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Computing grain boundary properties using atomistic simulations

Elizabeth A. Holm and Stephen M. Foiles
Computational Materials Science and Engineering
Sandia National Laboratories, Albuquerque, NM, USA

Eric R. Homer
Department of Mechanical Engineering
Brigham Young University, Provo, UT, USA

David L. Olmsted
Department of Materials Science and Engineering
University of California, Berkeley, CA, USA

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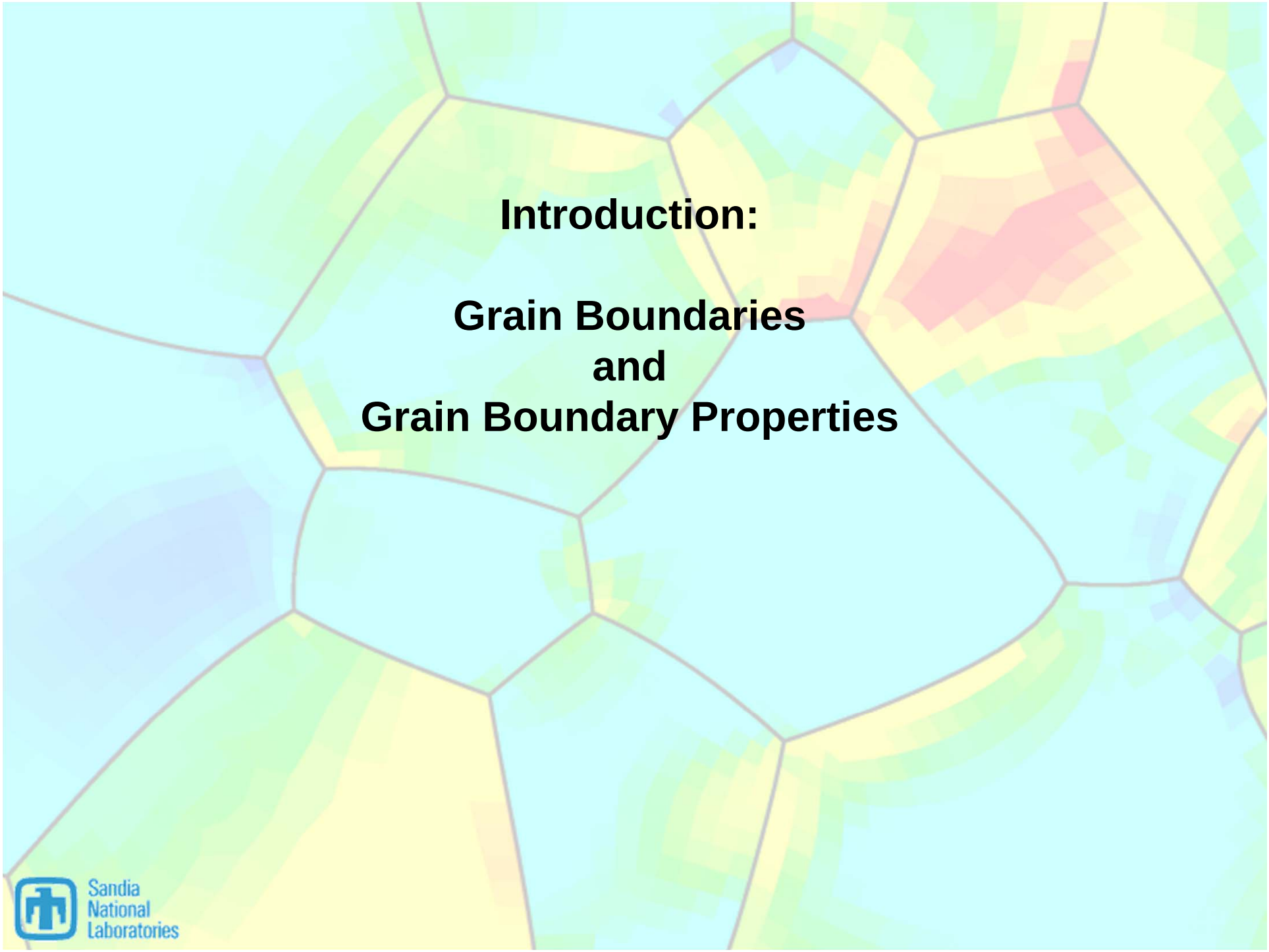

Introduction:

Grain Boundaries
and
Grain Boundary Properties

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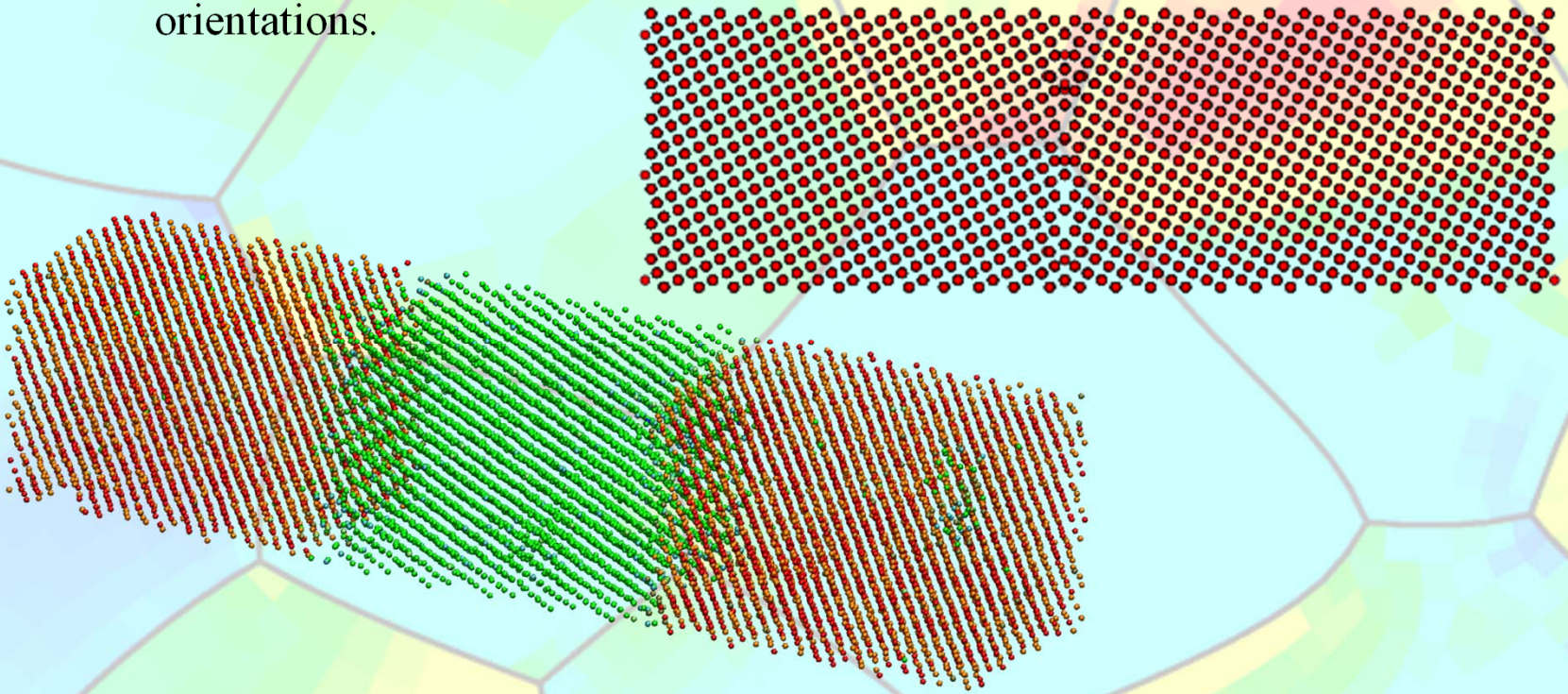
What is a grain boundary?

- A grain boundary is the atomic-scale interface between crystals of unlike orientations.



- Because atomic bonds are unfulfilled at the interface, grain boundaries have positive free energy.
- Atomic rearrangements at the interface can permit grain boundary motion in response to a driving force; thus, grain boundaries have finite mobility.
- Both energy and mobility can vary with grain boundary structure.

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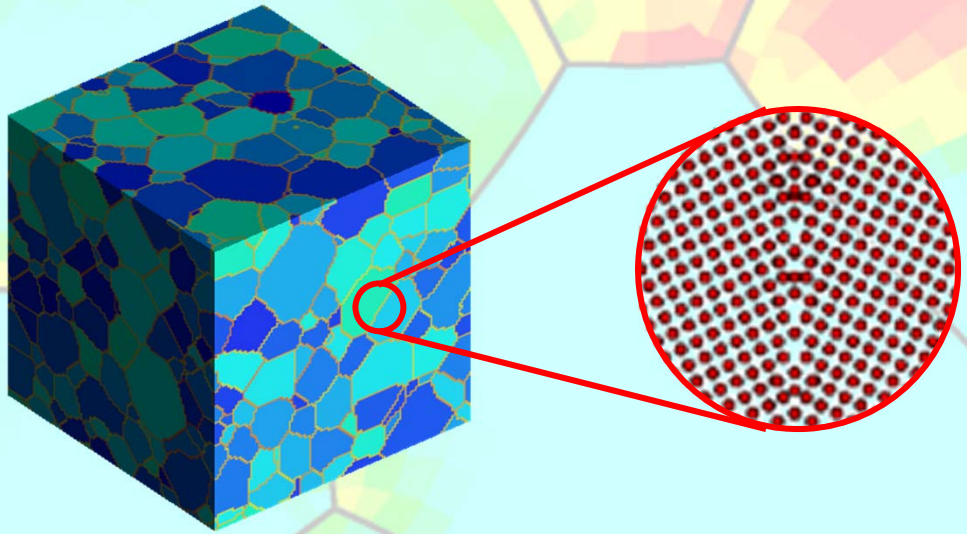
Why study grain boundary properties?

- To understand how grain boundaries behave in a microstructure, we need to know their atomic-scale properties.



- Goal: Efficiently measure the energy and mobility of a large set of grain boundaries.
- Tools: Because energy and mobility are atomic-scale properties, use atomistic simulation techniques: molecular dynamics.

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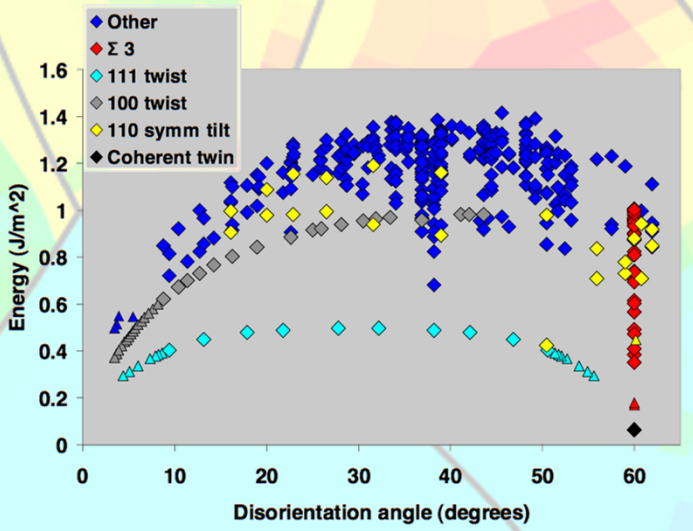
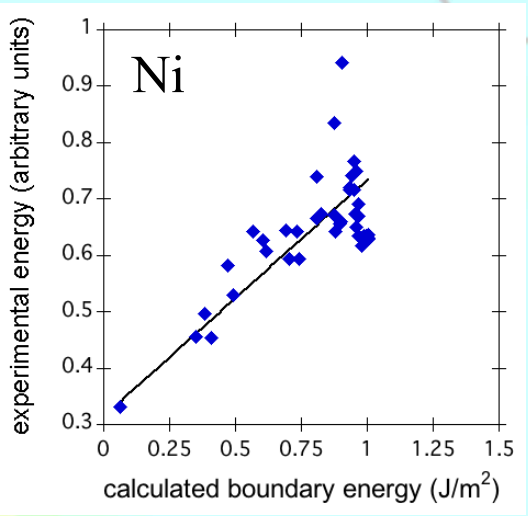
Determining atomic scale properties: Step 1: Build grain boundaries

- Method: Build a catalog of 388 minimum-energy grain boundary structures
  - Includes all boundaries that can fit inside a periodic box of size $15a_0/2$.
  - For each boundary, we minimize hundreds or thousands of configurations to find the lowest energy structure.

- Results: Publicly-available survey of grain boundary structures and energies
  - We can observe trends in energy as a function of boundary structure.
  - Calculated energies have been validated against experimental data for Ni and Al.





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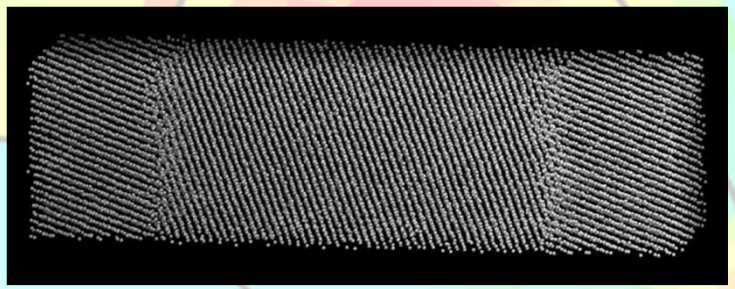
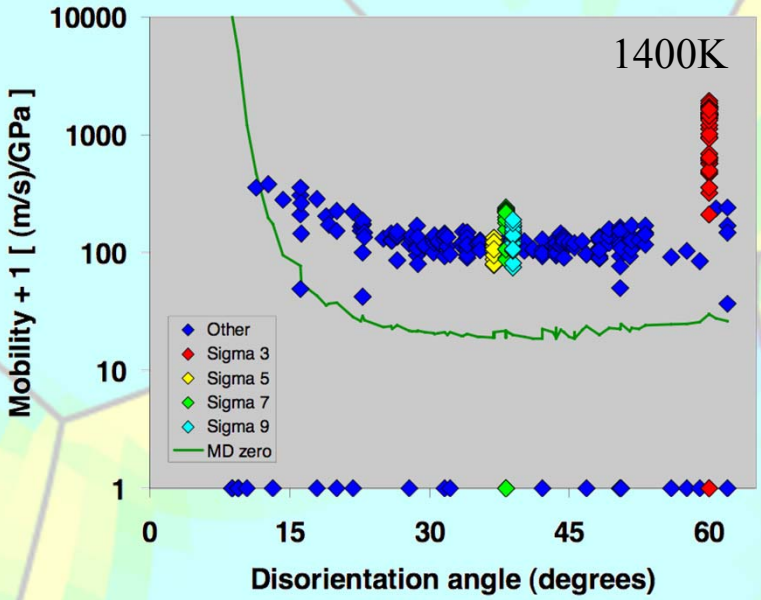
[Olmsted, Foiles, Holm, *Acta Mater.* **57** 3694 (2009),
Holm, Olmsted, Foiles, *Scripta Mater.* **63** 905 (2010),
Rohrer *et al.*, *Acta Mater.* **58** 5063 (2010),
Holm *et al.*, *Acta Mater.* **59** 5250 (2011)]

Determining atomic scale properties: Step 2: Calculate grain boundary mobility

- Method: Use synthetic driving force molecular dynamics to calculate the mobility of each grain boundary in our catalog.
  - 5 temperatures: 600, 800, 1000, 1200 and 1400K
  - Up to 4 driving forces: 0.005, 0.010, 0.025 and 0.050 eV/atom
  - 10,718 total mobility measurements



- Results: Publicly-available survey of grain boundary mobilities
  - Largest survey of boundary mobilities ever performed.
  - We are just beginning to mine this deep and rich data set.



