Last slide of my presentation at this workshop on February 7, 2006:

Conclusions

- Once very fashionable, the area of GB diffusion is not hot anymore. It is **not** considered to be cool enough. It cannot compete with carbon nanotubes and quantum dots
- It is only the Herzig group in Muenster that keeps GB diffusion measurements alive
- Development of GB diffusion theory stopped (June 1, 2005)
- Posterity will not forgive us

Grain boundary diffusion
The rest of the story

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Department of Physics
George Mason University
Virginia

Outline

- Quick overview of the field
- Diffusion along grain boundaries and their triple junctions in copper
- Diffusion along low-angle grain boundaries in aluminum

Importance of GB diffusion

GB diffusion is much faster than lattice diffusion

(E.g. $D_{gb}/D_L \approx 10^{10}$ at $0.5T_m$ in fcc metals)

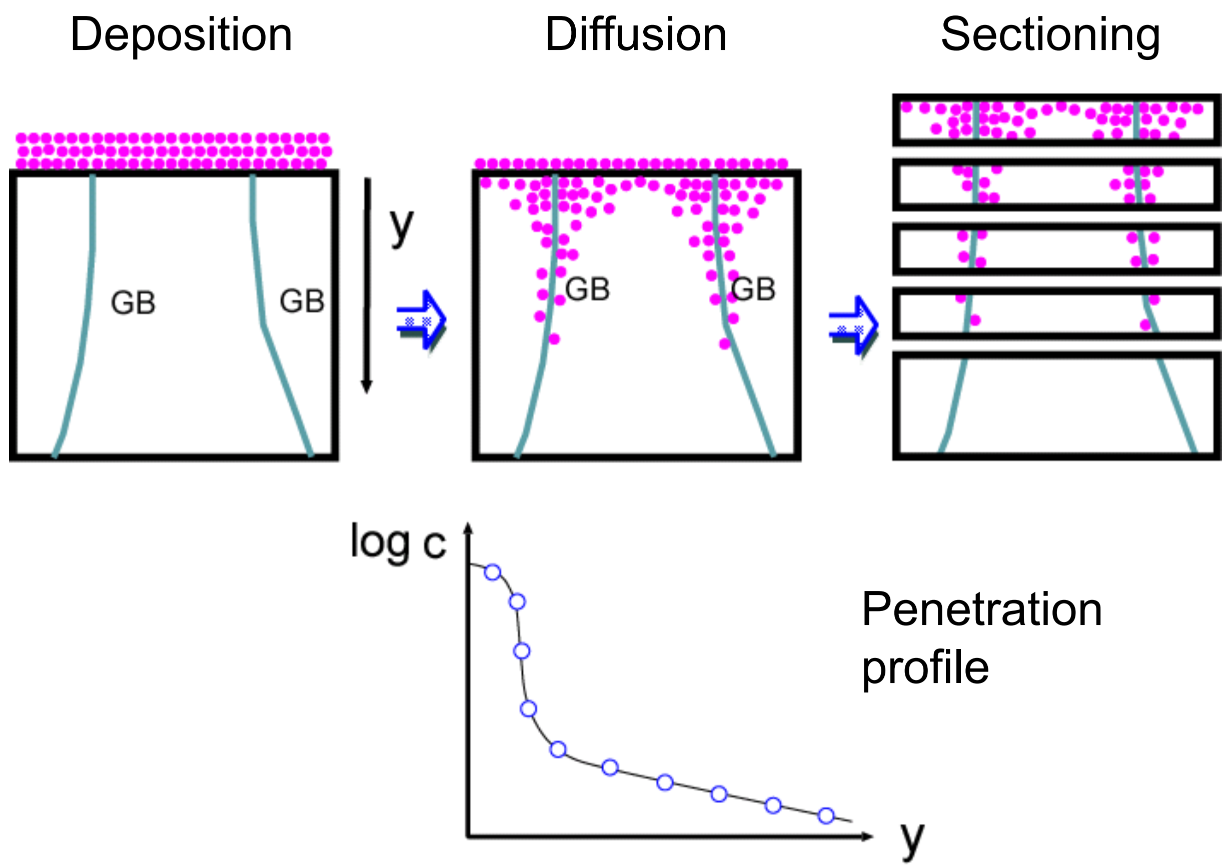
↓

Processes controlled/influenced by GB diffusion:

