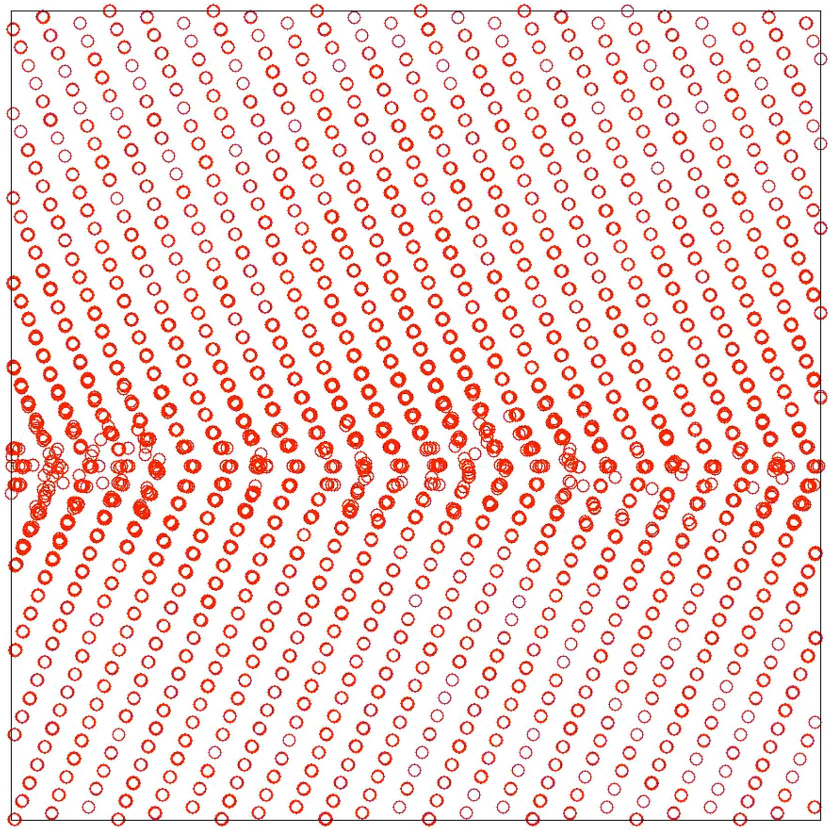
Polycrystalline sample



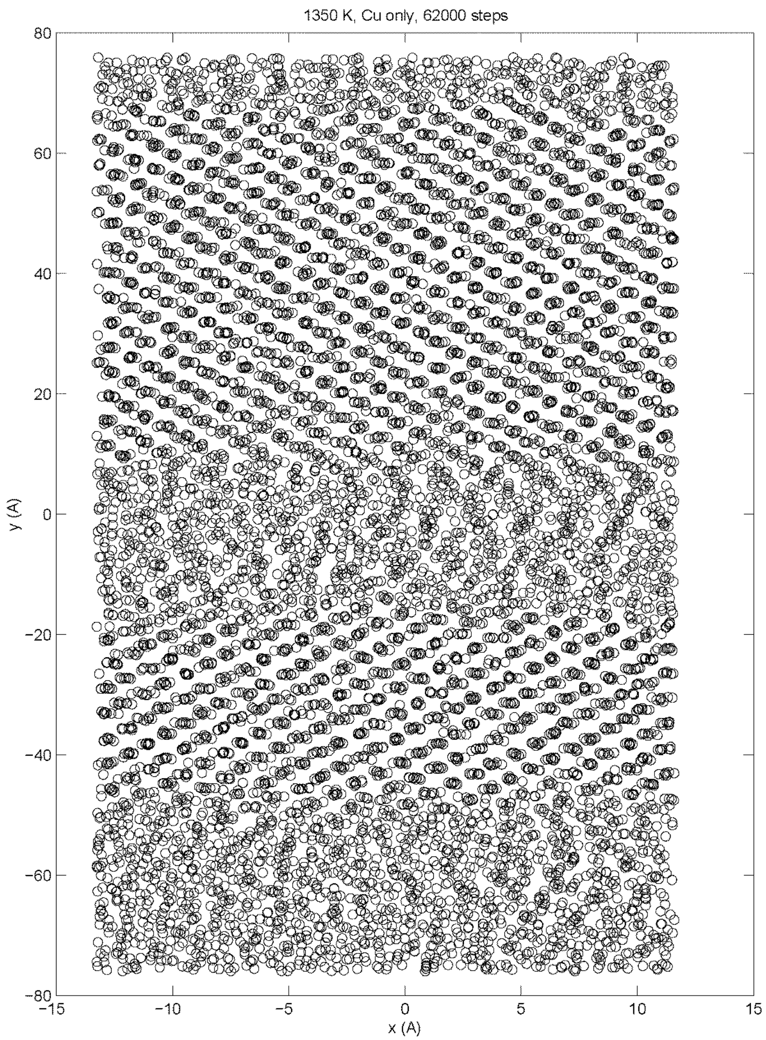


GBs at high temperatures

Disorder → pre-melting → melting



Σ21 GB in Al, 900 K



Σ5 GB in Cu, 1350 K

GB motion

Driving forces:

- Capillary forces
- Elastic anisotropy
- Magnetic anisotropy
- Many others

Driving force: $p = - dG/dV$

E.g. $p = 2\gamma/R$ – capillary force

Typically, $p \approx 0.01\text{-}1$ MPa

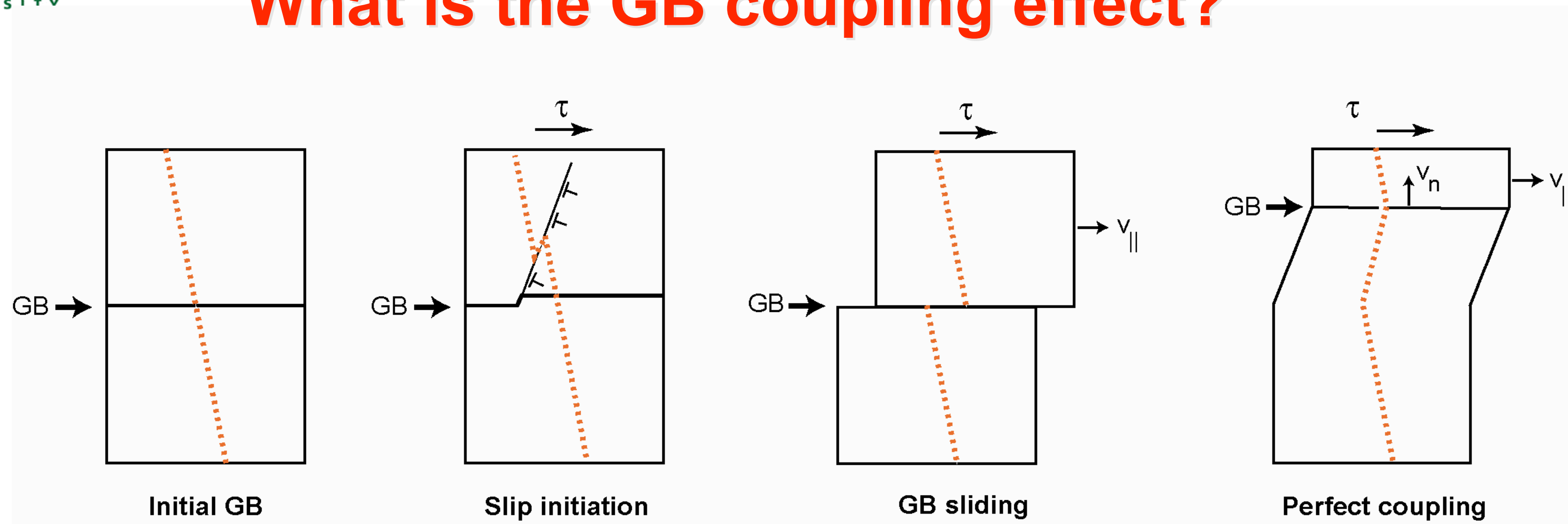
Typical velocities: $v = 1\text{-}100$ μm/s

Mechanisms:

- Diffusive
  - Assumes disordered structure
  - Diffusive jumps across the GB
  - Attachment-detachment concept
- "Military" (coupling effect)

Basic assumption: **$v = Mp$** (M = GB mobility)

What is the GB coupling effect?



$$v_{||} = \beta v_n$$

The coupling effect:

- Shear stress applied parallel to a GB induces its normal motion
- Normal GB motion produces shear deformation of the volume it traverses
- The driving force is linear in stress (not quadratic!)
- No diffusion required
- Particular cases of coupling: deformation twinning, martinsitic transformations.