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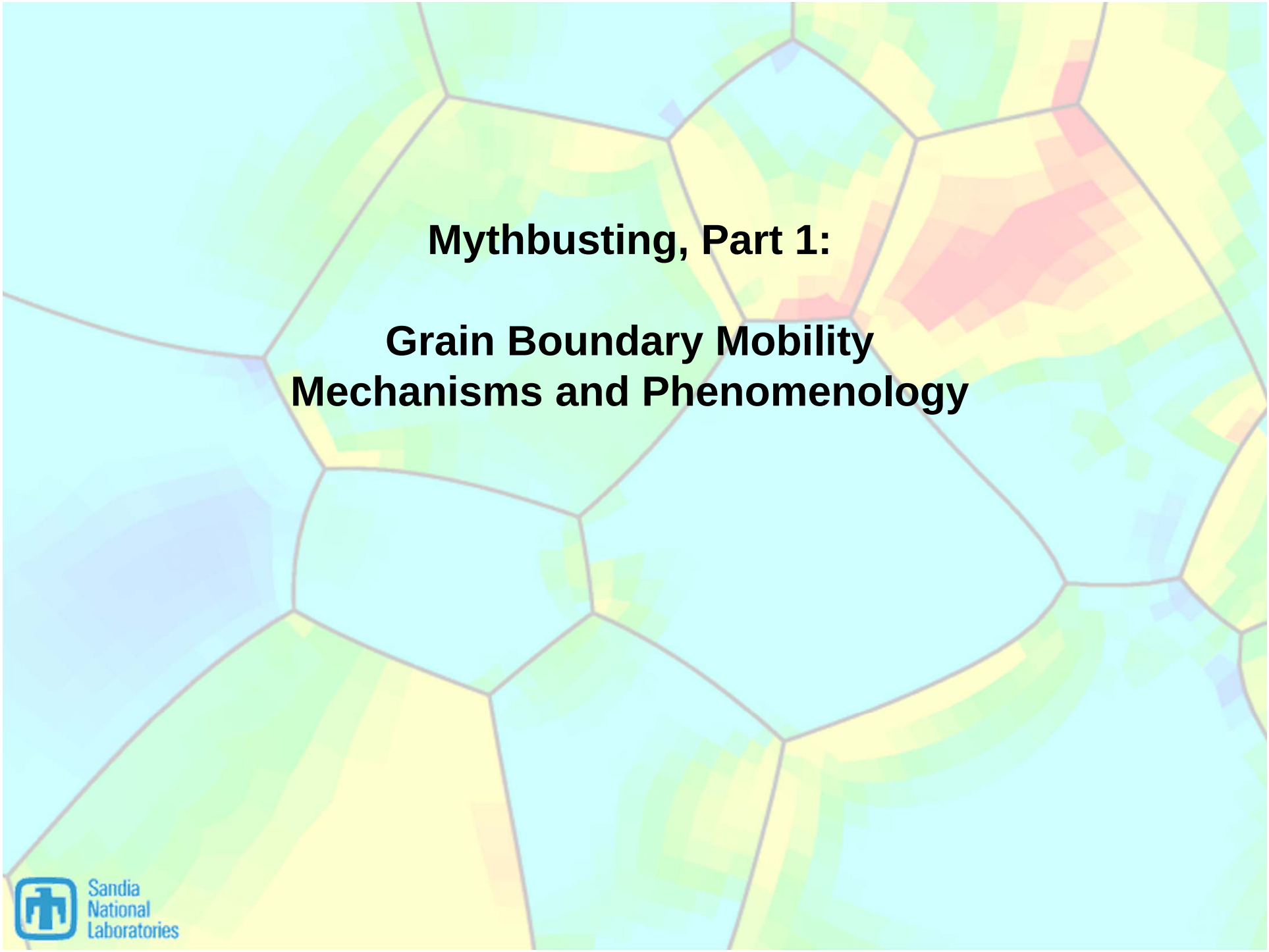
[Janssens *et al.*, *Nature Materials* **5**[2] 124 (2006), Olmsted, Foiles, Holm, *Scripta Mater.* **57** 1161 (2007), Olmsted, Holm, Foiles, *Acta Mater.* **57** 3704 (2009)]



Mythbusting, Part 1:

Grain Boundary Mobility Mechanisms and Phenomenology

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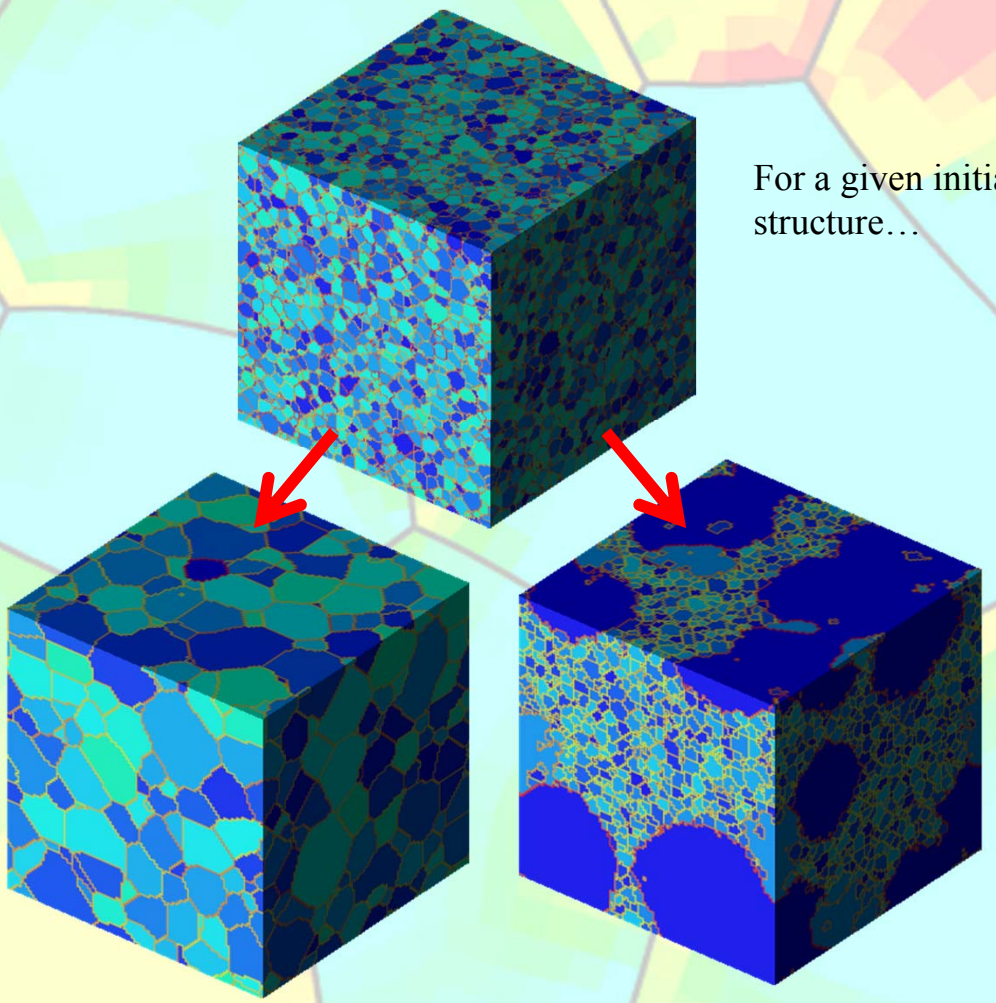
What is the grain boundary mobility?

- Grain boundary mobility is the **material constant** that scales the velocity of a grain boundary with the driving pressure applied to the boundary: $v = M P$



For a given initial grain structure…

Uniform boundary mobility results in normal grain growth.

Widely **varying grain boundary mobilities** can cause abnormal grain growth.

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Conventional wisdom:
Grain boundary motion is thermally activated

- Textbooks agree that grain boundary motion is a thermally activated process.

$$M = M_0 \exp\left(\frac{-Q}{kT}\right)$$

  - May be a single atom or multiatom process
  - For low angle grain boundaries, thermally activated dislocation climb is assumed to be the relevant process

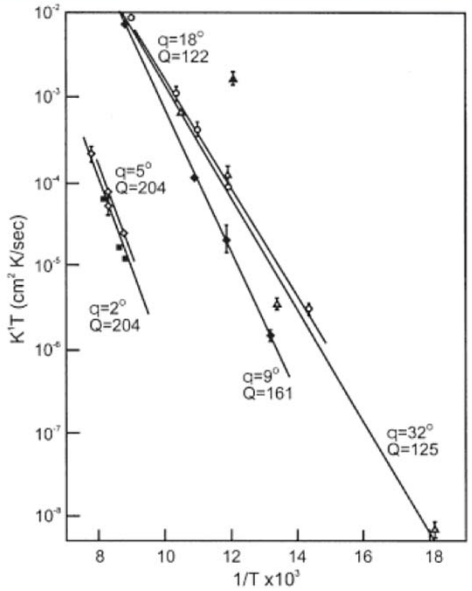

Fig. 5.4. Variation of boundary mobility parameter **K′** with temperature and misorientation for 99.999% copper. The activation energies (Q in kJ/mol) for each group of boundaries are also shown, (after Viswanathan & Bauer 1973).

"…the important process…appears to be the thermally activated transport of atoms across boundaries and the migration would seem to be controlled by the activation energy for this process."

-F. J. Humphreys and M. Hatherly,
Recrystallization and Related Annealing Phenomena

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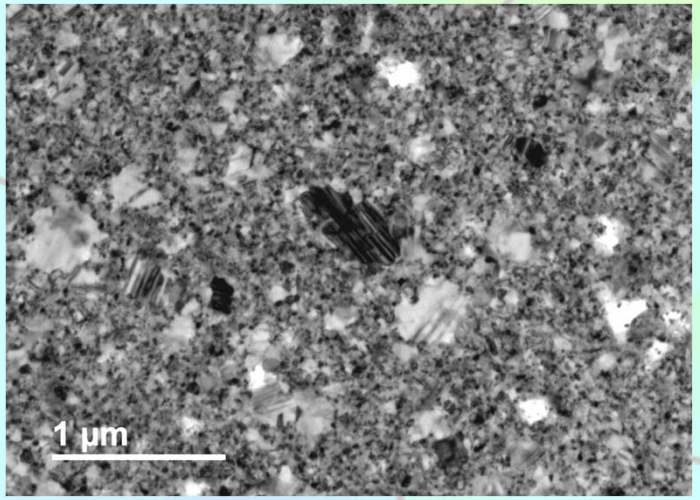
Observations of low temperature grain boundary motion contradict thermal activation



strain-free PLD Cu film, 6 years, R.T.
(D. Follstaedt, SNL)

boundary velocity $v = Mp$ — 10 nm grains

driving pressure $p \leq 60$ MPa

boundary mobility $M = M_0 \exp(-Q/kT)$

M_0: 10 m/s_MPa; Q: 1 eV

$T = 0.7\ T_m$ (annealing temperature) → $v \sim 12$ μm/s

$T = 0.3\ T_m$ (room temperature) → $v \sim 2 \times 10^{-7}$ nm/s

$T = 0.1\ T_m$ (cryogenic temperature) → $v \sim 6 \times 10^{-62}$ nm/s

•How did these grains grow?

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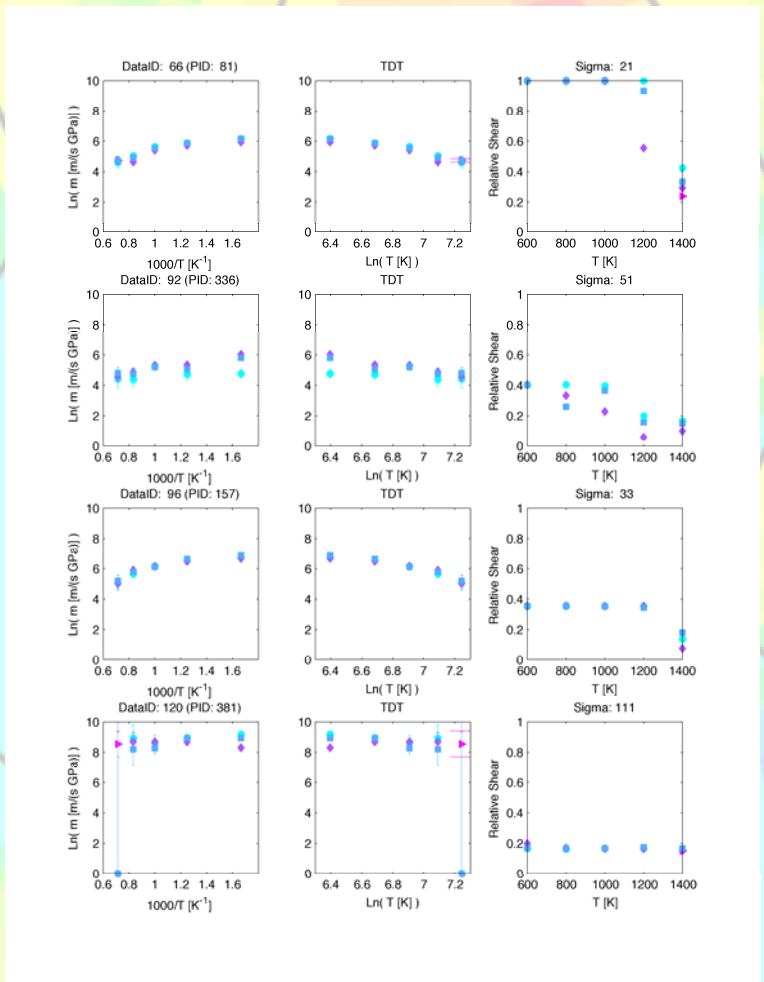
Mining the boundary mobility data set

- Used synthetic driving force molecular dynamics to calculate the mobility of 388 boundaries
  - 5 temperatures: 600, 800, 1000, 1200 and 1400K
  - Up to 4 driving forces: 0.005, 0.010, 0.025 and 0.050 eV/atom
  - 10,718 total mobility measurements
    [Olmsted, Holm, Foiles, *Acta Mater.* **57** 3704 (2009)]
- Plotted data in a variety of ways to probe for trends in mobility versus
  - Temperature
  - Shear coupling
  - Crystallography (symmetry, sigma, misorientation, etc.)



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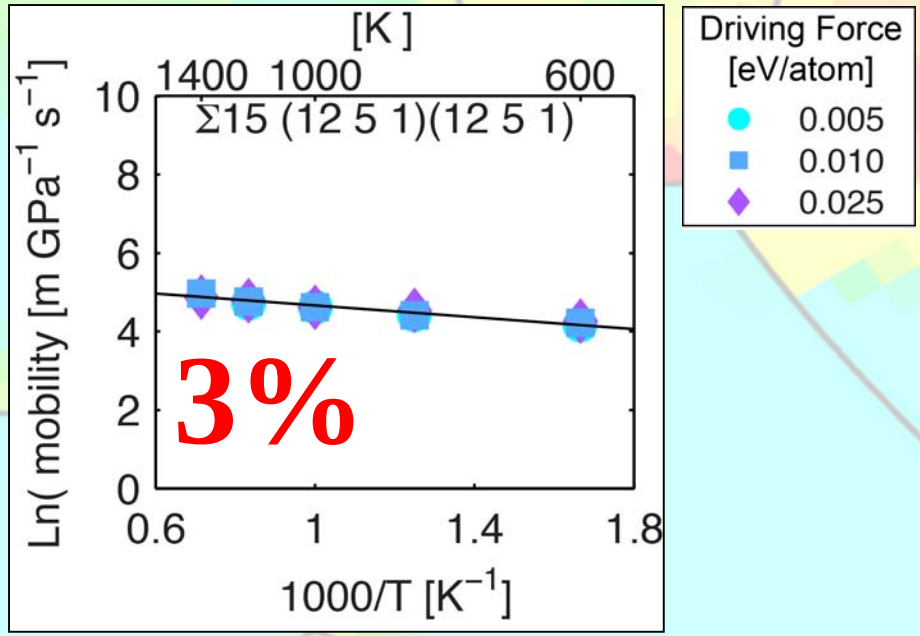
Results:
Thermally activated grain boundary motion



- Constant activation energy over the range of temperature
- No driving force dependence
- Moderate mobilities: 50-150 m/GPa_s
- **11 of 388 boundaries exhibit this behavior**