- Solid state reactions (discontinuous precipitation,…)
- Grain growth
- Deformation and fracture at elevated temperatures
- Coble creep
- GB dislocation climb
- Structural relaxation after fabrication (severe plastic deformation, etc.)

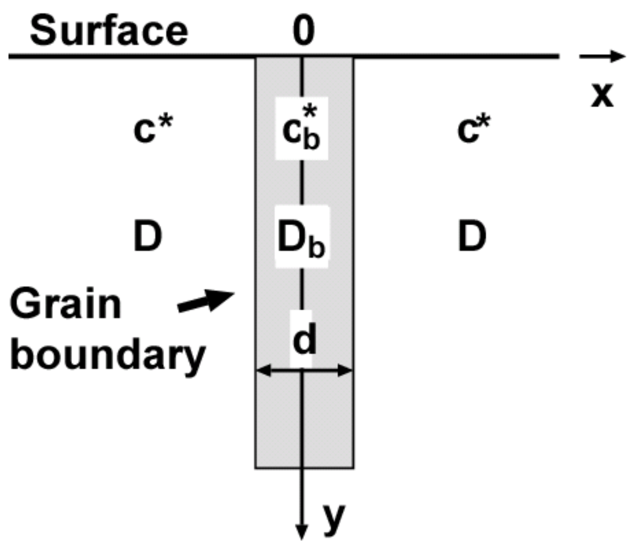
Diffusion is a structure-sensitive property

Radiotracer sectioning method



Need many GBs to achieve a high accuracy

Fisher model of GB diffusion



$$\frac{\partial c^*}{\partial t} = D\left(\frac{\partial^2 c^*}{\partial x^2} + \frac{\partial^2 c^*}{\partial y^2}\right)$$

$$\frac{\partial c_b^*}{\partial t} = D_b \frac{\partial^2 c^*}{\partial y^2} + \frac{2D}{\delta}\left(\frac{\partial c^*}{\partial x}\right)_{x=\delta/2}$$

<u>**Coupling conditions**</u>:

Self-diffusion A* → A: $c^*_b = c^*$

Impurity diffusion B* → A: $c^*_b = sc^*$, where $s = s_0 \exp(-E_s/kT)$

Self-diffusion in alloy B* → A-B: $c^*_b = sc^*$, where $s = c_b^B/c^B$

Solution of the Fisher model

Under typical experimental conditions

$$\log \bar{c} \propto -\left[\frac{4\pi D}{(s\delta D_b)^2}\right]^{3/10} y^{6/5}$$