Is the coupling effect real?

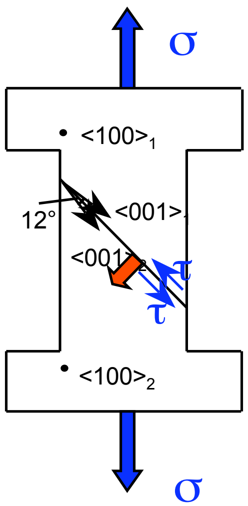
Experimental observations of coupling

- **First experimental observation of coupling** (low-angle GB in Zn)

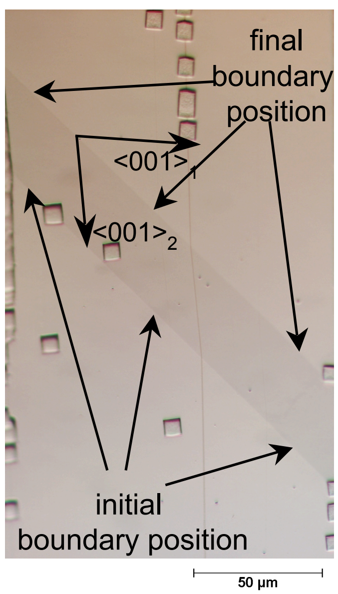
  C.H. Li et al., *Acta Metall*. **1**, 223 (1953)

- **Extension to high-angle GBs:**
  - M. Biscondi and C. Goux, *Mem. Sci. Rev. Met*. (1968): Al tilt GBs, θ up to 70^o
  - H. Fukutomi *et al*., *Acta Mater*. **39**, 1445 (1995): Al <110> Σ11 tilt GB
  - M. Winning *et al*., *Acta Mater*. **49**, 211 (2001): Al tilt GBs, θ up to 32^o
  - D. A. Molodov, V. A. Ivanov & G. Gottstein, *Acta Mater*. **55**, 1843 (2007): Al <100> tilt GBs, the first accurate quantitative study of coupling
- **Coupling is observed in both metals and ceramics**

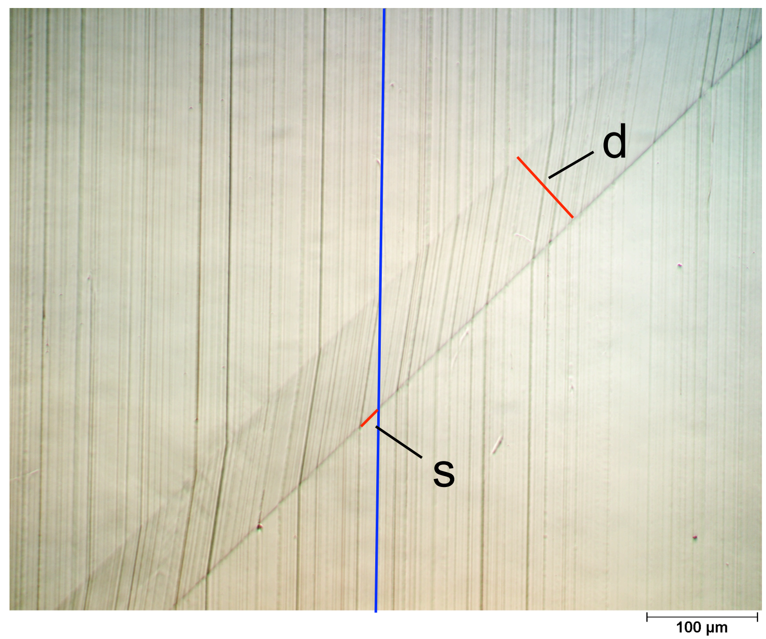
Observations of coupling in Al [001] tilt bicrystals



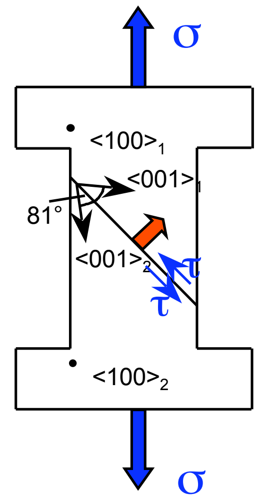
θ=12°, 325°C,
50 min

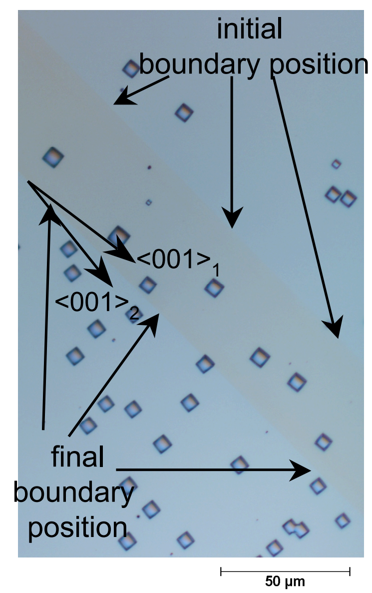


θ=17.8°, 375°C,
68 min



θ=81°, 320°C,
40 min

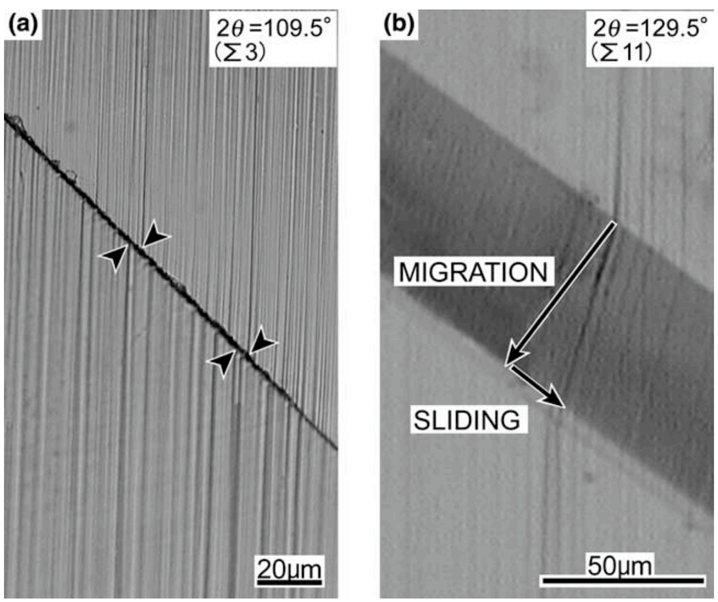




The β values exactly match the geometric model!

D. A. Molodov, V. A. Ivanov & G. Gottstein, *Acta Mater*. **55**, 1843 (2007)

Coupling in ceramic materials

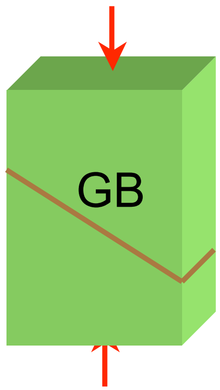


Sliding Coupling

High-temperature GB sliding and coupling in ZrO_2

T = 1400 °C, σ = 100 MPa

H. Yoshida *et al.*, *Acta Mater*. **52**, 2349 (2004)



Compressive creep test

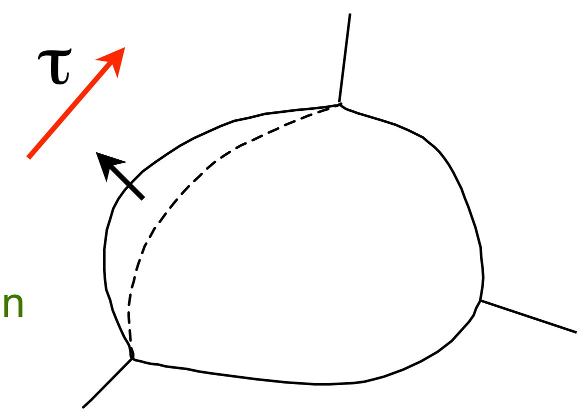
Possible implications of the coupling effect

- GB motion can be induced not only by volume driving forces or curvature, but also by shear stresses.
- Motion of high-angle GBs can occur without diffusion. This was only known for twin GBs. In fact, there is a large class of high-angle GBs which can move in a coupled manner similar to twin GBs. Diffusion and coupled motion do not exclude each other.
- Grain rotation observed in many materials is a likely result of coupled motion of curved GBs.
- Stress-induced GB migration can produce grain shape changes, rotation, and thus plastic deformation without diffusion or slip in the grains. This is another deformation mechanism, which can be especially important in nano-crystalline materials.