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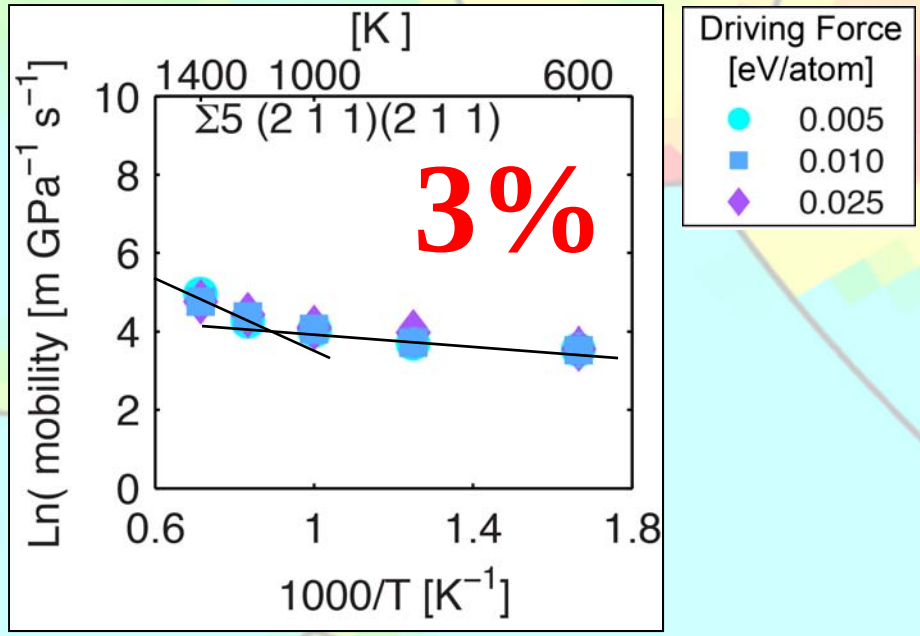
Results:
Two thermally activated motion regimes



- Thermally activated motion over the range of temperature, with a change in activation energy, presumably due to a change in motion mechanism
- Activation energy at high T > activation energy at low T
- Has been observed experimentally [Maksimova, Shvindlerman, Straumel, *Acta Metall.* **36** 1573 (1998)]
- **10 of 388 boundaries exhibit this behavior**

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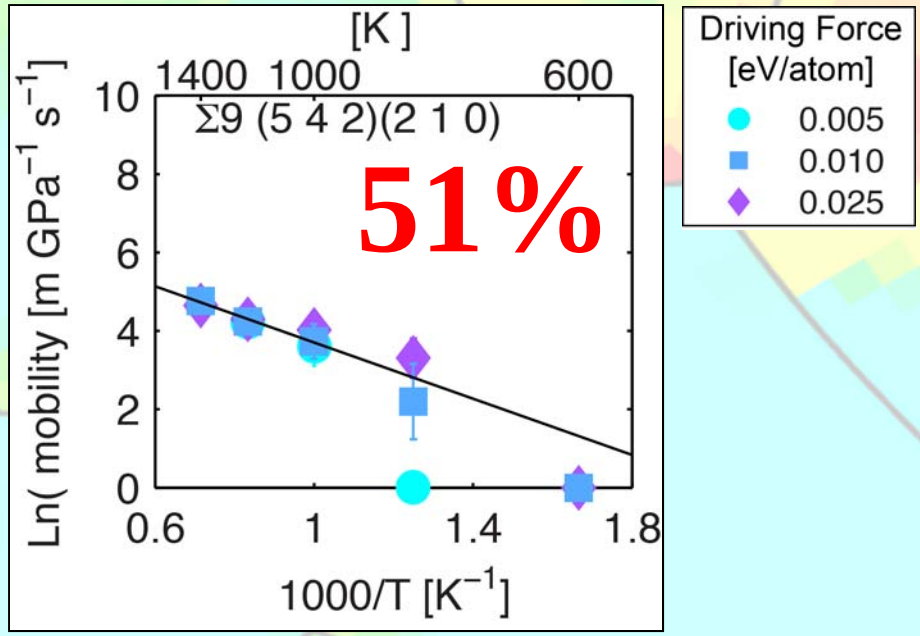
Results:
Thermally activated with boundary roughening



- Thermally activated with moderate mobilities at high temperatures
- Sudden drop in M at a characteristic T_r corresponds to a transformation from atomically rough to atomically smooth [Olmsted, Foiles, Holm, *Scripta Mater.* **57** 1161 (2007)]
- Often, the roughening transformation is driving force dependent, i.e. kinetic roughening
- **200 of 388 boundaries exhibit this behavior**

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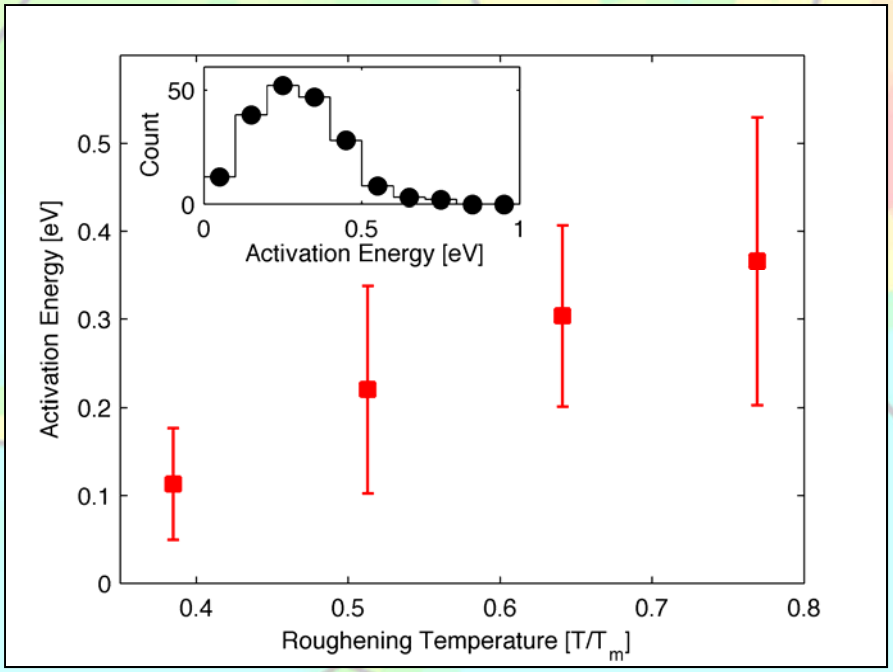
Activation energy trends in thermally activated grain boundary motion



- We observe an essentially normal distribution of activation energies, Q
  - There is no single, characteristic Q
  - Q's are lower than experimentally measured, consistent with other MD studies
- Mean activation energy $\langle Q \rangle$ increases with the roughening temperature T_r
  - Reasonable to correlate tendency toward smooth boundary structure with high Q
  - Suggests that most or all boundaries can kinetically roughen

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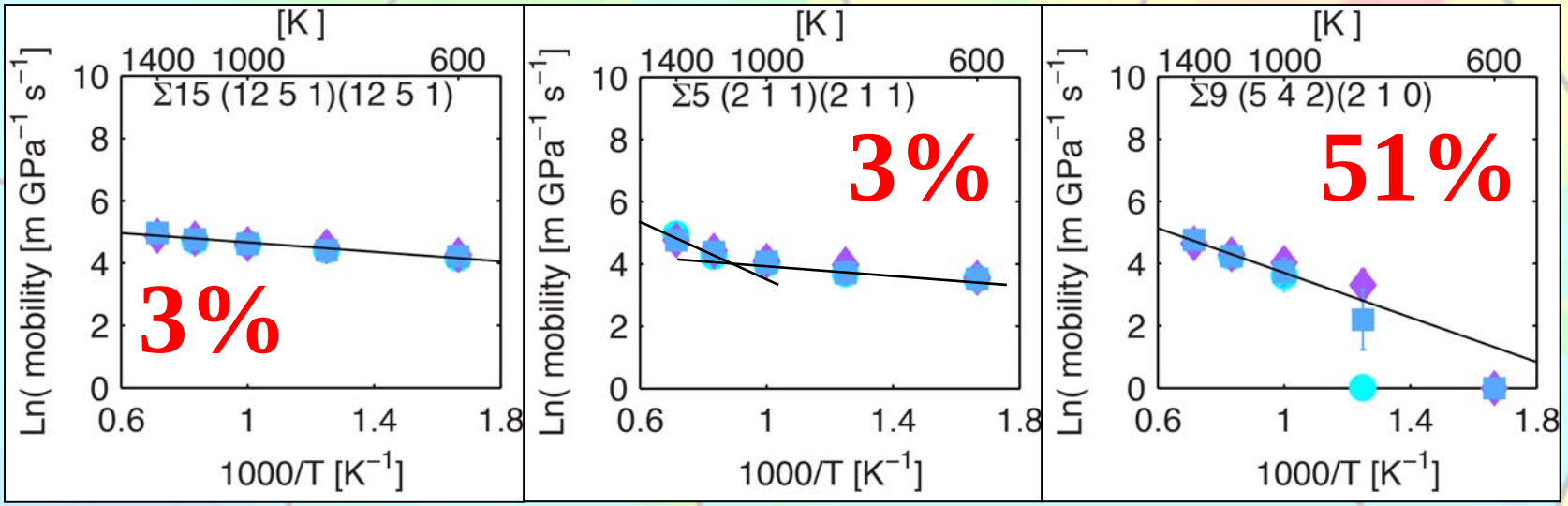
Summary:
Thermally activated grain boundary motion



- Thermally activated grain boundary motion occurs in 57% of our grain boundaries
- The vast majority of these undergo thermal roughening at a characteristic temperature
- Roughening temperature and activation energy are strongly correlated

How do the remaining 43% of grain boundaries move?

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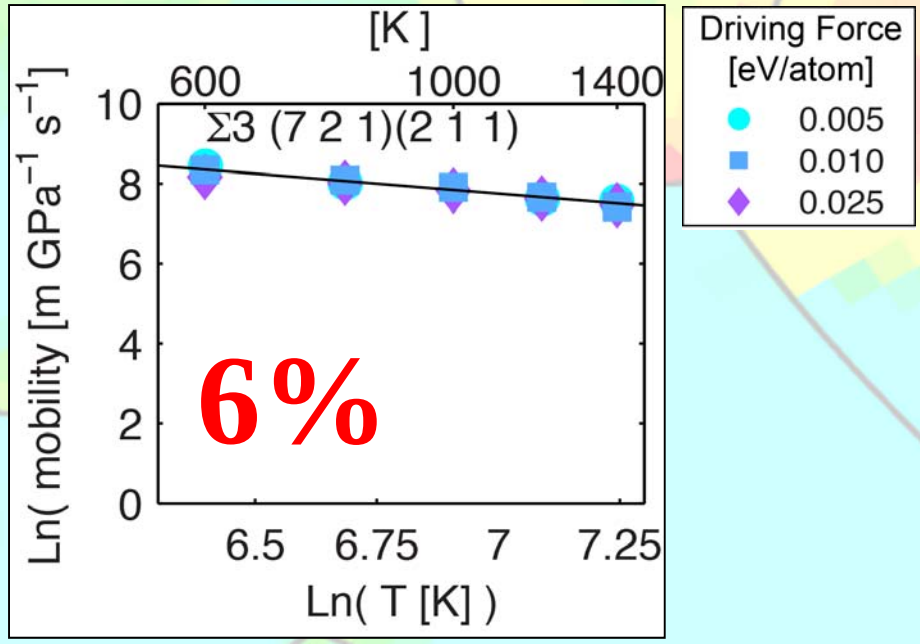
Results:
Thermally damped grain boundary motion



- *M* decreases as *T* increases, such that $M \propto 1/T$ – **boundaries move faster as *T* decreases!**
- Suggests a phonon-damped motion, similar to dislocation glide
- All thermally damped boundaries we have observed are Σ3 boundaries
- *M* is exceptionally high (800-4000 m/GPa_s) and not driving force dependent
- **25 of 388 boundaries (25 of 41 Σ3 boundaries) exhibit this behavior**

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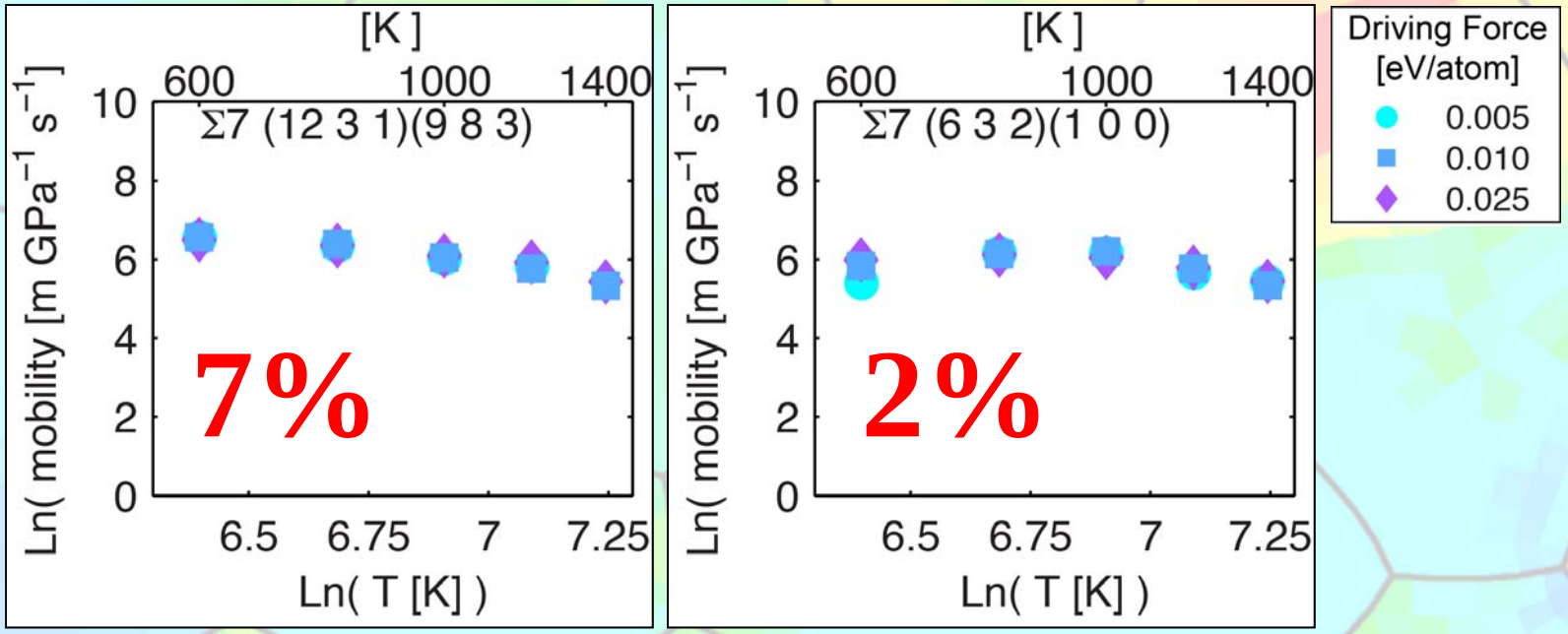
Results:
Anti-thermal grain boundary motion



- *M* decreases as *T* increases, but *M* is not proportional to *1/T*. Instead, *M* is concave in *T*, with or without a local maximum.
- None of these boundaries are Σ3 boundaries.
- *M* is moderate (150-700 m/GPa_s), lower than Σ3 thermally damped boundaries, and comparable to thermally activated boundaries at high *T*.
- **33 of 388 boundaries exhibit this behavior**

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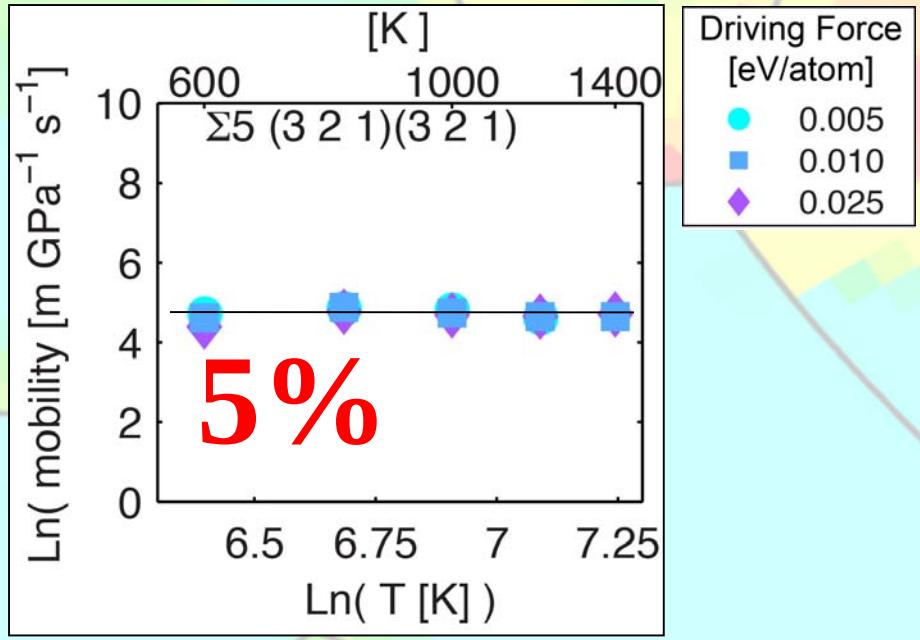
Results:
Athermal, constant grain boundary motion