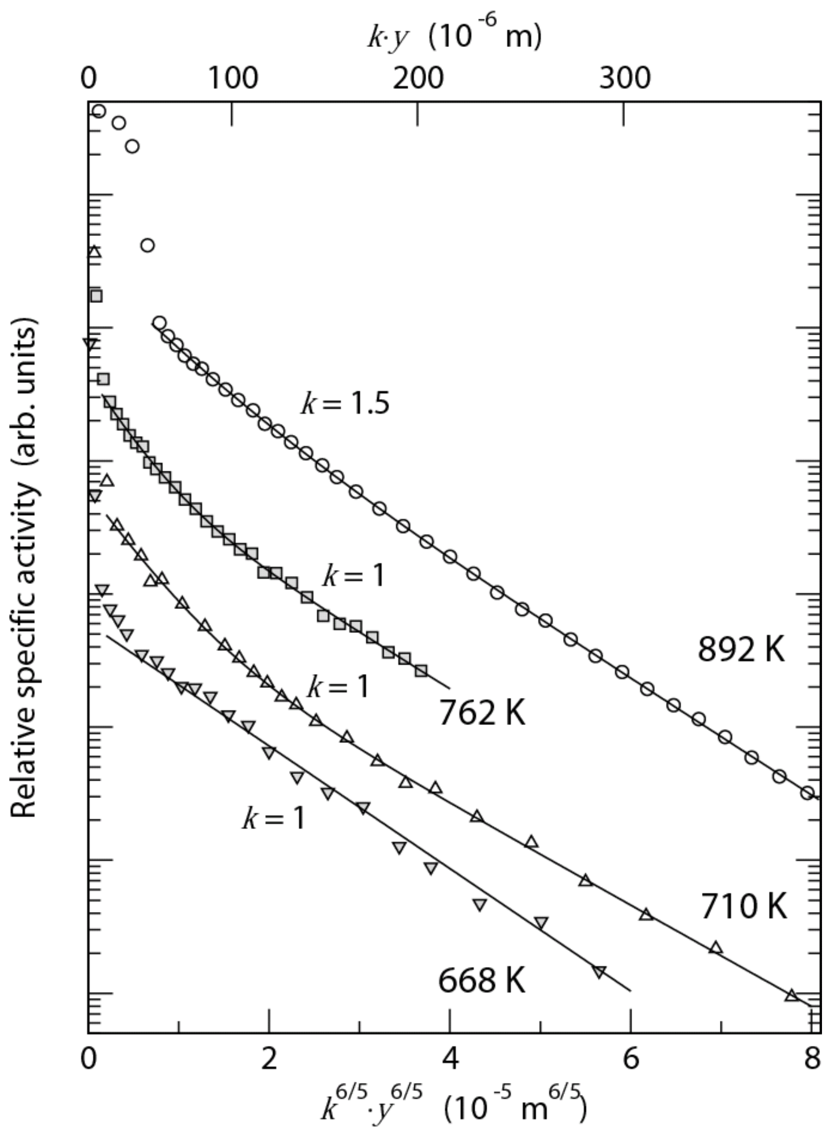
$$\Downarrow$$

$$s\delta D_b = q\left(\frac{D}{t}\right)^{1/2}\left(-\frac{\partial \ln \bar{c}}{\partial y^{6/5}}\right)^{-5/3}$$

q – numerical factor depending on the surface condition

- Assume δ = 0.5 nm
- Must know D from independent measurements

Examples of GB diffusion profiles



Ag in Cu-0.2at%Ag

Divinski et al., *Interface Science* **11**, 21 (2003)

Combined B and C regime measurements

Regime B (high temperatures)

$$(Dt)^{1/2} >> s\delta \;\Rightarrow\; \bar{c}(y, s\delta D_b) \;\Rightarrow\; s\delta D_b$$

Regime C (low temperatures – extremely difficult measurements!)