Implications of the coupling effect (cont'd)

- In nanocrystalline materials, stress-induced GB motion can trigger grain growth at low temperatures [Kevin Hemker & and co-authors, JHU]. It could also be responsible for grain growth at cryogenic temperatures found in nanoindentation creep experiments [K. Zhang, J.R. Weertman and J.A. Eastman, APL 87 (2005)].
- In nanocrystalline materials, coupled GB motion can be jerky and can be accompanied by stress-peaks (stick-slip behavior).

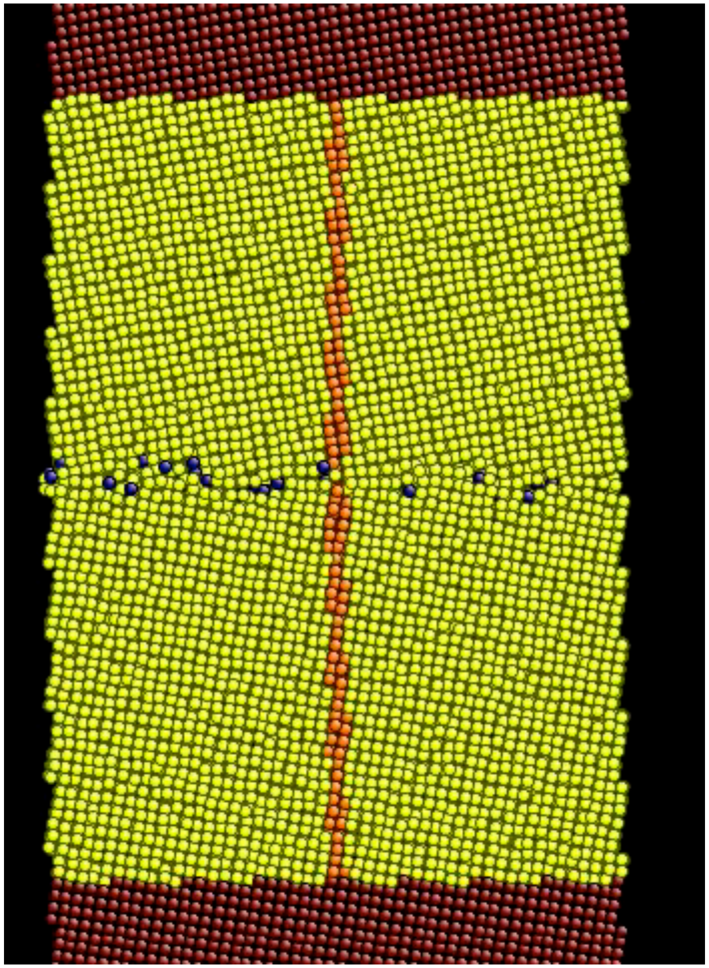
Deformation-induced GB motion



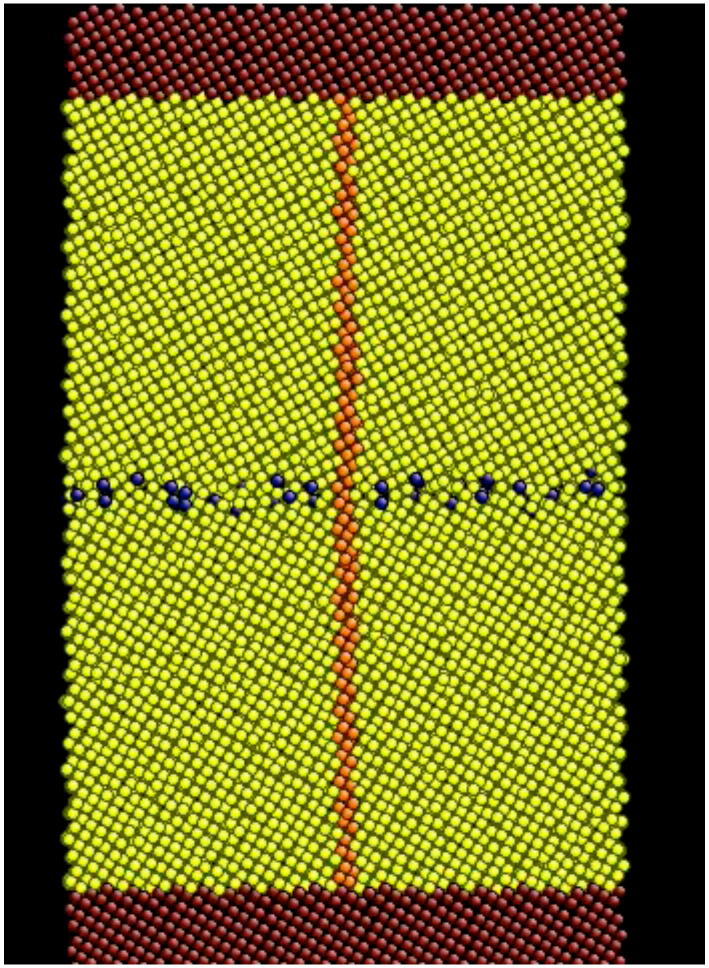
Stress-induced GB migration:

coupling can be positive or negative

$T = 800$ K, $v_{||} = 1$ m/s normal to the tilt axis

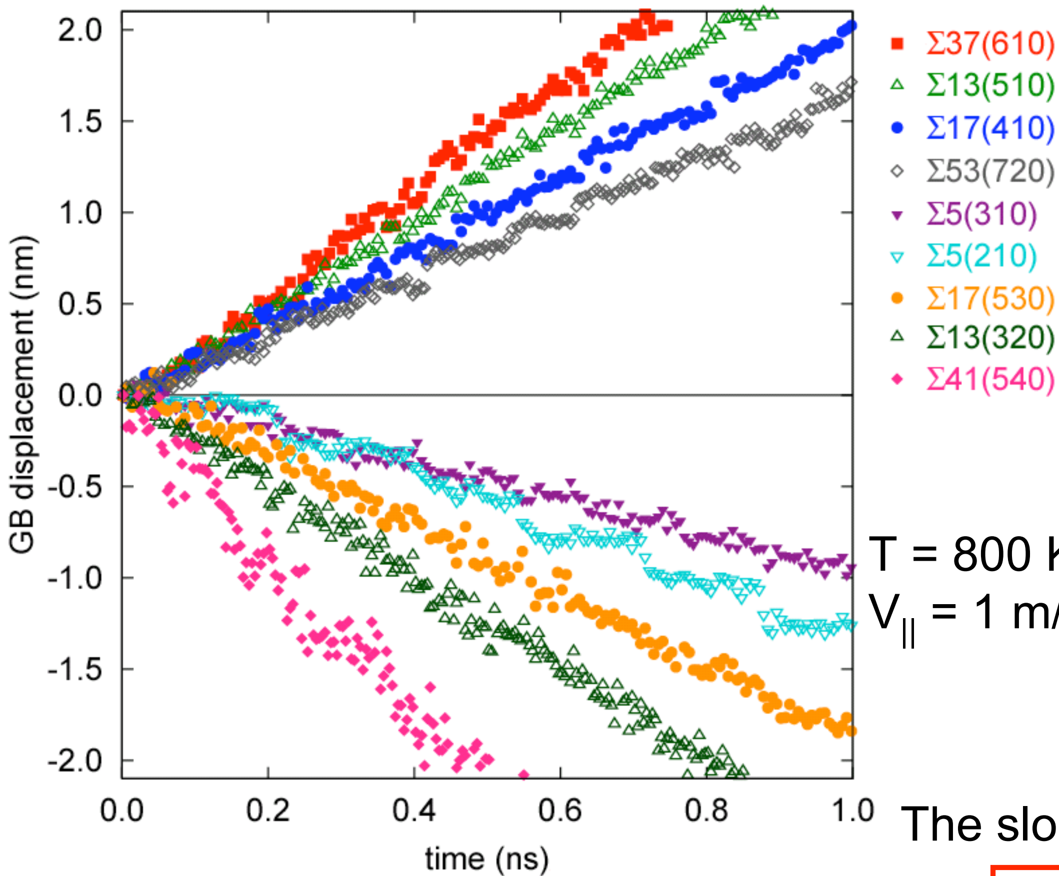


Σ37 (610) Cu θ
=18.92°



Σ17 (530) Cu θ
=61.93°

GB displacement vs time



T = 800 K

$V_{||}$ = 1 m/s

The slopes give β:

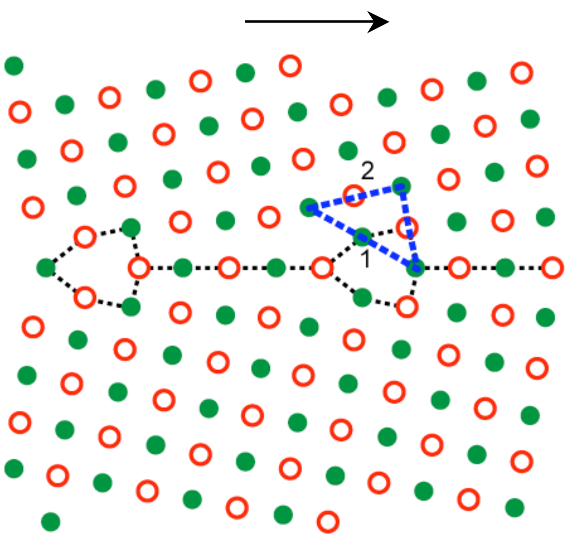
$$\mathbf{v_{||} = \beta v_n}$$

β depends on the GB crystallography only!