- Moderate *M*, constant over the range of *T*, with no driving force dependence
- Indicates an athermal, undamped motion; potentially a velocity saturation effect
- A high fraction of these boundaries exhibit shear coupled motion
- Athermal *M* has been observed in faceting boundaries and attributed to a speed of sound limitation [Kopetskii, Sursaeva, Shvindlerman, *Scripta Metall.* **12** 953 (1978)]
  - **21of 388 boundaries exhibit this behavior**

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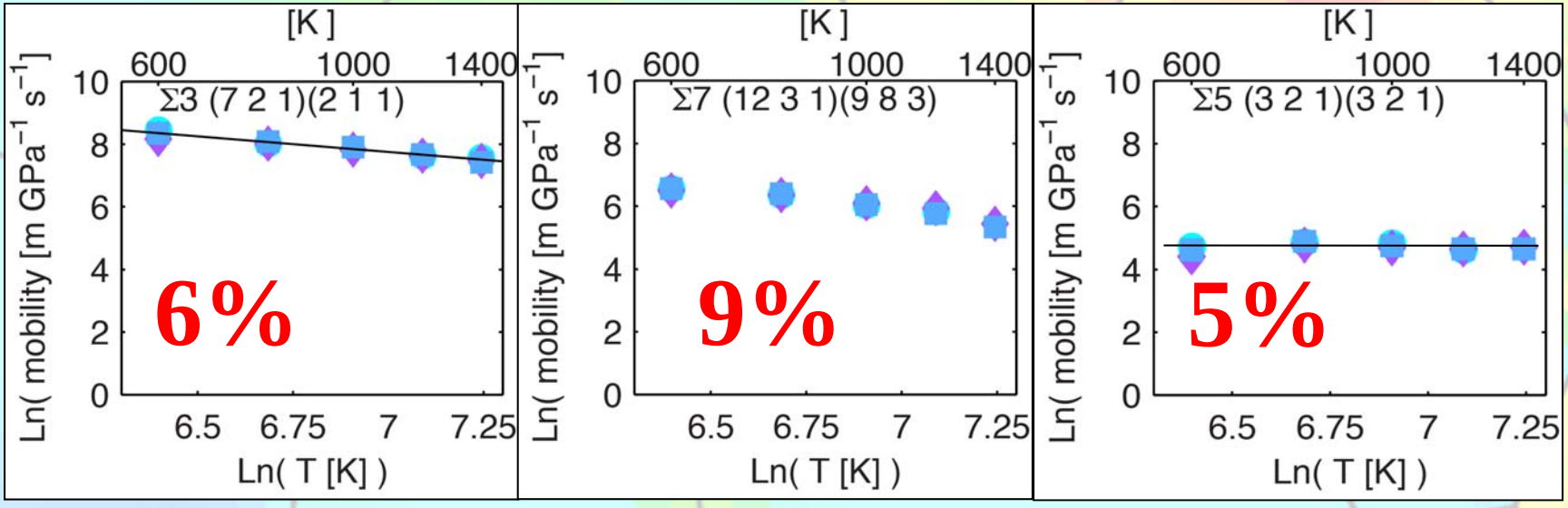
Summary:
Non-activated grain boundary motion



- Non-activated grain boundary motion occurs in 20% of our grain boundaries.
- The mechanisms of non-activated motion are unknown.
- **Non-activated motion offers the possibility that a substantial fraction of grain boundaries could be mobile at very low temperatures.**

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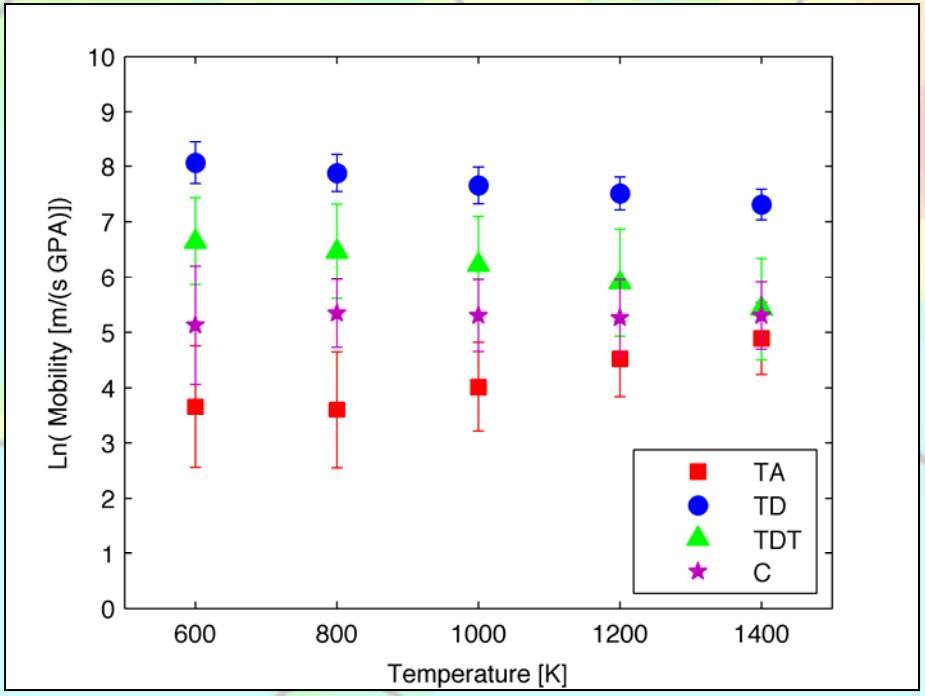
Temperature dependence of mobility



- At a given *T*, the <*M*> varies with mobility mechanism
- At high *T*, all mechanisms (excluding thermally damped motion) converge
- At low *T*, thermally damped and thermally activated mobilities differ by 2 orders of magnitude
- **As *T* decreases, the importance of non-activated boundaries increases**

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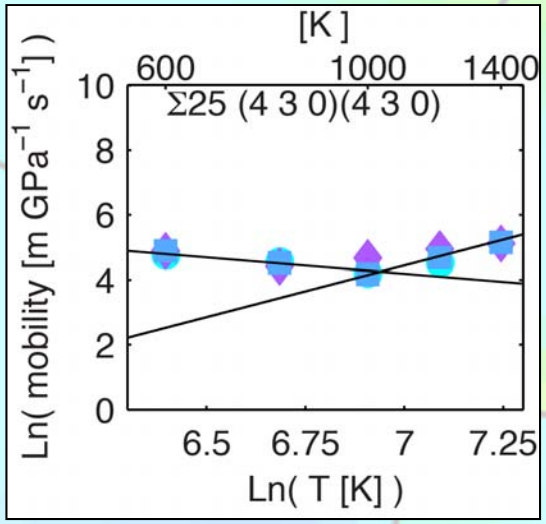
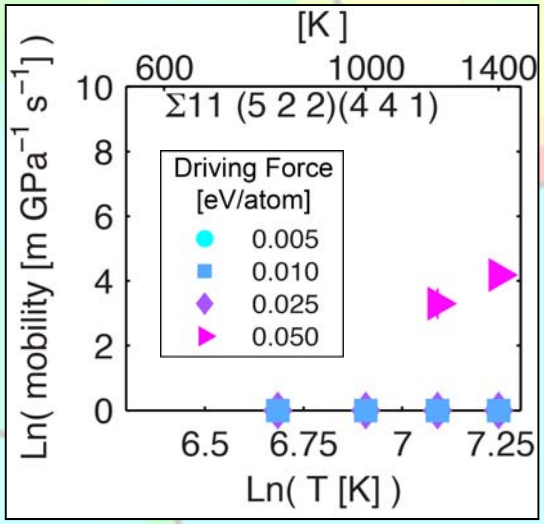
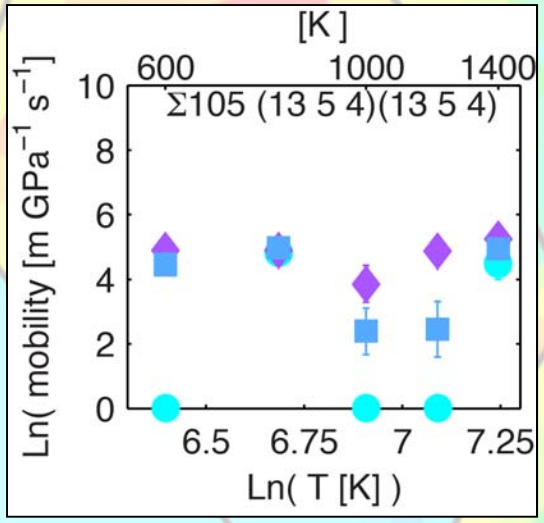
The final 23%:
Miscellaneous motion mechanisms



- **14%** move by a combination of mechanisms
- The observed combinations are reasonable
- Roughening appears possible for all boundary types



- **6%** are immobile at all temperatures
- We can force motion using extremely high driving forces
- Possibly includes boundaries that roughen at temperatures above 1400K



- **3%** move in ways that are simply unclassifiable

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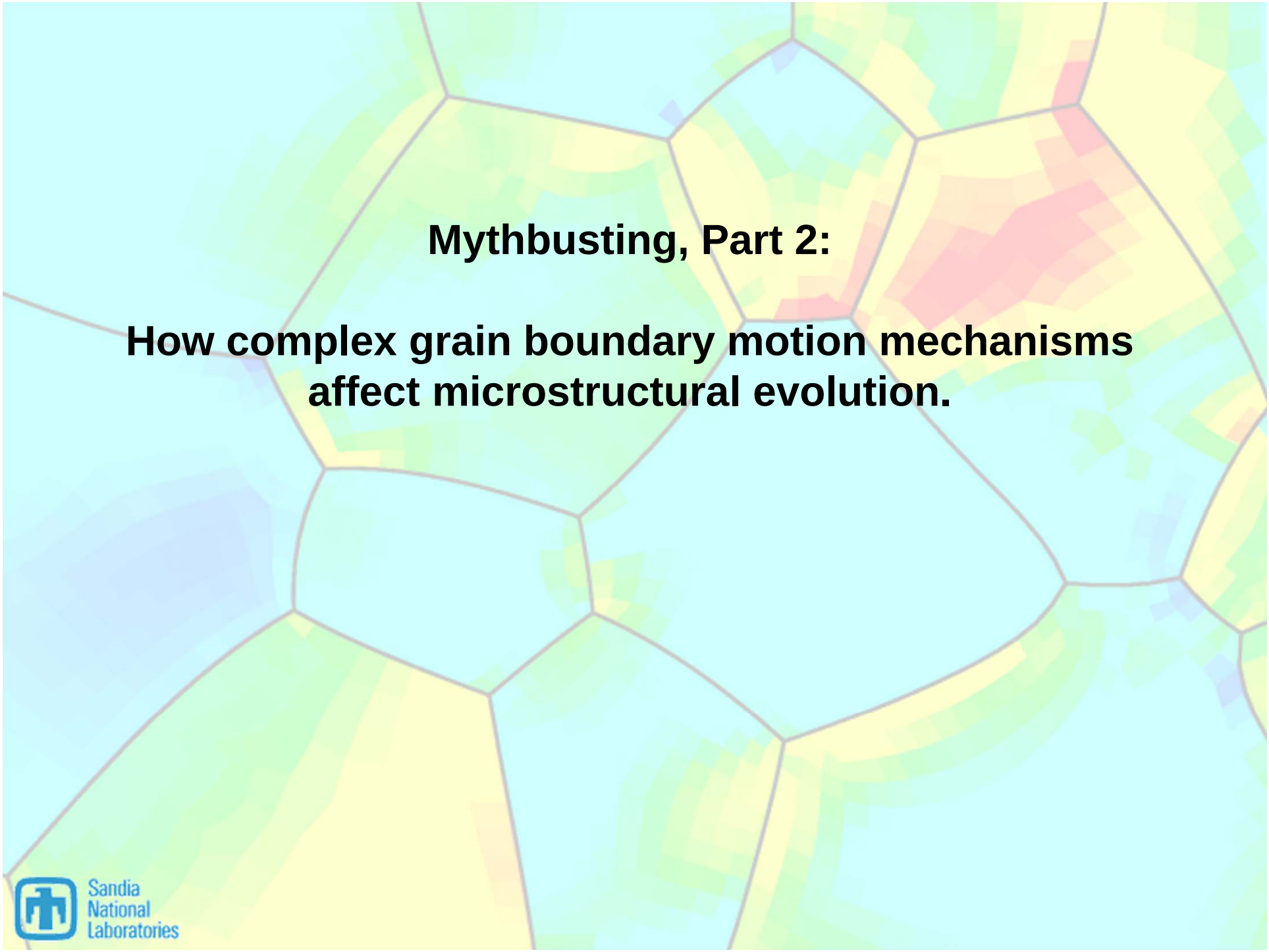
Grain Boundary Mobility Myths: BUSTED

- **Myth: Grain boundary motion is thermally activated.**
  - **Fact: Thermally activated motion occurs in just over half of boundaries – and most of those undergo a thermal roughening transition.**
- **Myth: Grain boundaries are slow at low temperatures.**
  - **Fact: Non-activated motion can yield high mobility at low temperatures in almost a quarter of boundaries.**
- **Myth: Grain boundary motion is relatively simple.**
  - **Fact: About a quarter of boundaries are mixed mode, immobile, or otherwise unclassifiable.**

Mythbusting, Part 2:

How complex grain boundary motion mechanisms affect microstructural evolution.



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The longstanding problem of grain growth stagnation at high temperatures

- The equilibrium state of crystalline materials is a single crystal.

- However, grain growth only rarely proceeds to the single crystal state.
  - Stagnation is pervasively observed in experiments
  - Assumed – without physical justification – in most grain growth models

- **Conventional wisdom attributes grain growth stagnation to solute drag or particle pinning, even in high purity materials.**

If grain growth did not stop, the cost of Si photovoltaics would decrease dramatically.

$$\frac{dR}{dt} = M\gamma\left(\frac{1}{R} - \frac{1}{R_c}\right)$$

Most grain growth models assume a maximum attainable grain size.

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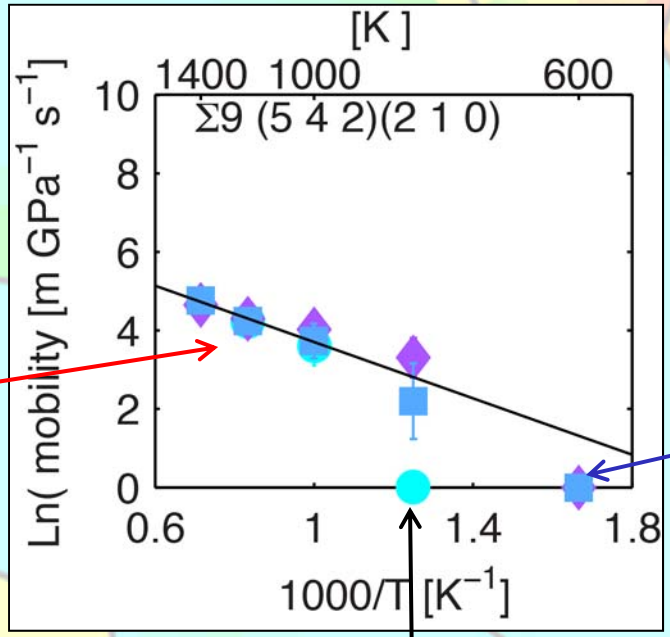
Atomic-scale simulations reveal the pervasive phenomenon of thermal roughening

- A thermal roughening transition has been observed with all boundary motion mechanisms except thermally damped motion.