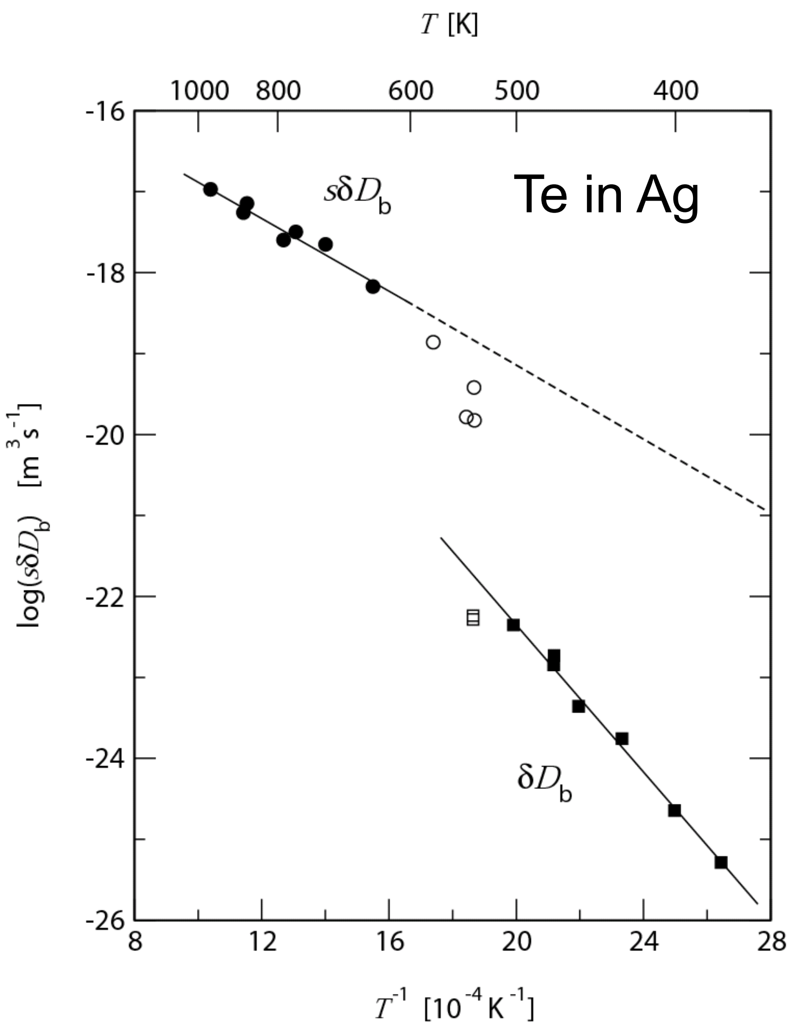
$$(Dt)^{1/2} << s\delta \;\Rightarrow\; \bar{c} \propto \exp\left(-\frac{y^2}{4D_b t}\right) \;\Rightarrow\; D_b$$

$$\Downarrow$$

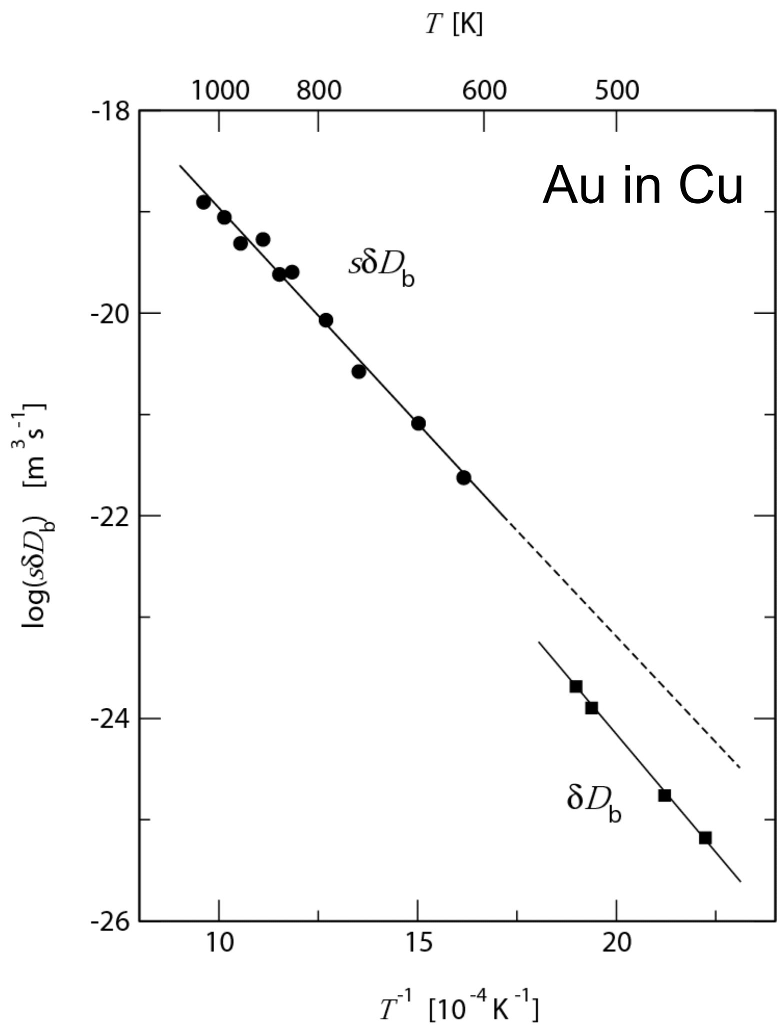
$$s\delta = \frac{(s\delta D_b)_B}{(D_b)_C}$$