Atomic mechanisms of GB motion

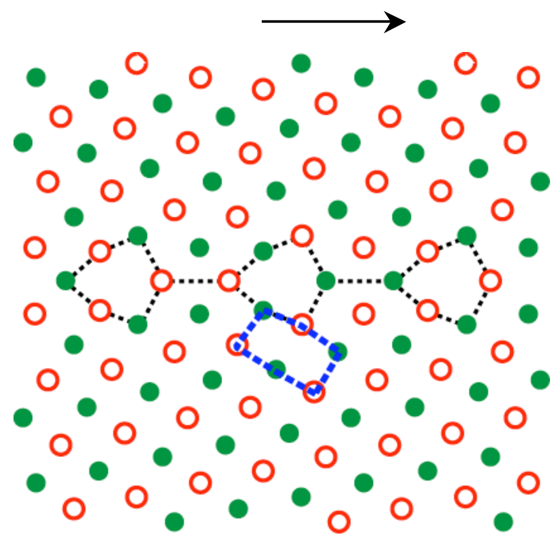
Determined by MD simulations

Σ37 (610)
θ=18.92°



<100>- mode

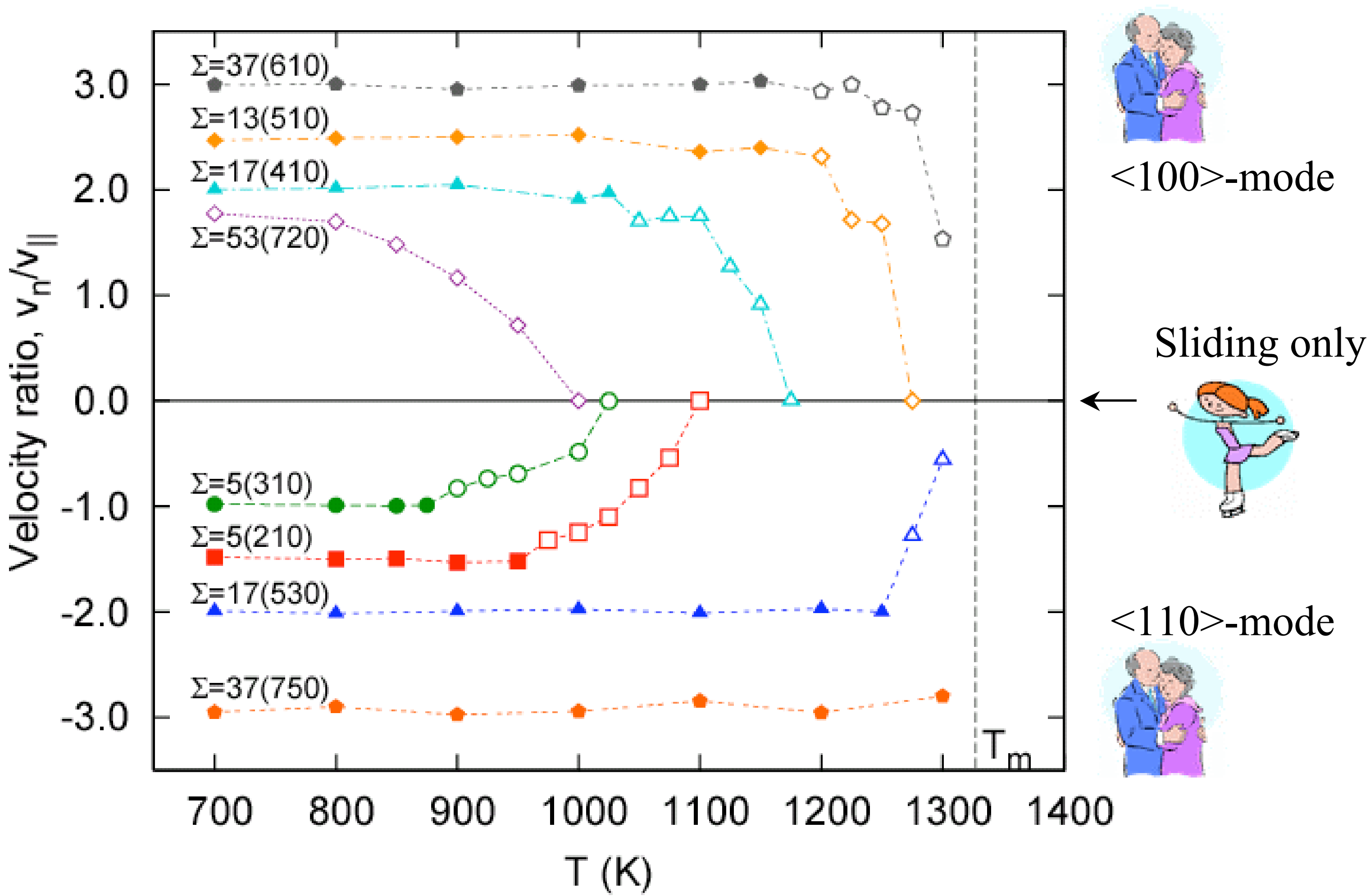
Σ13 (320)
θ=67.38°



<110>- mode

- GBs move by distortion and rotation of structural units. This requires thermal activation
- No vacancy diffusion is involved. "Military" or "glissile" GB motion
- For low-angle GBs the process reduces to collective dislocation glide: **b** = <100> {100} or 1/2<110> {110}
- Structurally, each GB is prepared to move in either mode, hence the duality of coupling

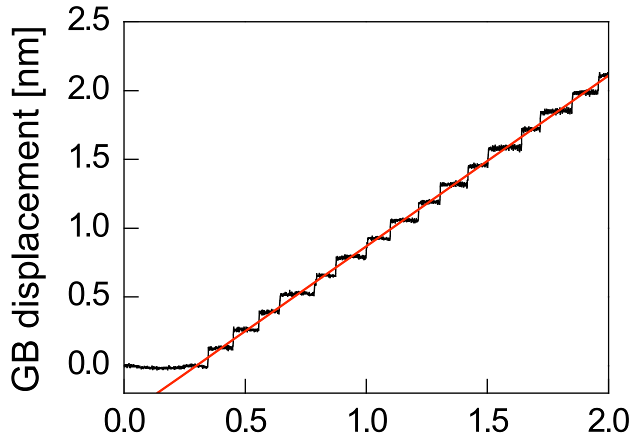
Temperature dependence of the velocity ratio



- Low-angle GBs remain coupled up to ~T_m .
- High-angle GBs switch from coupling to sliding at ~$0.7T_m$