High T:
Atomically rough
Highly mobile
Continuous motion

Low T:
Atomically smooth
Nearly immobile
Stepwise motion

Roughening temperature T_r

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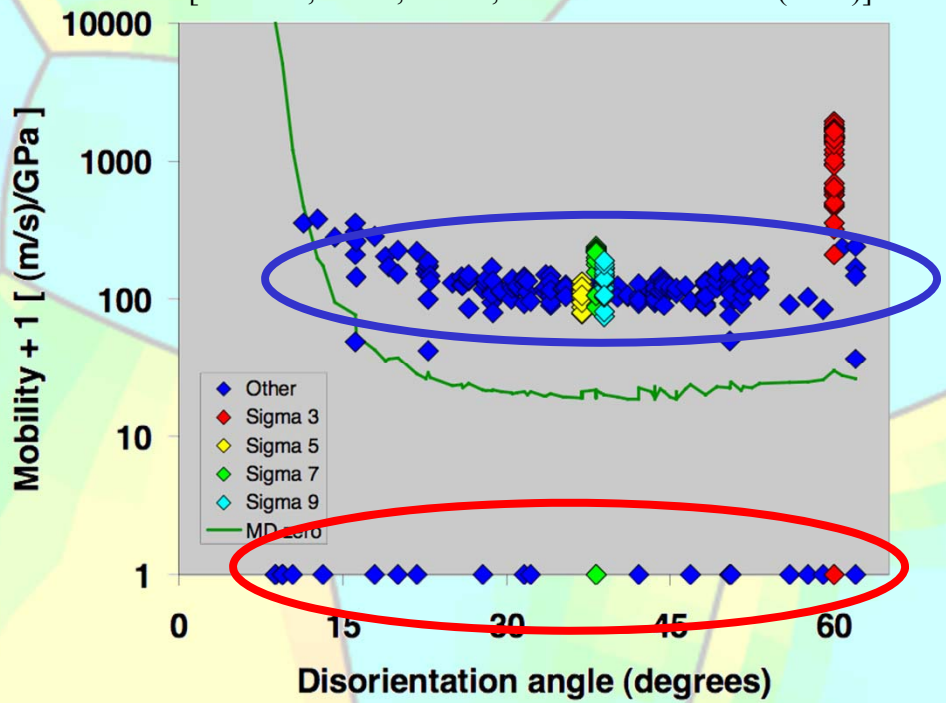
How thermal roughening affects the distribution of grain boundary mobilities

- At a given temperature, grain boundary mobilities fall into two groups:

  -Rough, mobile boundaries (M ≥ 100 m/s_GPa at 1400K)

  -Smooth, immobile boundaries (M ~ 0 m/s_GPa)

[Olmsted, Holm, Foiles, *Acta Mater.* **57** 3704 (2009)]



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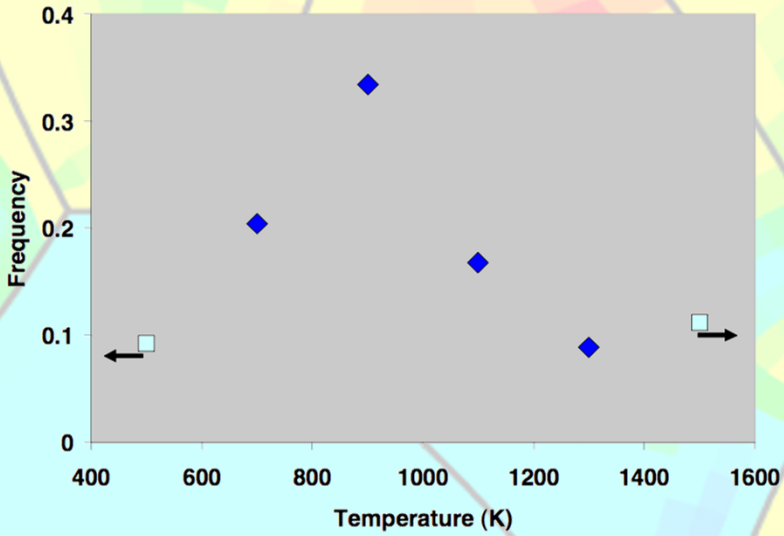
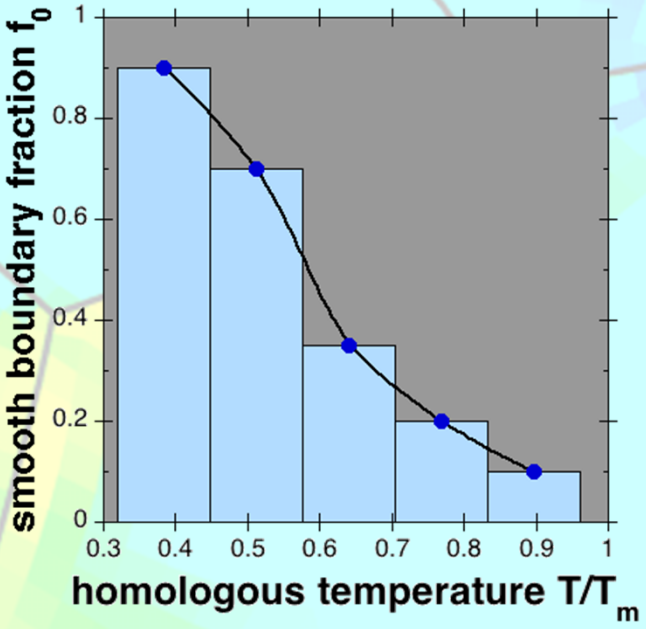
The roughening temperature varies widely; smooth/slow boundaries are always present

- Data mining provides the distribution of grain boundary roughening temperatures



- The cumulative distribution of roughening temperatures gives the fraction of smooth/immobile boundaries as a function of temperature.



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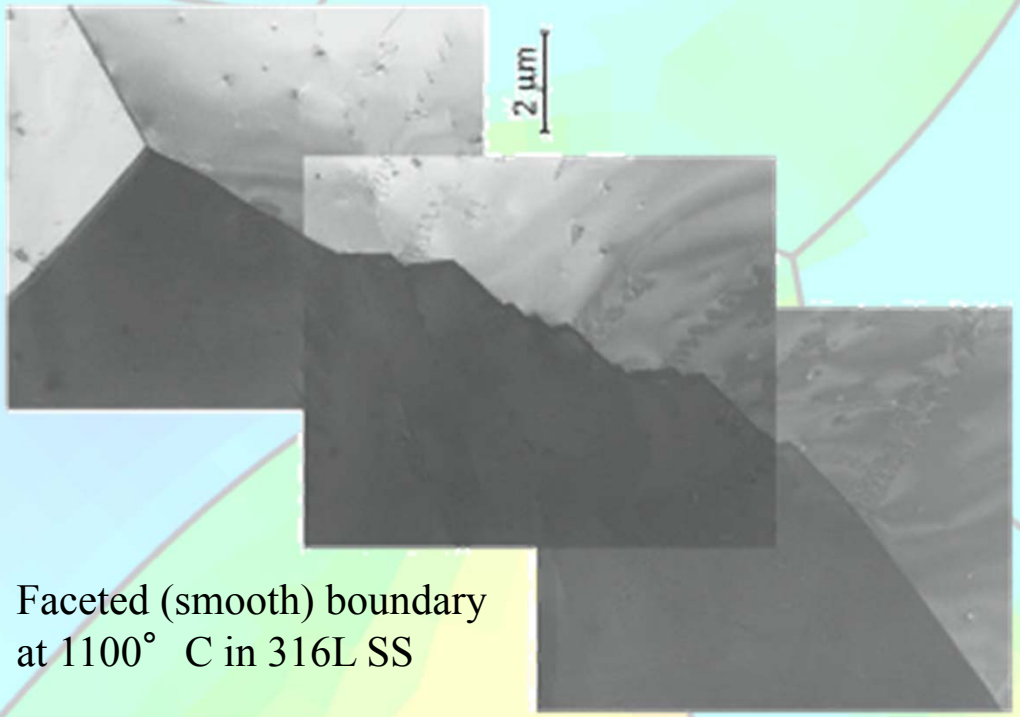
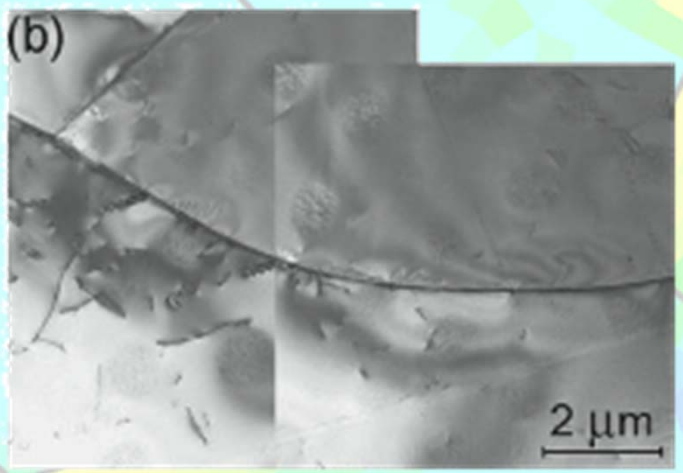
Experiments suggest further study

- Yoon and Cho [*J. Mater. Sci.* **40** (2005) 861] surveyed boundary roughening:

  "In many metals and oxides, abnormal and normal grain growth behaviors were observed to be correlated with grain boundary roughening."



Faceted (smooth) boundary at 1100° C in 316L SS



Unfaceted (rough) boundary at 1350° C in 316L SS

⇒ How does grain boundary roughening affect grain growth in polycrystals?

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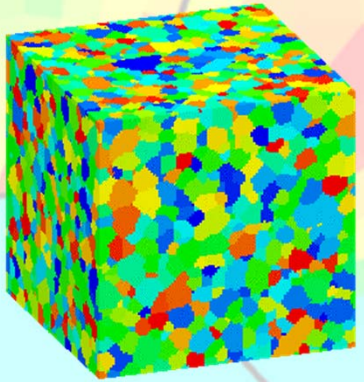
Incorporate boundary roughening data into microstructural evolution simulations

- Begin with an equiaxed polycrystalline microstructure
  - uniform boundary energies
  - slightly pre-coarsened
  - 100x100x100 lattice
- Assign boundary mobilities at random
  - smooth boundaries $M \sim 0$
  - rough boundaries $M \sim 1$
  - fraction of smooth boundaries f_0 depends on T
- Allow system to evolve via normal grain growth physics
  - Monte Carlo Potts model
  - 16 independent runs for each f_0
  - SPPARKS parallel code package
    http://www.sandia.gov/~sjplimp/spparks.html



T (K)	f_0
600	0.9
800	0.7
1000	0.35
1200	0.2
1400	0.1

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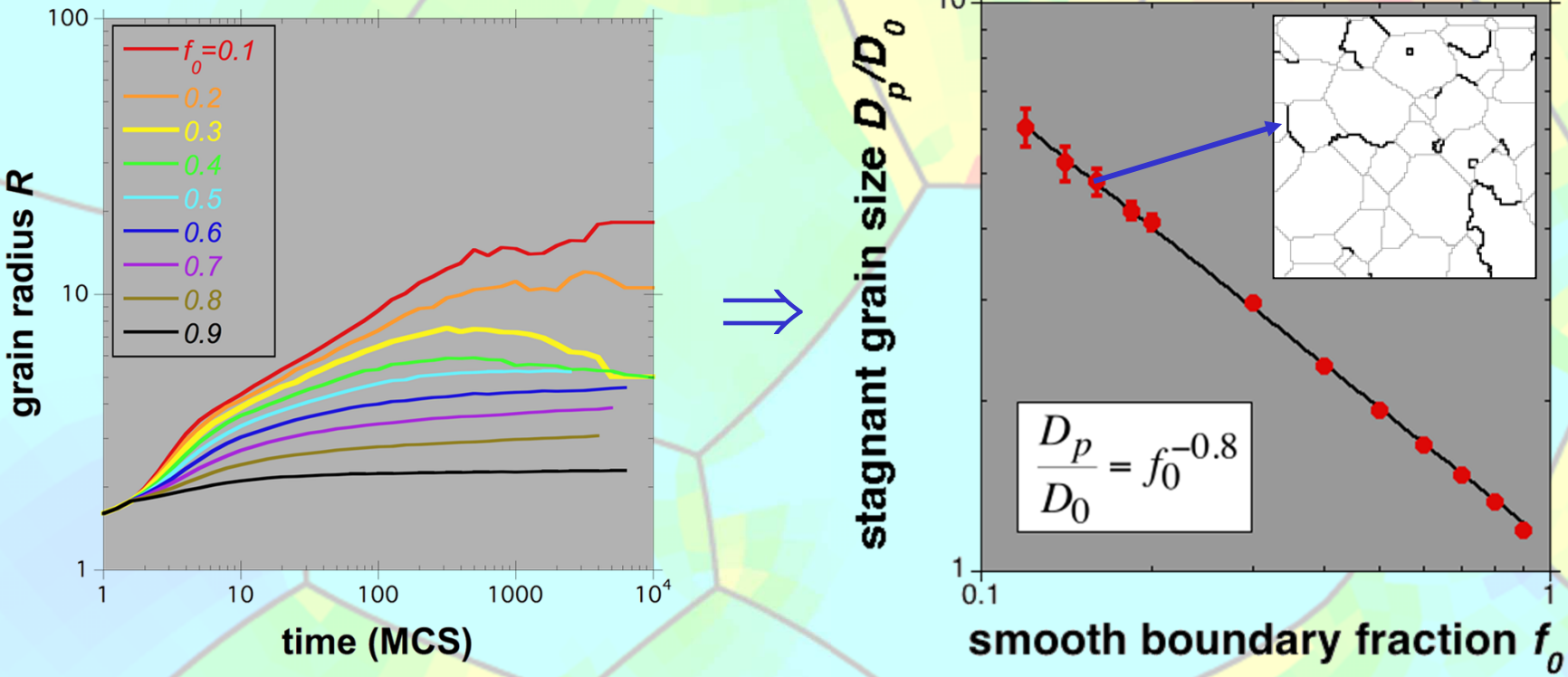
Grain growth kinetics



- Grain growth stagnates in the presence of smooth boundaries
- The stagnant grain size has a power law dependence on smooth boundary fraction f_0
- Not all boundaries must be immobile for the structure to be stagnant

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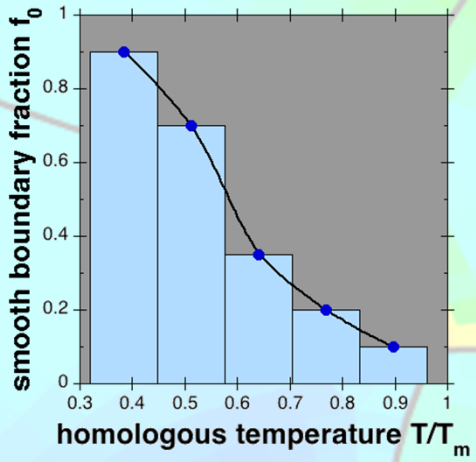
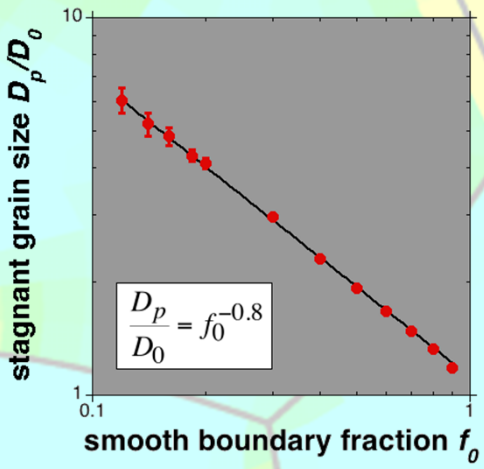
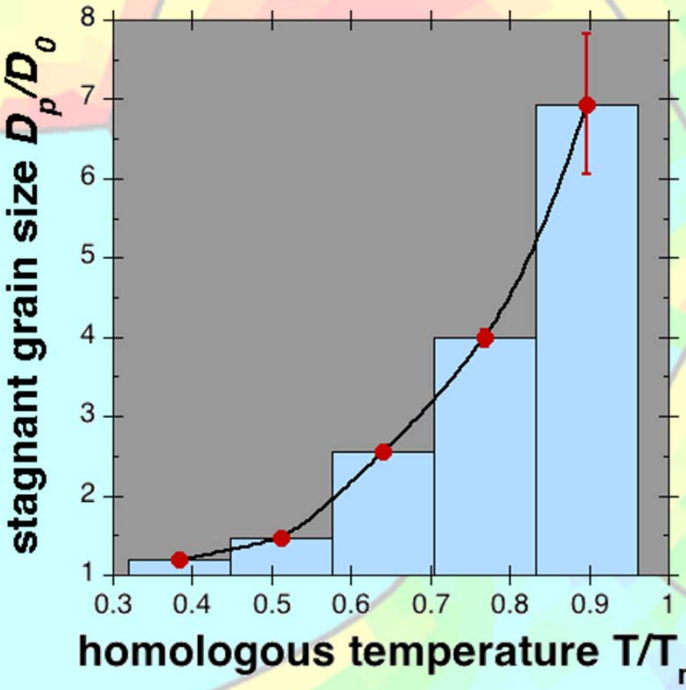
Mesoscale simulations connect atomic-scale phenomena to microstructure