Self-diffusion: s = 1 ⇒ δ ≈ 0.5 nm (Atkinson and Taylor 1981; Sommer and Herzig 1992; Gas, Beke and Bernardini 1992)

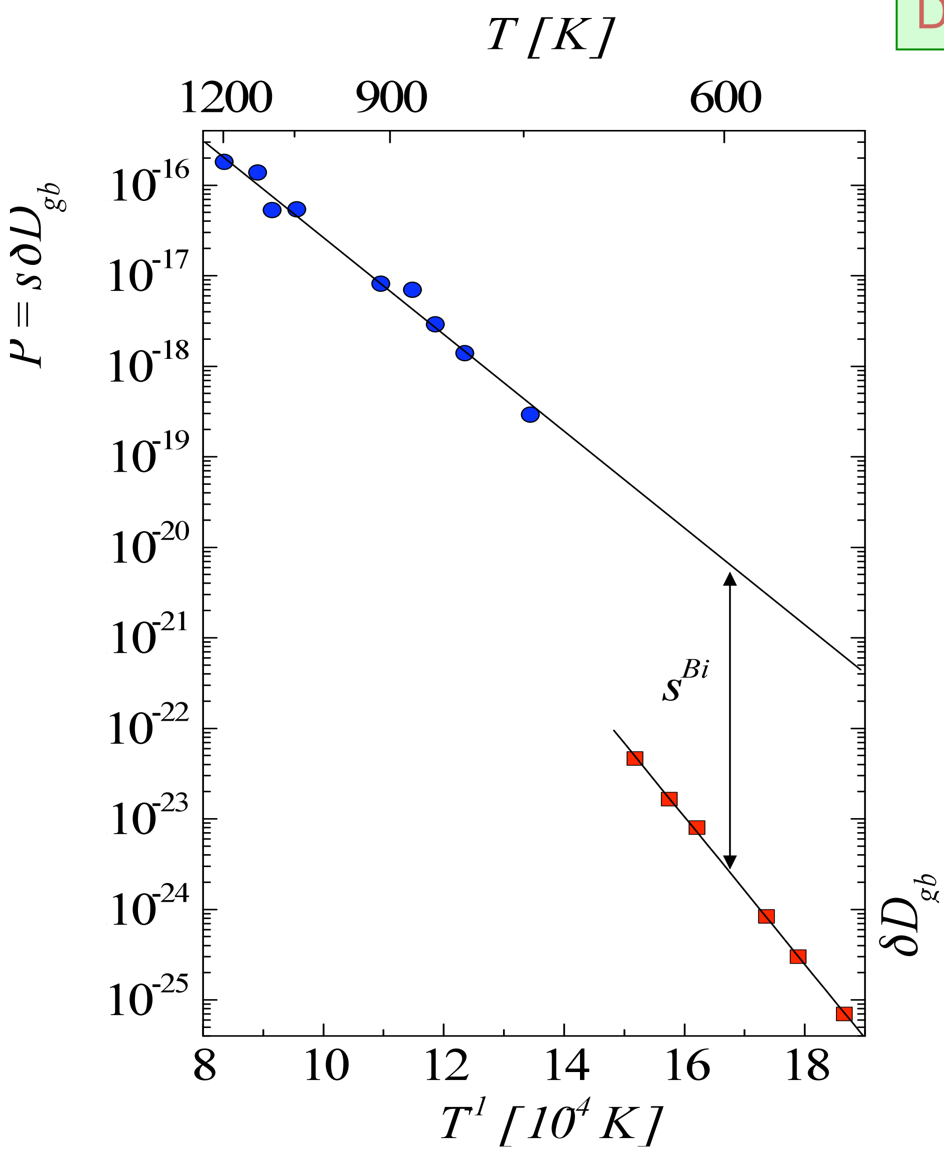
Example of combined B and C regime measurements