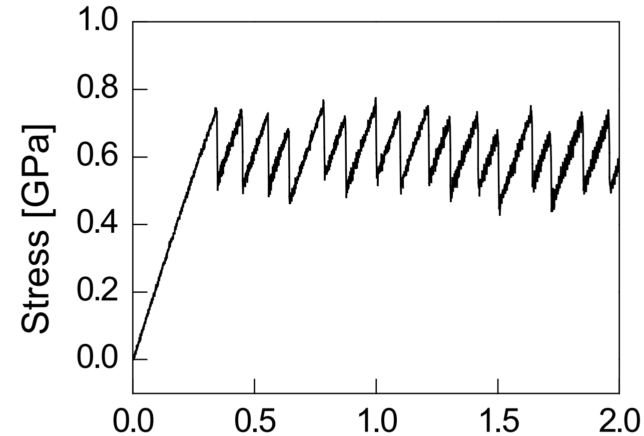
Dynamics of coupled GB motion

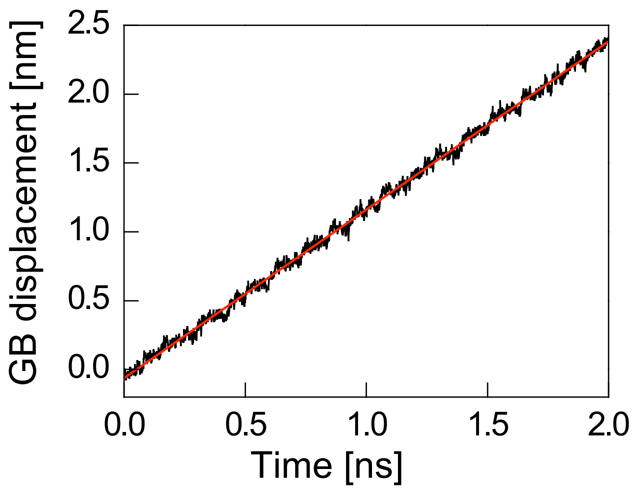
$\Sigma 21$ $\theta = 44.4°$ GB in Al



"Stick-slip"regime

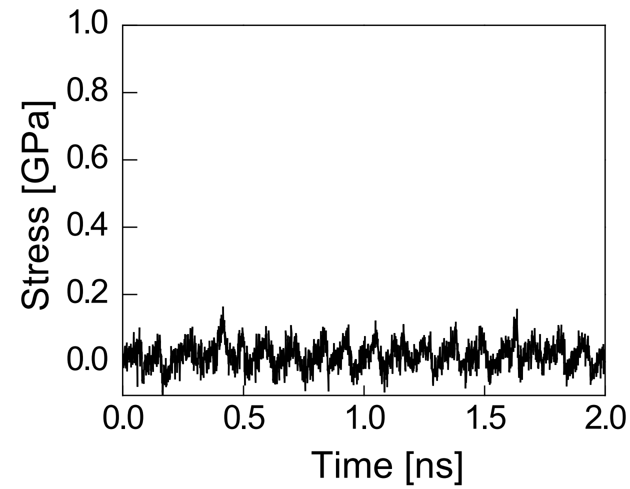
T = 100 K; $V_{||}$ = 1 m/s





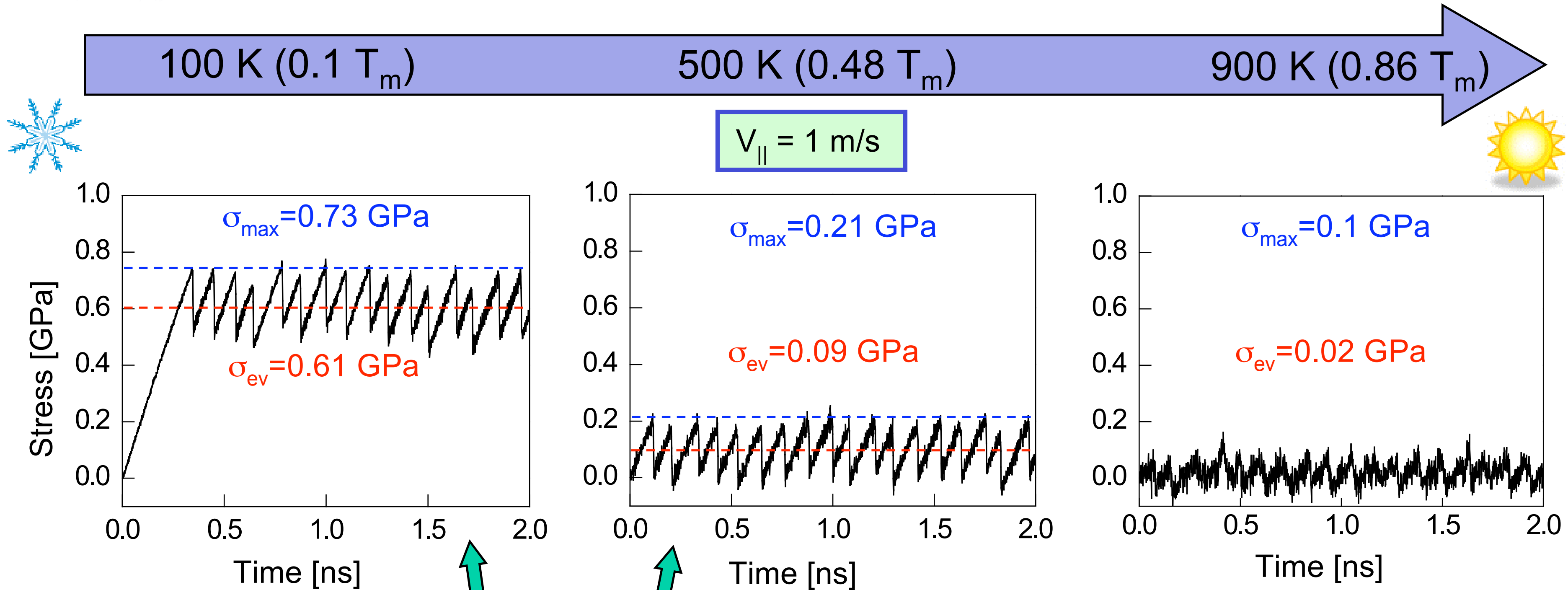
Brownian regime

T = 900 K; $V_{||}$ = 1 m/s



- The peak stress nucleates a disconnection
- Parallel with dry friction
- The dynamics depend on three factors: • System size • Temperature • GB velocity

Temperature effect on stick-slip dynamics



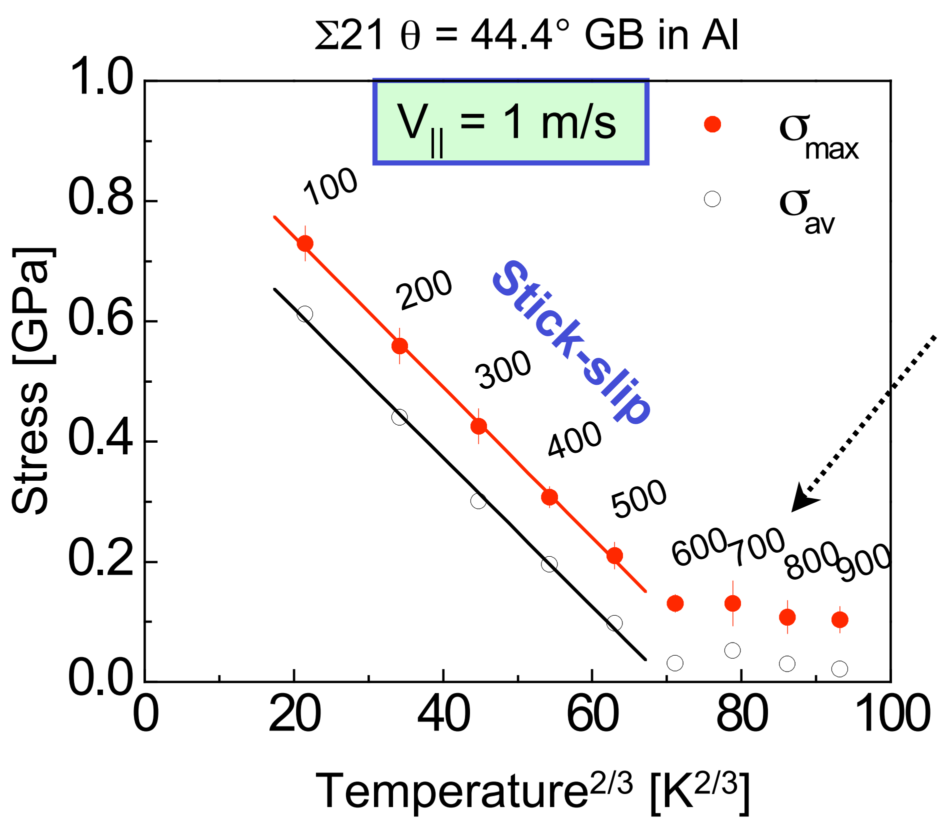
Stick-slip mode

Transition to driven Brownian motion

- Jumps only forward
- Thermal fluctuations assist in overcoming the barrier → σ_{max} decreases with T
- Theoretical prediction: $\sigma_{max} \propto \sigma_c - BT^{2/3}$.