Atomistic results + Mesoscale simulations ⇒ Microstructural insights







- Grain growth does not proceed to completion at any temperature
- The stagnant grain size increases with T

⇒**Boundary roughening may play a critical role in grain growth stagnation.**

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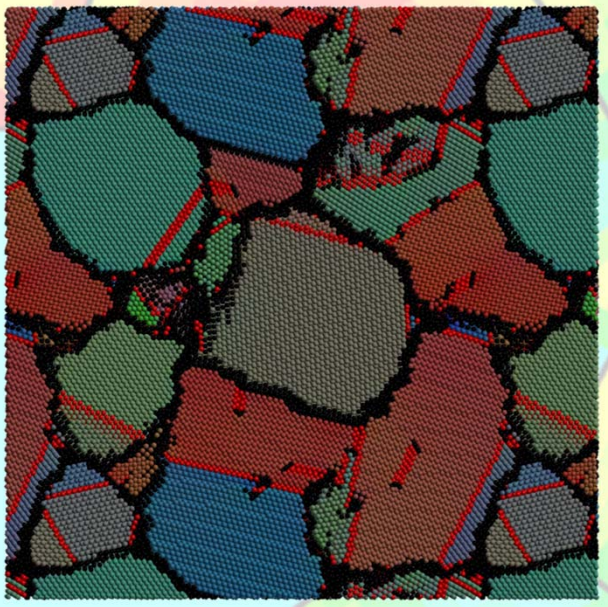
Coupling back to atomistic simulations provides physical validation

Direct MD simulation of annealing of nanograined Ni

- 3-D Cubic cell with periodic boundary conditions
  - 55 or 110 a_0 (~20 or 40 nm) on a side
- Initial structure
  - 100 or 800 randomly centered and oriented Voronoi grains
  - Initial average grain diameter: ~5 nm
  - 650k or 5.2M atoms
- Foiles-Hoyt EAM Potential for Ni
- Temperatures: 0.85 T_M, 0.75 T_M, 0.65 T_M
  - T_M = 1565 K for this potential



Visualization key:

- Color reflects local orientation of fcc neighbor shell
- Red: HCP configuration of nearest neighbors
- Black: Unidentified neighbor structure

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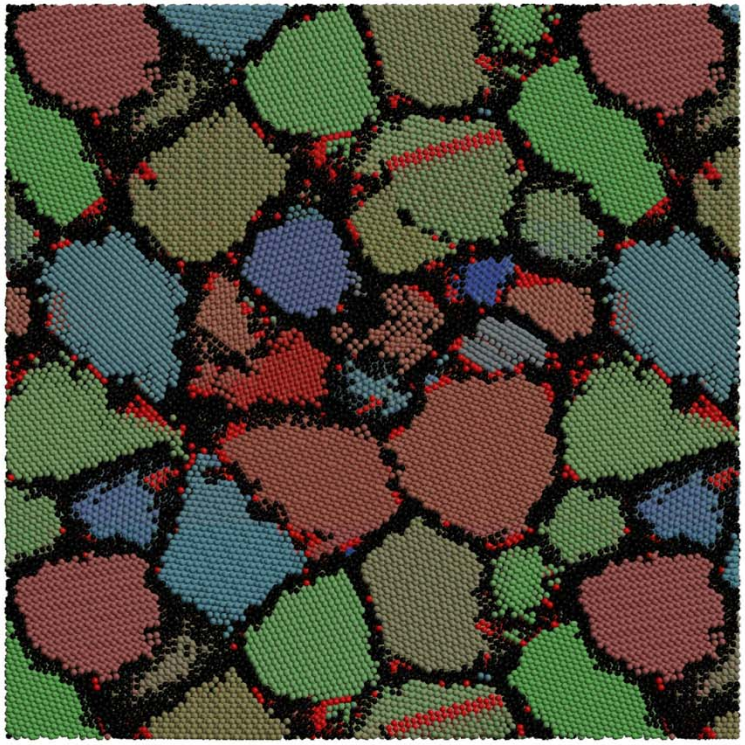
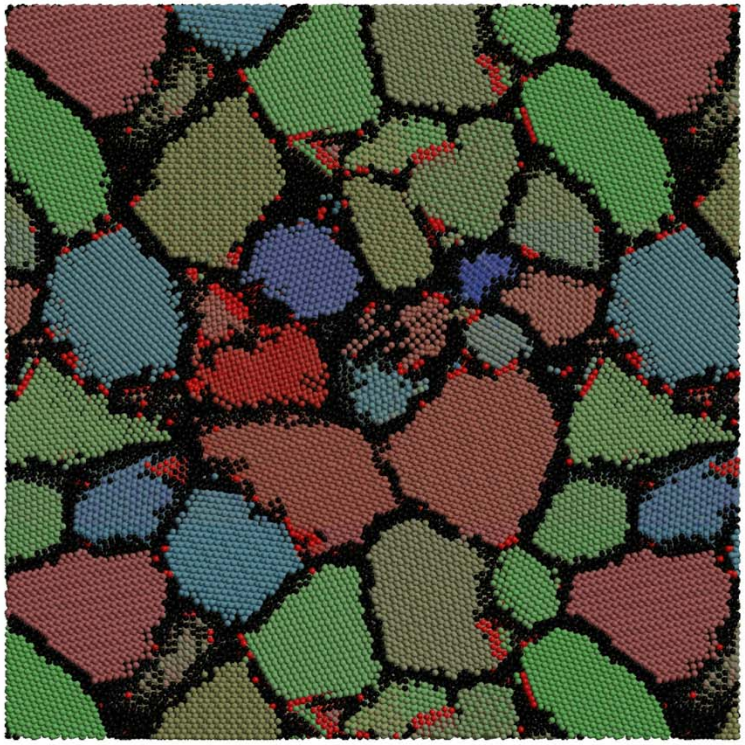
Time evolution of microstructure differs with temperature



$T = 0.85\ T_M$
0.6 ns



$T = 0.65\ T_M$
10.0 ns

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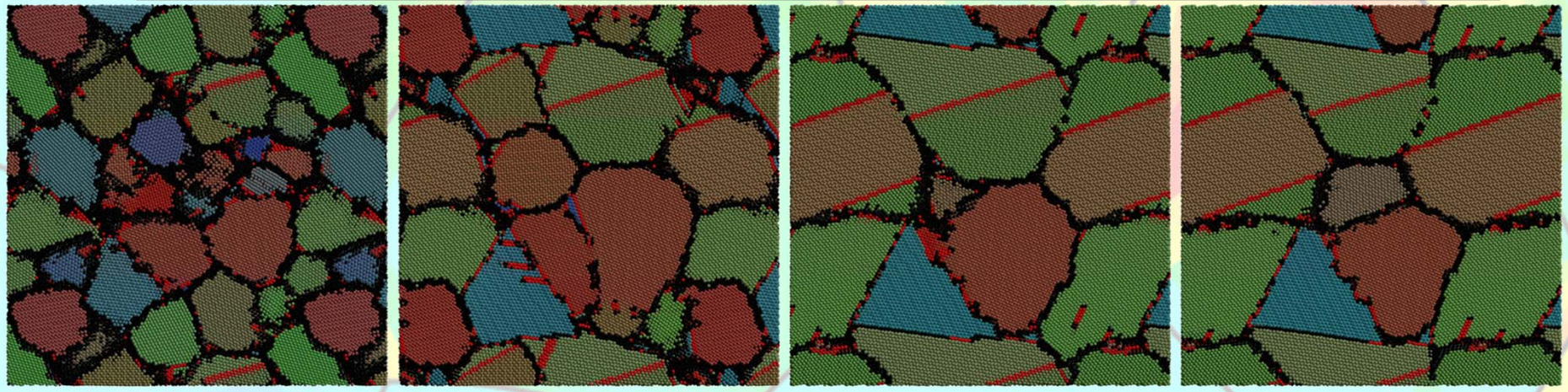
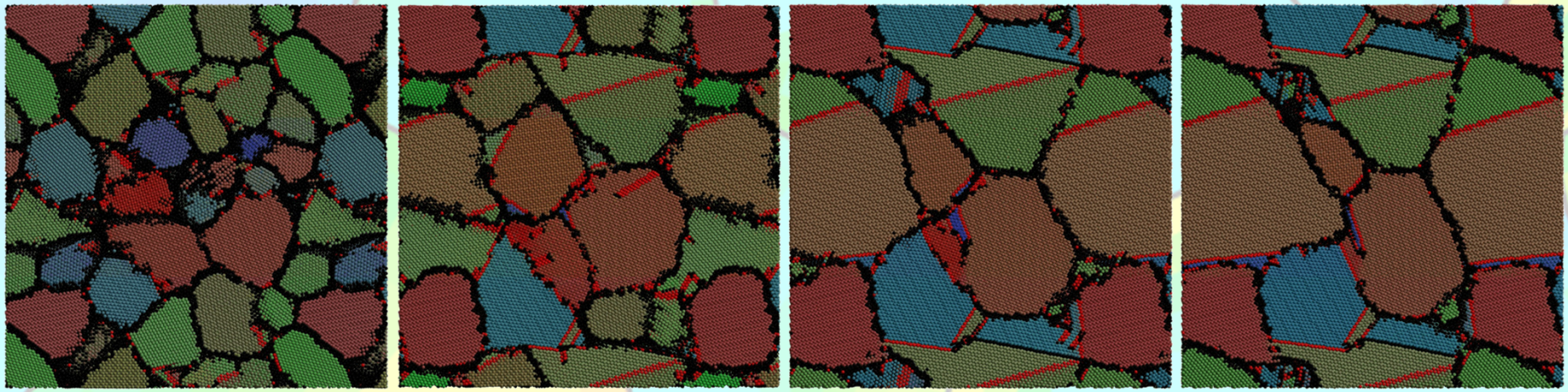
Time evolution of microstructure differs with temperature



$T = 0.85\ T_M$, *initial* | 0.2 ns | 0.4 ns | 0.6 ns



$T = 0.65\ T_M$, initial | 2 ns | 7 ns | 10 ns

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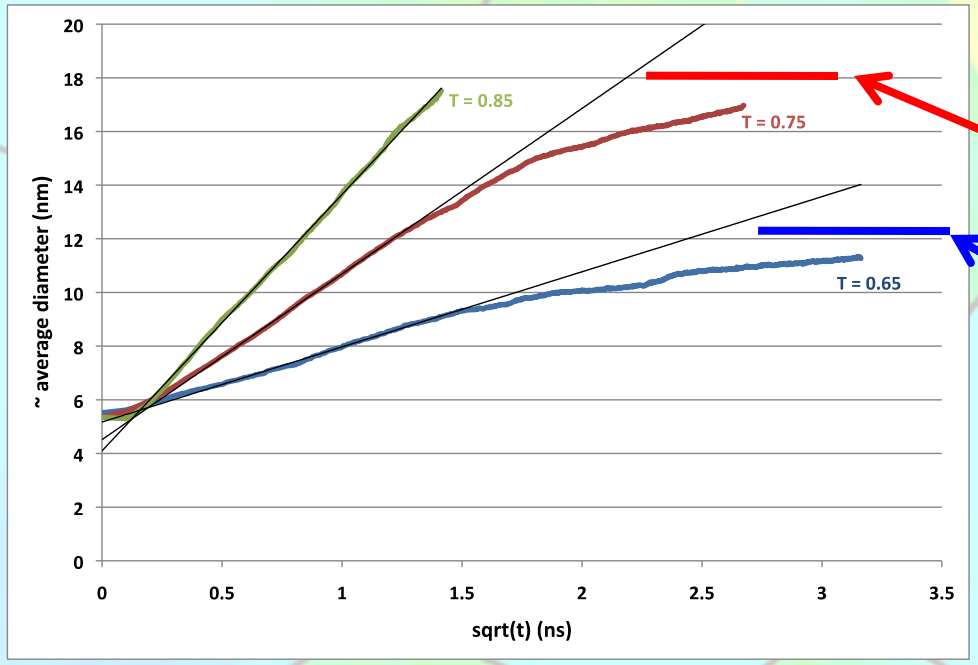
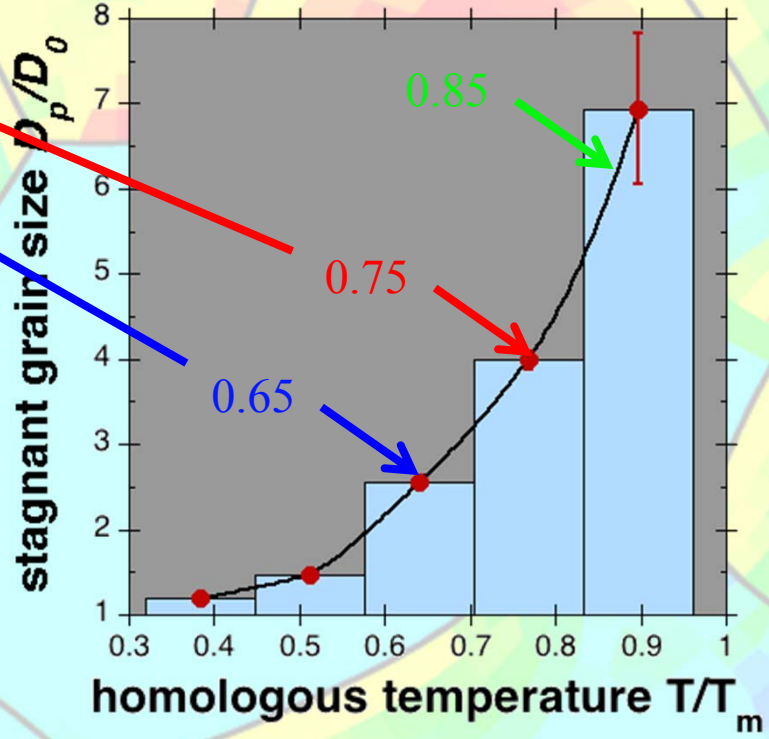
Atomic-scale results support mesoscale model for roughening stagnation





- 0.65 and 0.75 T_M samples stagnate at grain sizes consistent with the predictions of the microstructural simulation.
- Sample size is too small to reach stagnant size predicted for 0.85 T_M sample.

⇒Atomistic simulations quantitatively validate microstructural results and support the roughening stagnation model.

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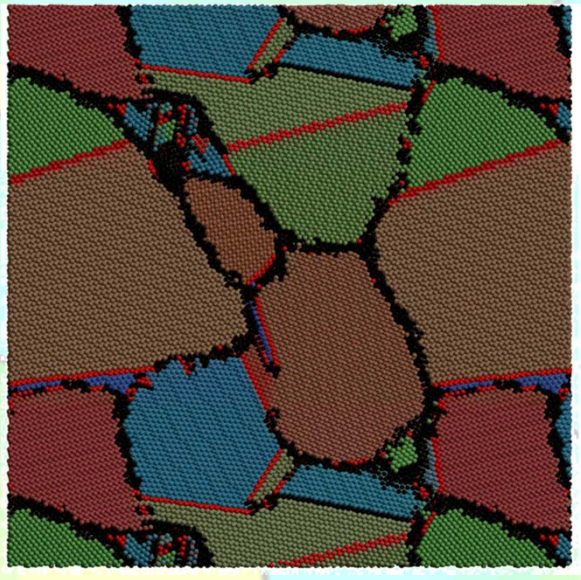
Grain Growth Stagnation Myth: BUSTED

- **Myth: Grain growth stagnation is caused by impurities.**
  - **Fact: Smooth grain boundaries stop grain growth, even in perfectly pure materials.**



E. A. Holm and S. M. Foiles,
Science **328** 1138 (2010).

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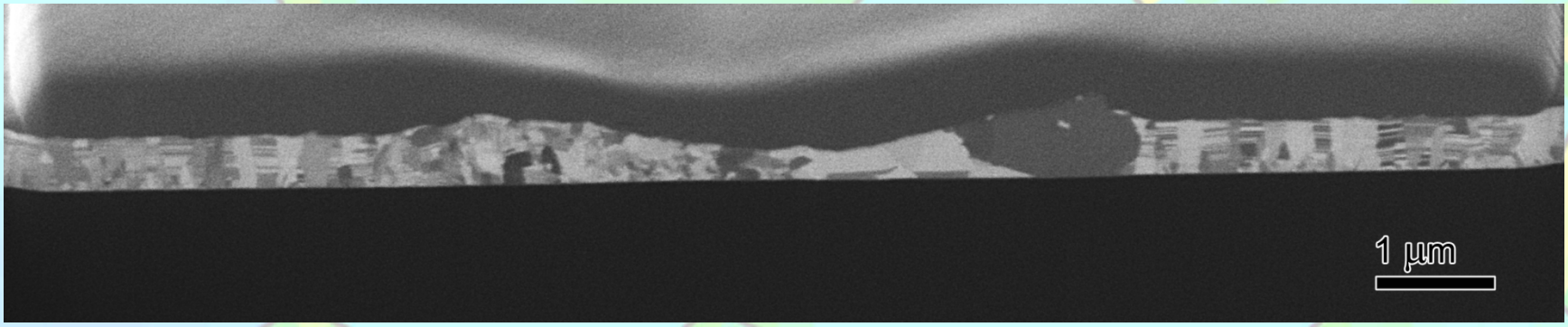
Next steps in Mythbusting: Anomalous low temperature boundary motion

- **Conventional Wisdom: Grain structure is frozen in at low temperatures.**
  - **Fact: We observe substantial grain growth at 4K in indented Cu that contains large numbers of Σ3 boundaries.**



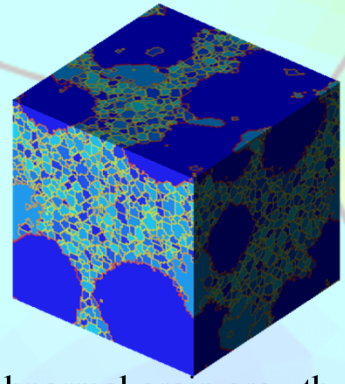
  - Many incoherent Σ3 boundaries have very high mobility at low temperatures due to the thermally damped motion mechanism. **Coincidence or not?**

Conclusions

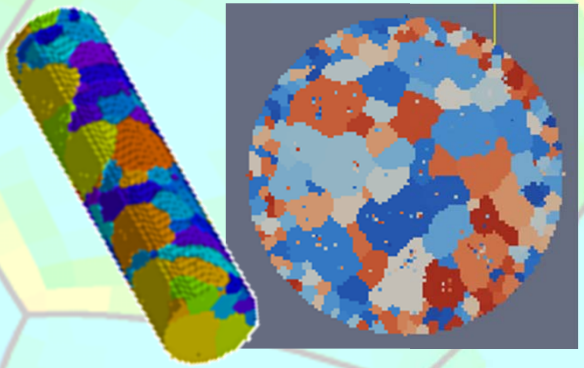
- Most of what we've presumed about grain boundary mobility is wrong – at least for some boundaries at some temperatures.
- Our new understanding of grain boundary motion answers longstanding questions about microstructural evolution.
- We move beyond the old myths by integrating new results from atomistic simulations with mesoscale models and experimental results.

Beyond Grain Boundaries: Computational Materials Science at the Mesoscale

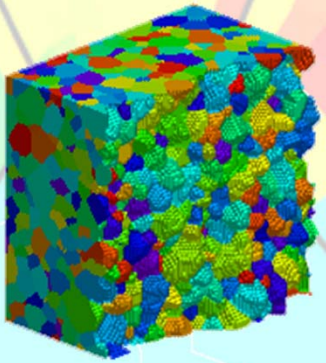
- Mesoscale models link structure, processing and properties.



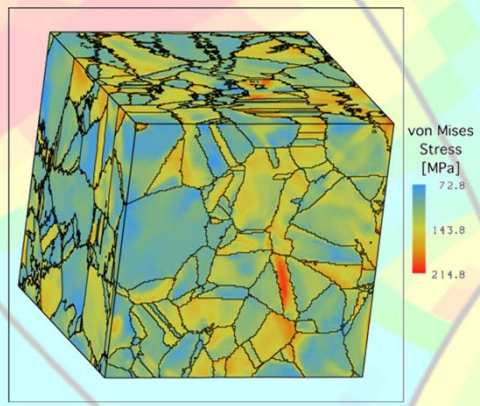
abnormal grain growth



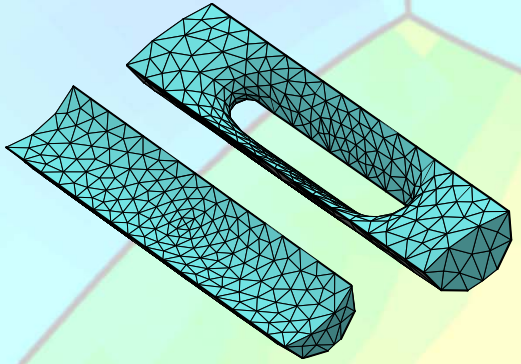
static and dynamic recrystallization



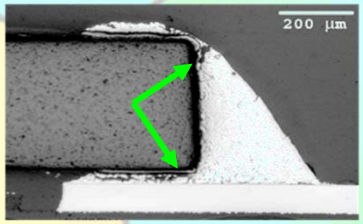
brittle fracture



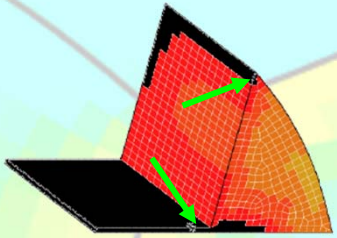
polycrystal plasticity



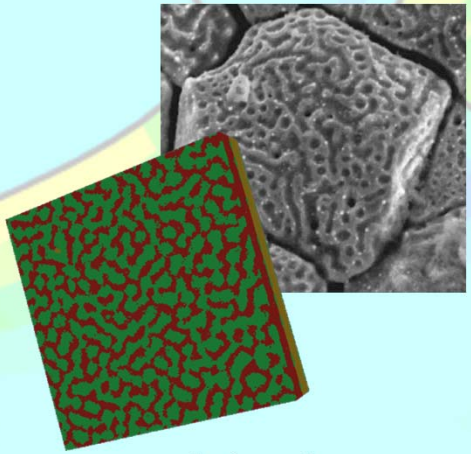
weld pool shape and hot tearing



1000 cycles



thermomechanical fatigue and failure



percolation phenomena and void link-up

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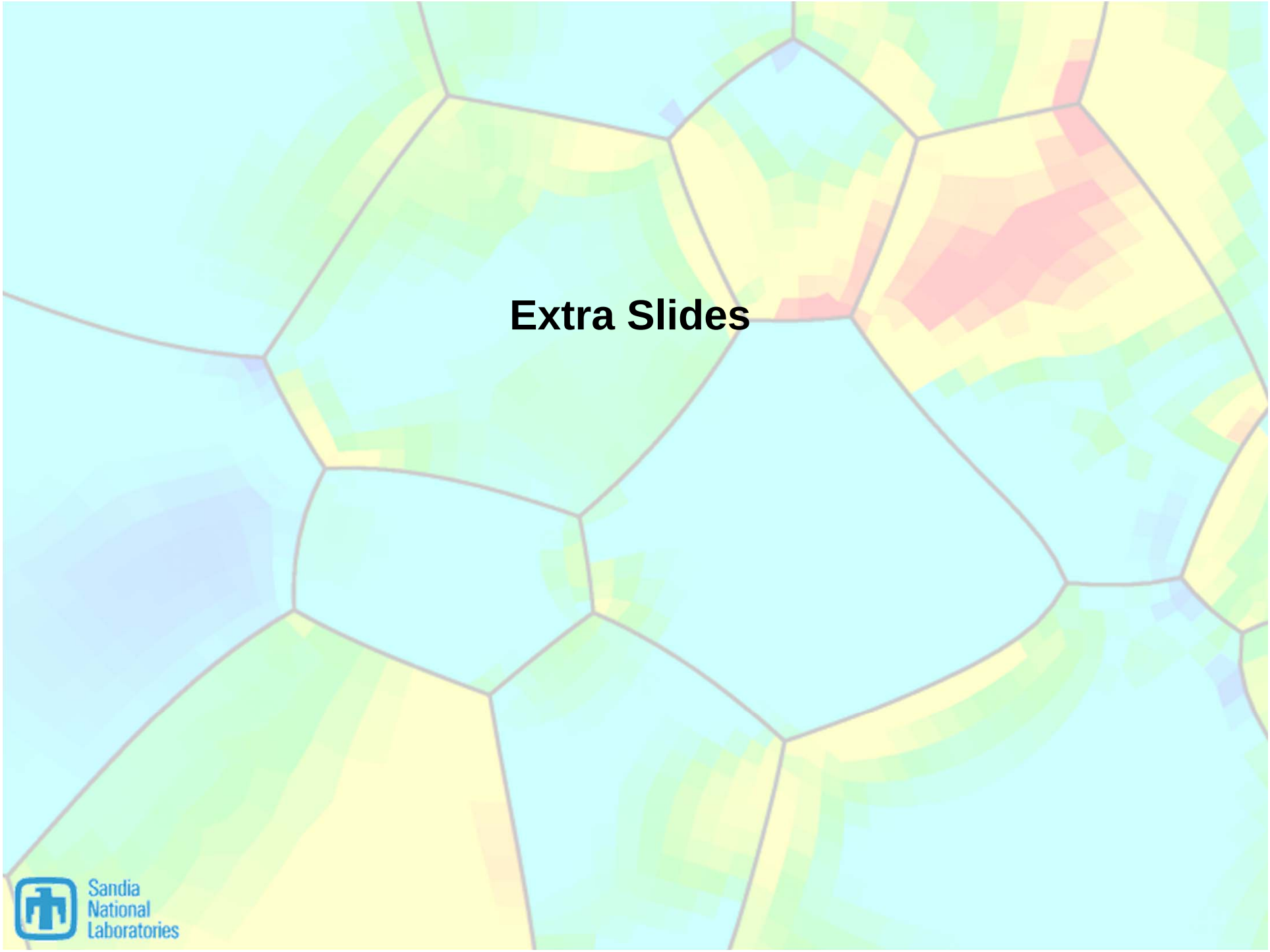
Extra Slides



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Step 1: An automated grain boundary energy method

(1) Choose a periodic box size (here, $15a_0/2$).

(2) Determine which orientation pairs can fit inside the y-z periodic box (here, 388 pairs)

(3) For each pair of grains, construct and minimize boundaries for

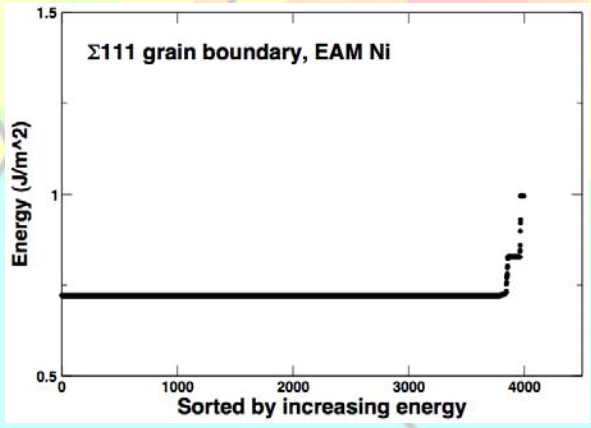
-A sampling of offset vectors spread uniformly in the DSC cell (here, either 8 or 27 offsets)

--Each non-equivalent boundary plane placement in the x direction

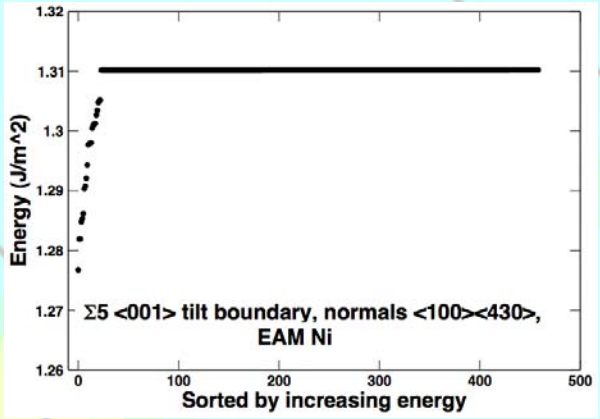
---Three different atom removal methods, each over a range of cutoff radii

- For typical boundaries, we minimize several hundred to several thousand configurations.

- For most boundaries:



- For a few boundaries



⇒ Careful boundary construction is critical to finding the minimum energy configuration.

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An efficient boundary mobility calculation method

- Apply a synthetic driving force for boundary motion:

For an atom in the favored/growing grain: $\varphi = \varphi_{EAM}$

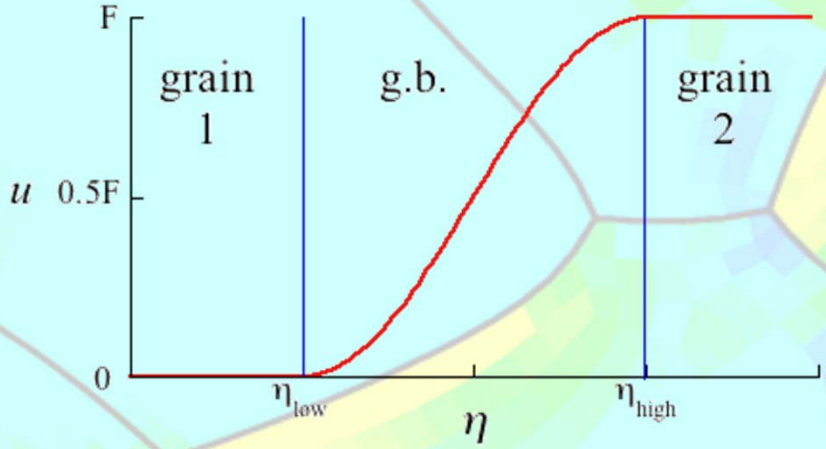
For an atom in the unfavored/shrinking grain: $\varphi = \varphi_{EAM} + u$

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

- Define the excess free energy function as:

$$u(r_i) = \begin{cases} 0 & \eta_i \le \eta_{low} \\ \frac{F}{2}(1-\cos 2\omega_i) & \eta_{low} < \eta_i < \eta_{high} \\ F & \eta_{high} \le \eta_i \end{cases}$$

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.