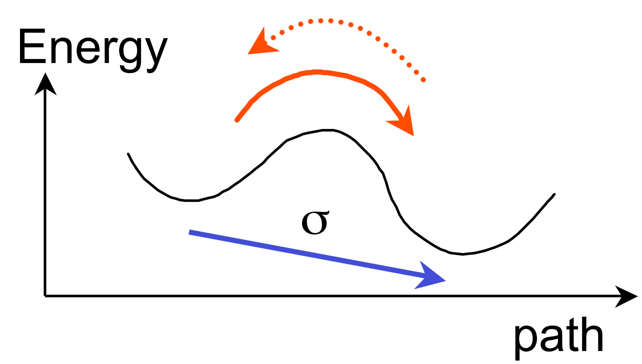
- Both forward and backward jumps by thermal fluctuations
- The stress biases the jumps
- σ_{max} makes no sense, need to use σ_{av}

Stick-slip dynamics of Al GBs

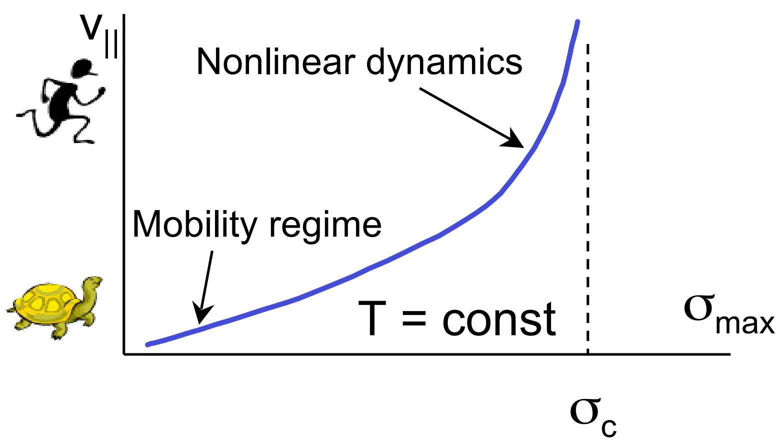


Transition to driven Brownian dynamics

- Occasional reversal jumps
- Brownian motion in the absence of stress



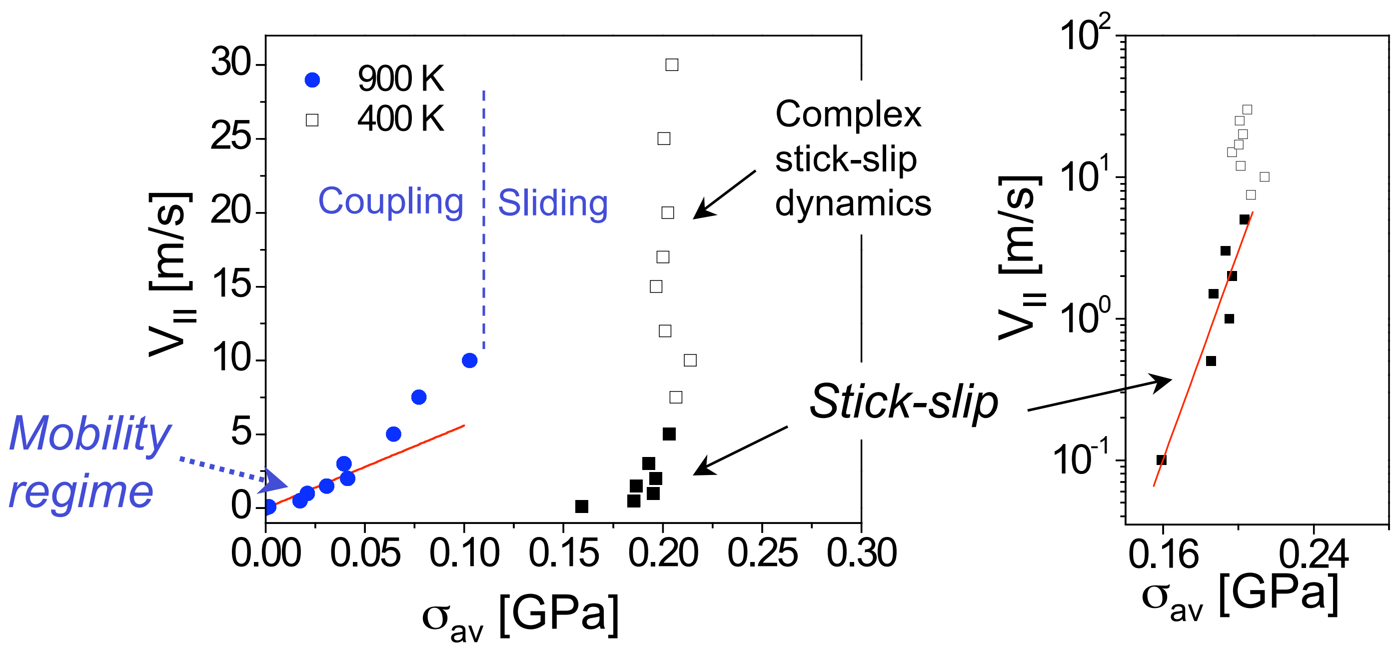
Strain rate effect on GB dynamics



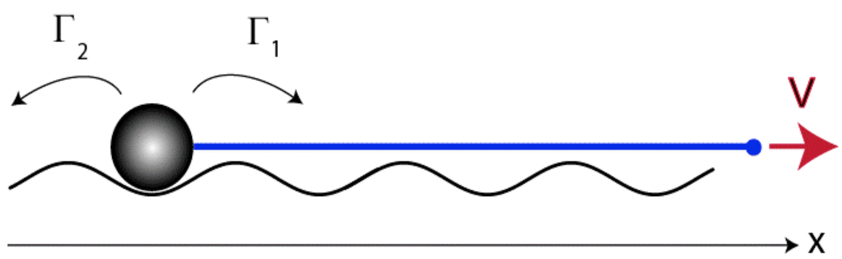
- Brownian (mobility) regime $v = M\sigma_{av}$

- Strongly driven regime (forward jumps):

$$v = A(T)\exp\left(-\frac{E_0(1-\sigma_{max}/\sigma_c)^{3/2}}{kT}\right)$$



Mechanical analog of coupled GB motion



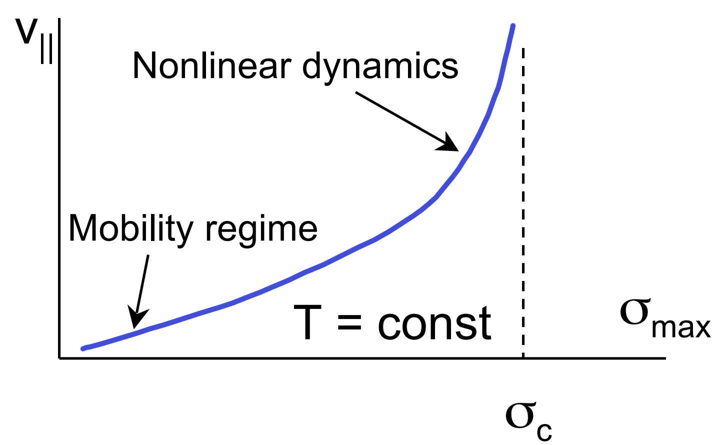
The particle is dragged by an elastic rod through a periodic potential

- MD simulation: $m\ddot{x} = -\dfrac{dU(x)}{dx} + 2C(vt - x) - \gamma\dot{x} + \xi(t,T)$
- KMC: $\Gamma_+ = \nu\exp(-E_+/kT)$, $\Gamma_- = \nu\exp(-E_-/kT)$, $E_{+/-} = E_0 \pm A\sigma$
- Analytical:
  - Brownian regime $v = M\sigma_{av}$
  - Strongly driven regime (forward jumps only):