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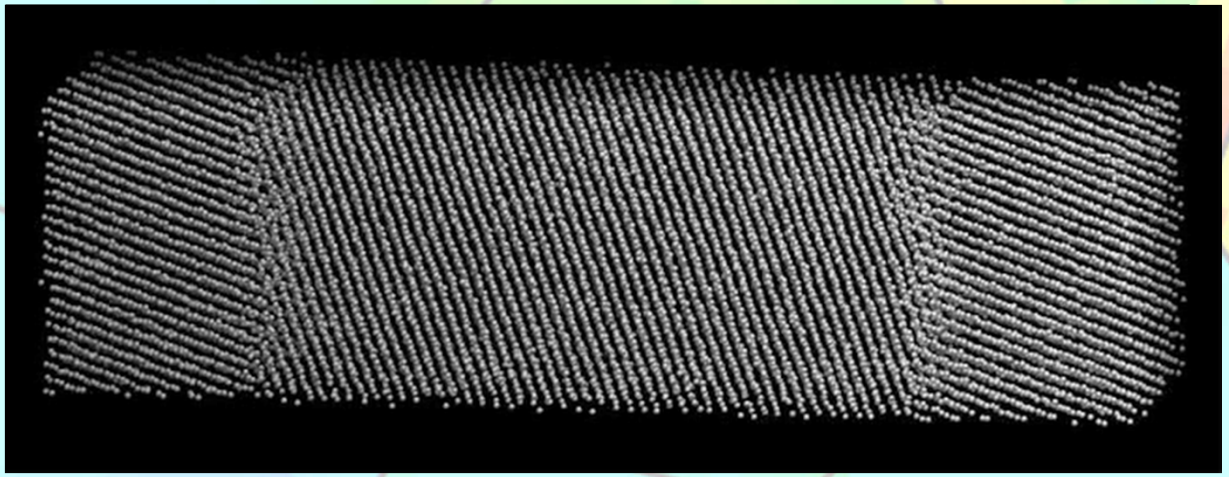
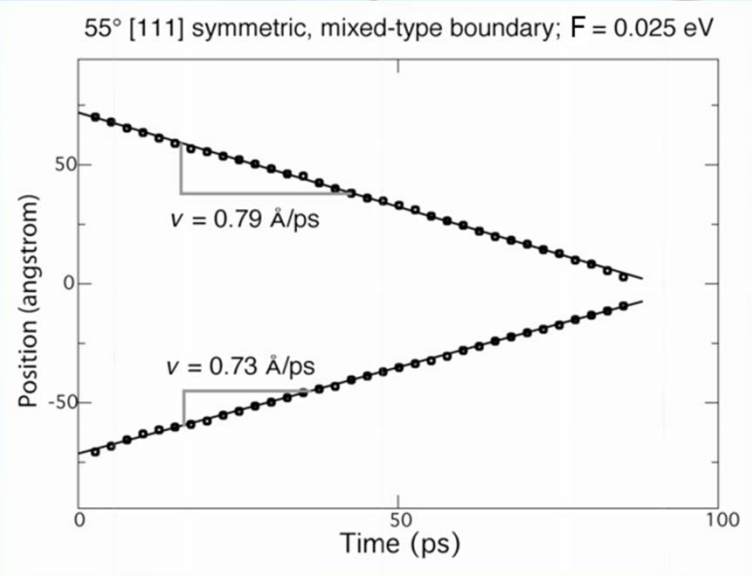
Atomic-scale evolution of flat grain boundaries via a synthethic driving force



Qualitatively:

•Fully periodic system; 26,057 atoms; Σ3 mixed-type boundary

•Grain 2 in the center; boundaries move towards the center



Quantitatively:

- To calculate M, we input F, measure v, and use $v = MF$
- Constant velocities over time, well below the speed of sound
- M does not change with F, with ensemble (NVE, NPT) or with direction of motion
- M agrees with results from simulations with physical driving forces (i.e. stress driven)

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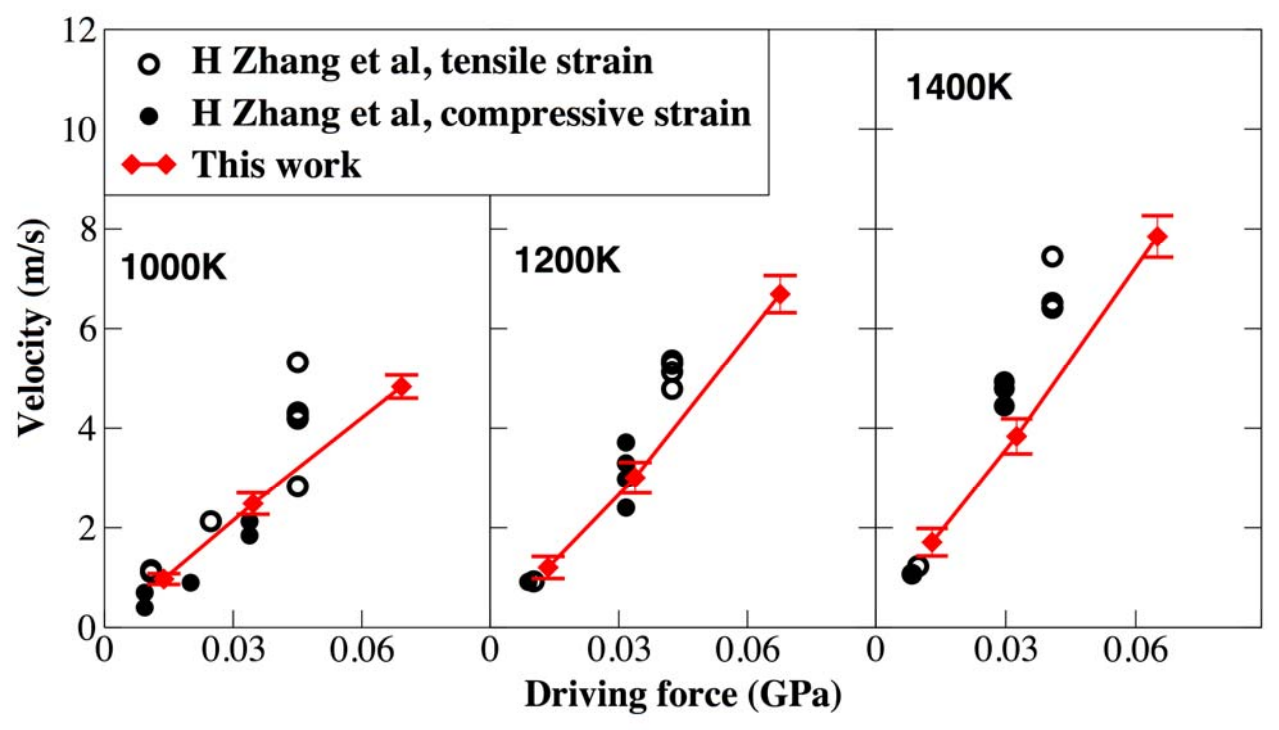
Are the results realistic?

- Compare our artificial driving force calculations to realistic elastic driving force calculations [H. Zhang, M.I. Mendelev, D.J. Srolovitz, *Acta Mater.* **52** (2004) 2569]
- We use the same interatomic potential (Voter-Chen Ni), the same range of driving forces, the same temperatures, and the same Σ5 <100> asymmetric tilt boundary.



The artificial driving force gives realistic results.

D. Olmsted, S. M. Foiles, E. A. Holm, *Scripta Mater.* **57** 1161-1164 (2007).

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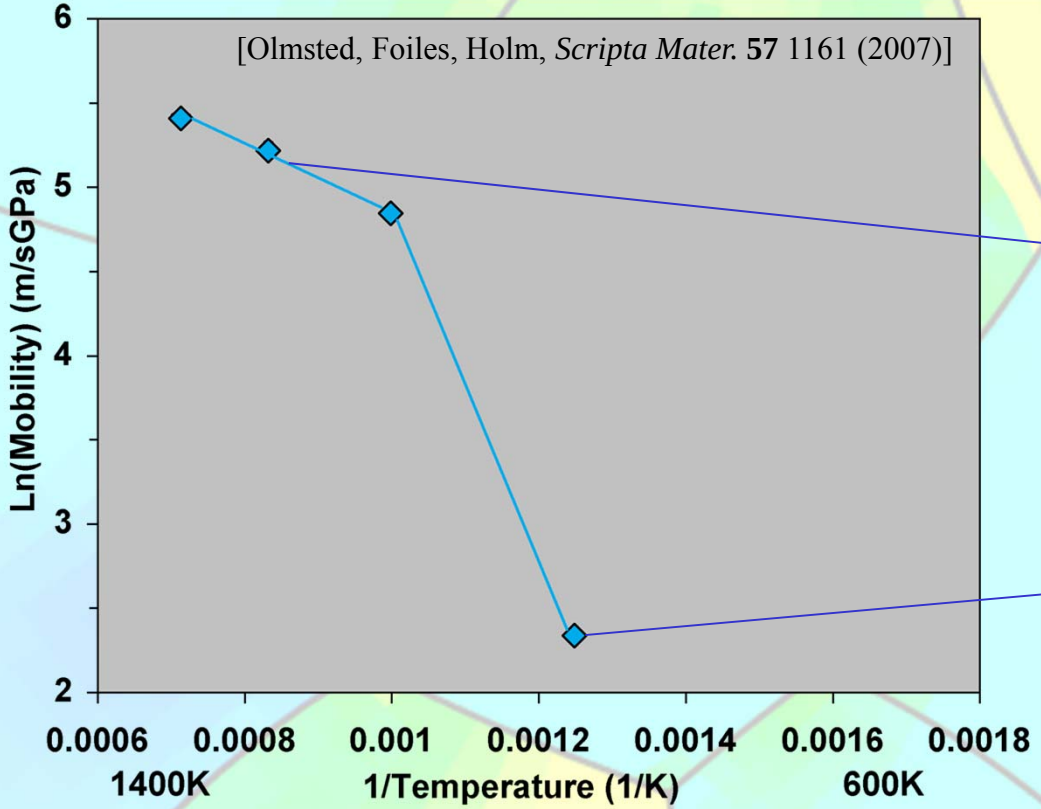
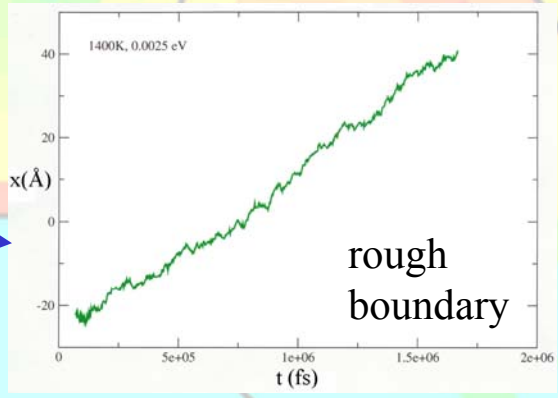
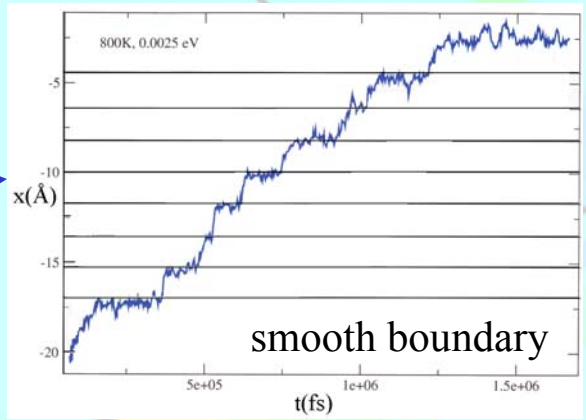
What do the mobility clusters represent?







- High T: high mobility, atomically rough, continuous motion
- Low T: low mobility, atomically smooth, stepwise motion
- Each boundary has a characteristic roughening temperature T_r

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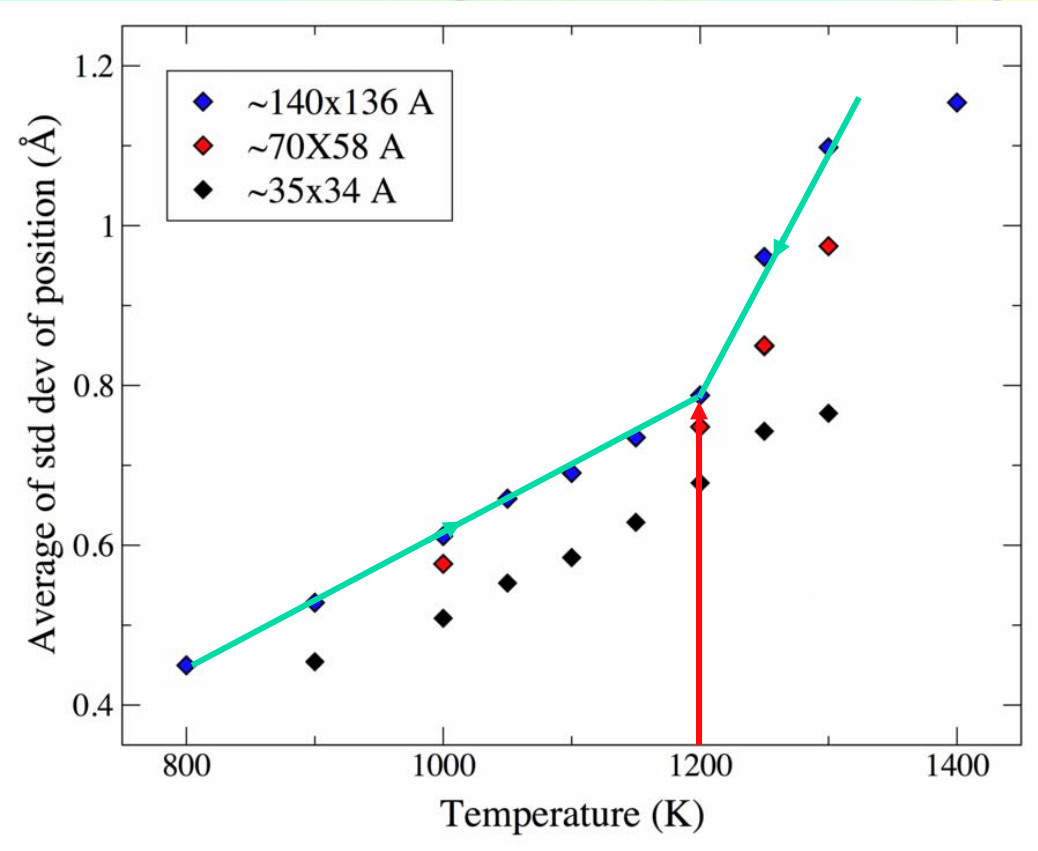
Can we measure roughness directly?

Ni Σ5 <010> symmetric tilt boundary, <301><-301>



- We measure roughness as RMS displacement.
- For large systems, we observe a transition in roughness at a characteristic temperature T_R.
- T_R from roughness measurements agrees with T_R from mobility analysis.
- For small systems, we cannot resolve a transition in roughness, though the change in mobility is evident.

We use the abrupt change in mobility as the signature of the roughening transition.

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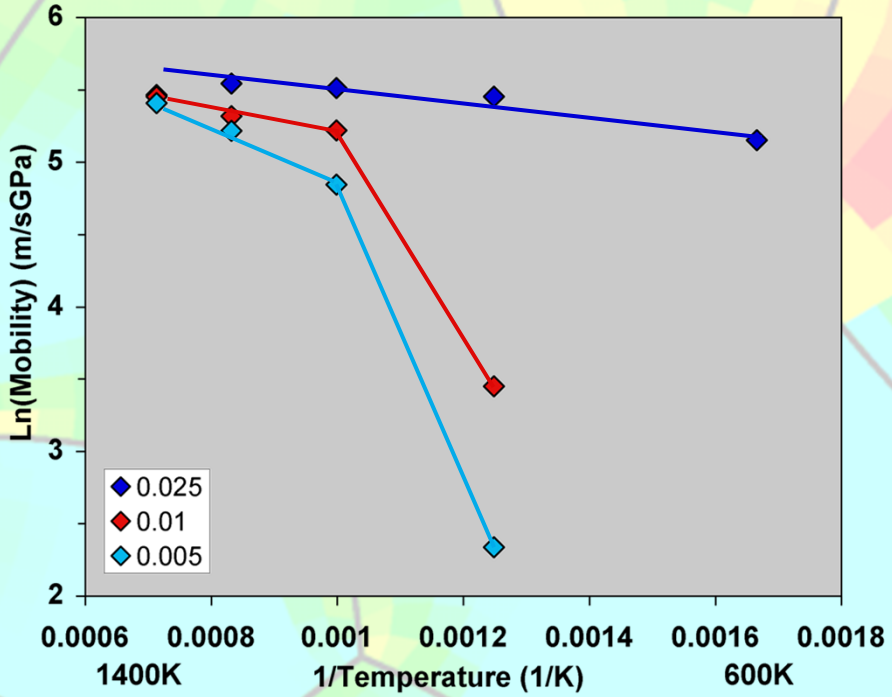
What factors affect roughening?



- At low driving forces, boundaries roughen at a characteristic roughening temperature – thermal roughening.
- At high driving forces, boundaries remain rough at all temperatures – kinetic roughening.
- The driving force for kinetic roughening is typically much larger than the driving force for grain growth.

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Results:
Mixed mobility modes

		low temperature				
high temperature	f_o (%)	thermally activated	anti-thermal	athermal	immobile	thermally damped
	thermally activated	5%	3%		52%	
	anti-thermal		8%	5%	3%	
	athermal	2%		5%	0.5%	
	immobile				6%	
	thermally damped					6%

- About **14%** of boundaries move by a combination of mechanisms
  - TA→A, AT→TA, A→AT, I→AT, I→A **(14%)**
  - Thermal roughening (I→TA) **(51%)**
- While not all combinations are represented in our data, the observed mechanism combinations are reasonable
- Roughening appears possible for all boundary types

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