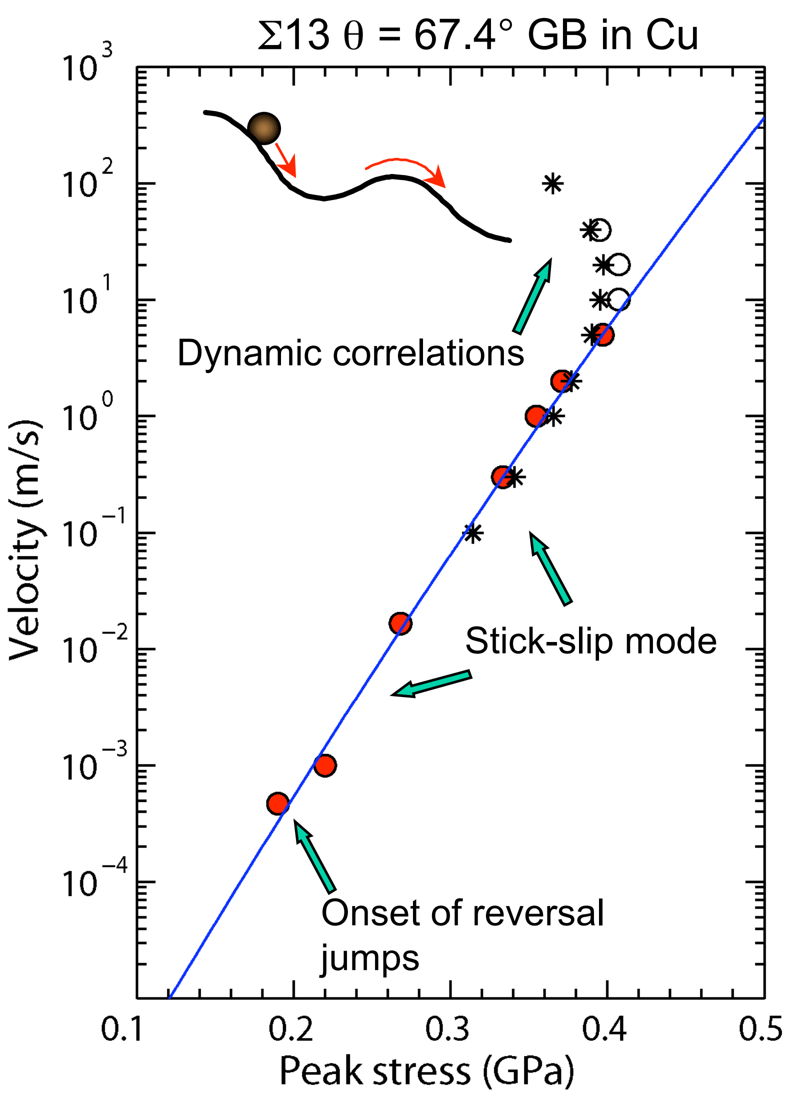
$$v = A(T)\exp\left(-\frac{E_0(1 - g\sigma_{max}/\sigma_c)}{kT}\right)$$

$$\Downarrow$$

$$v = A(T)\exp\left(-\frac{E_0(1 - \sigma_{max}/\sigma_c)^{3/2}}{kT}\right)$$

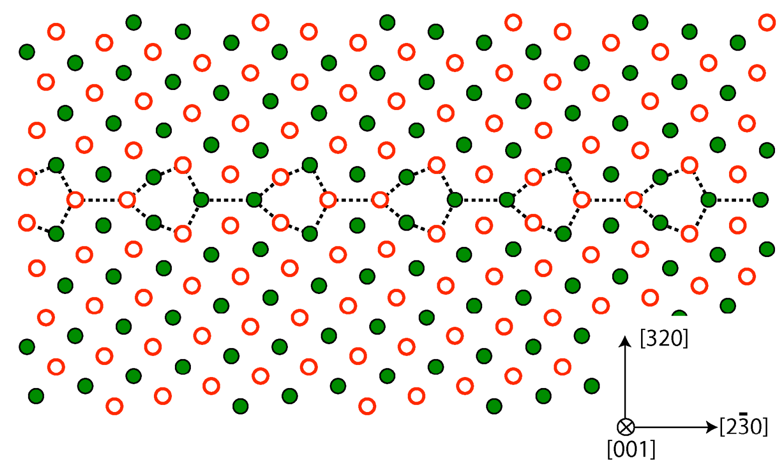


Strain rate effect on stick-slip dynamics



Parallel-replica MD at 500 K

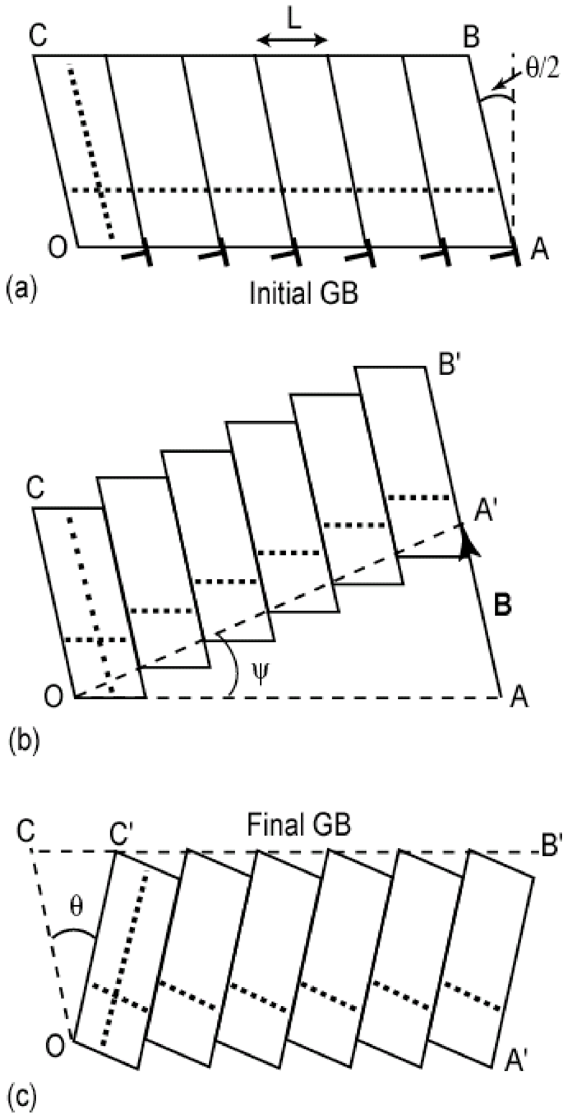
(with Suzuki, Uberuaga and Voter)
Phys. Rev. B **75**, 224101 (2007)



Conclusions

- GBs are important elements of materials microstructure
- Their atomic structure is well ordered at low temperatures, becomes increasingly disordered at high temperature, and turns to a liquid layer near the melting point
- Many GBs can be driven by applied shear stresses. This GB motion is thermally activated but does not require diffusion and can occur at low temperatures.
- Coupled GB motion can produce permanent shear deformation of the material and might contribute to deformation behavior of polycrystalline materials, especially on the nano-scale. It may constitute a significant part of the so-called “GB processes”.
- Coupled GB motion display interesting dynamics, ranging from driven Brownian motion to the stick-slip behavior. It has similarities with atomic friction observed by AFM (FFM).

Dislocation model of coupling



Low-angle GBs with θ → 0:

Slip of **b** = [100] dislocations on {100} planes

Frank equation: $B = 2\sin(\theta/2)$

OA=OA' and $\psi = \theta$

$\beta = 2\tan(\theta/2)$

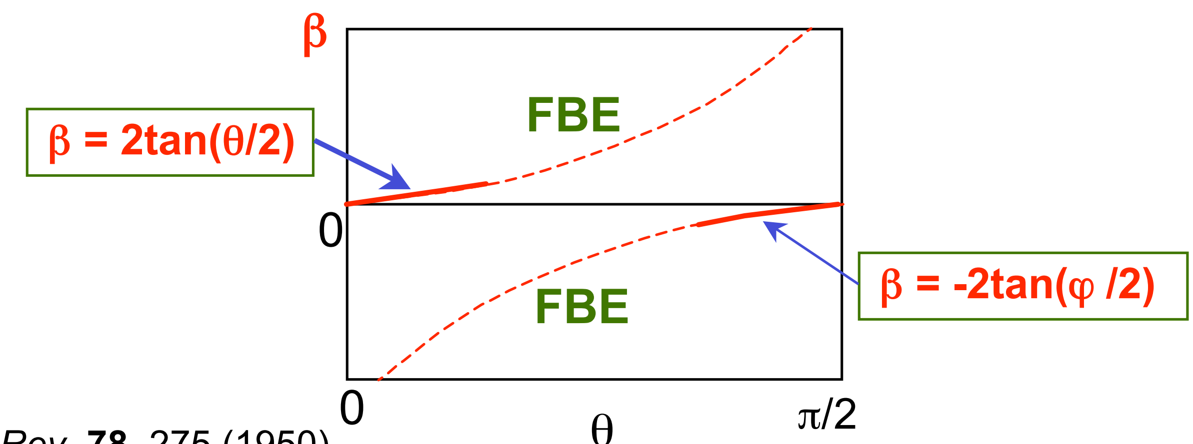
Low-angle GBs with θ → π/2:

Slip of **b** = -1/2[110] dislocations on {110} planes

Frank equation: $B = 2\sin(\varphi/2)$

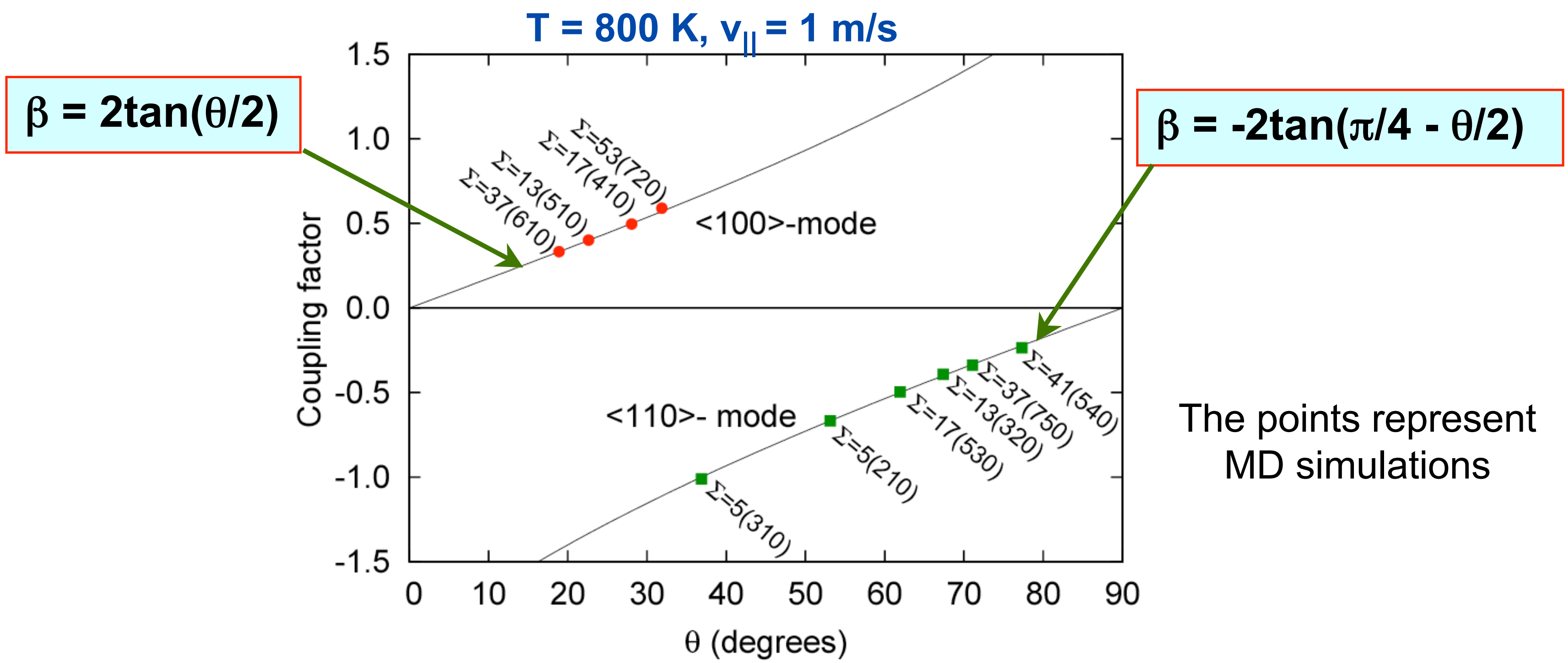
where $\varphi = \pi/2 - \theta \to 0$

$\beta = -2\tan(\varphi/2)$



W.T. Read and W. Shockley, *Phys. Rev*. **78**, 275 (1950)

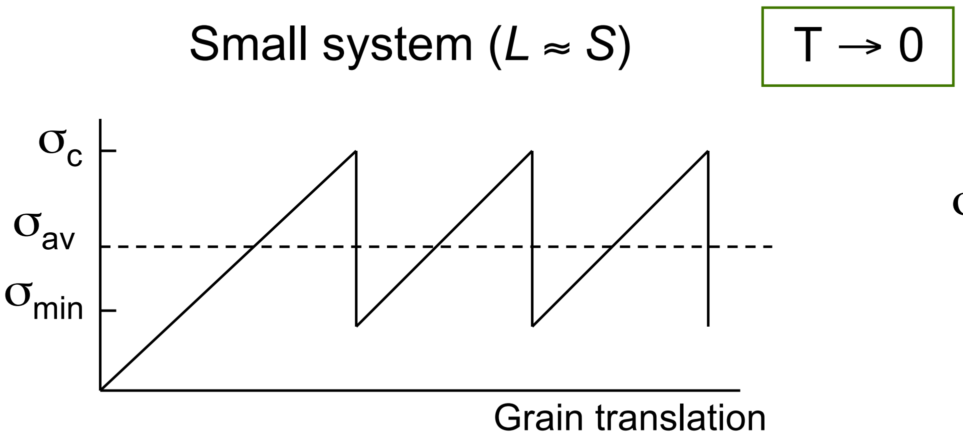
MD results for Cu: Misorientation dependence of β

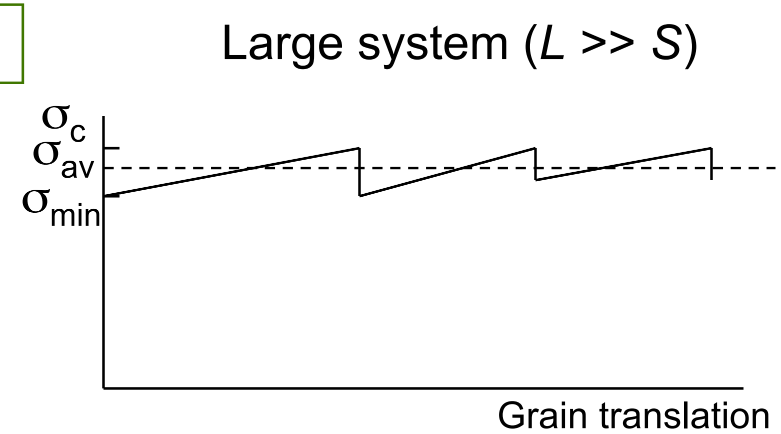


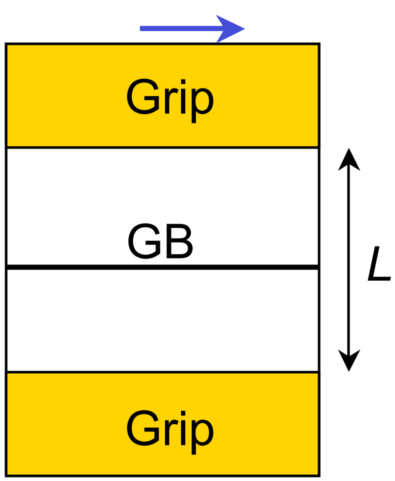
The points represent MD simulations

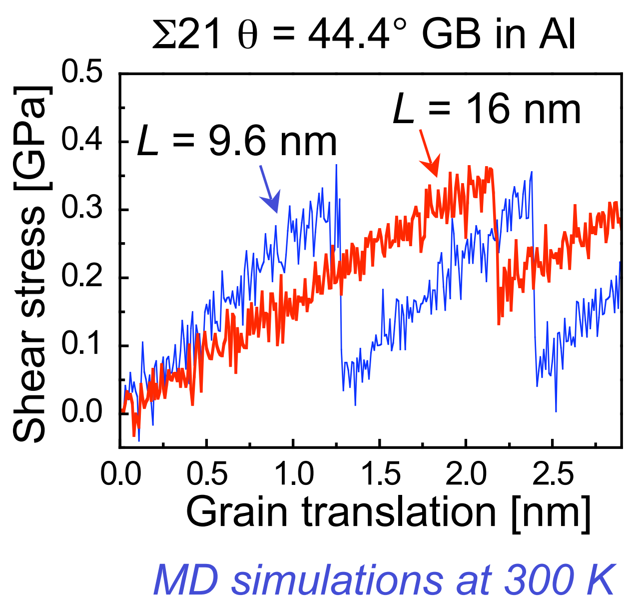
- Excellent agreement between the dislocation model and MD for **all** θ. The Frank-Bilby equation works! The "effective" dislocation content makes sense!
- β_{MD} is shear-rate independent (at least for $v_{||} < 10$ m/s)
- β is a multivalued geometric factor
- β has a discontinuous change of sign between θ=31.9° and θ=36.9°
- **Two modes of coupling: <100>-mode and <110>-mode**

Size effect of stick-slip behavior









- Nucleation and propagation of disconnections at σ_c
- The peak stress σ_c is a better measure of GB resistance than σ_{av}
- As *L* increases, $\sigma_{min} \rightarrow \sigma_{av} \rightarrow \sigma_c$ – motion at a constant stress

Methodology of simulations

- Symmetrical tilt GBs
  - [001] with 0<θ<90º in Cu
  - [211] with 0<θ<180º in Al
- EAM potential for Cu and Al
- MD simulations at temperatures 0 -T_m. Thermal expansion included
- Block contains 10,000-90,000 atoms
- Fixed boundary condition in *y*
- Constant shear rate $v_{||}$ = 0.001-10 m/s. Shear stress varies.
- Automatic GB tracking by the structure factor or the centrosymmetry parameter