C. Herzig et al., *Acta Mater*. **41**, 1683 (1993)



T. Surholt et al., *Phys. Rev. B*. **50**, 3577 (1994)



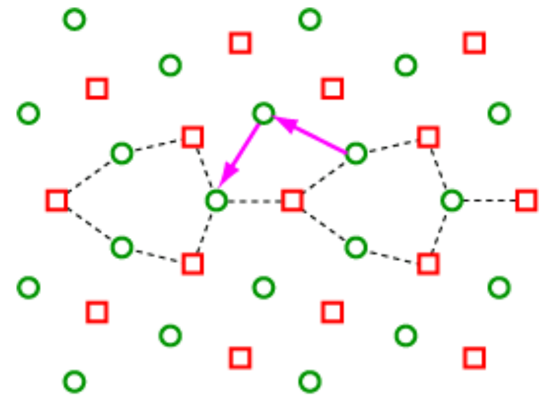
Divinski, Herzig, et al Acta Mater (2004)

Bi GB diffusion in Cu

Non-destructive evaluation of GB segregation factors

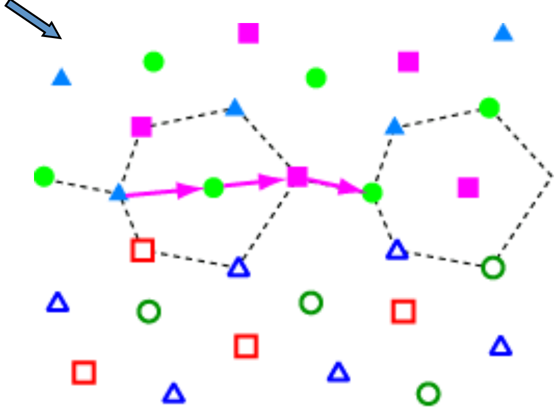
Diffusion mechanisms in GBs

- <u>Vacancy mechanisms</u>
  - Simple vacancy-atom exchanges
  - Long vacancy jumps (2-3 atoms)
- <u>Interstitial mechanisms</u>
  - Direct jumps
  - Collective jumps (2-4 atoms)
- <u>Ring mechanisms </u>(up to 6 atoms)



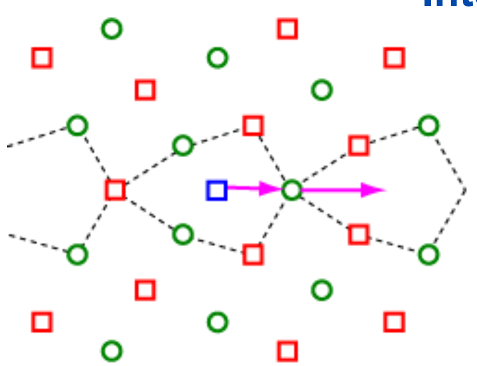
Σ5(310)[001]

Vacancies

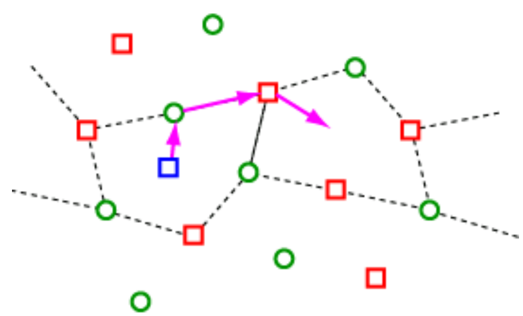


Σ7(231)[111]

Interstitials



Σ5(210)[001]



Σ9(122)[011]

Comparison of GB and lattice diffusion

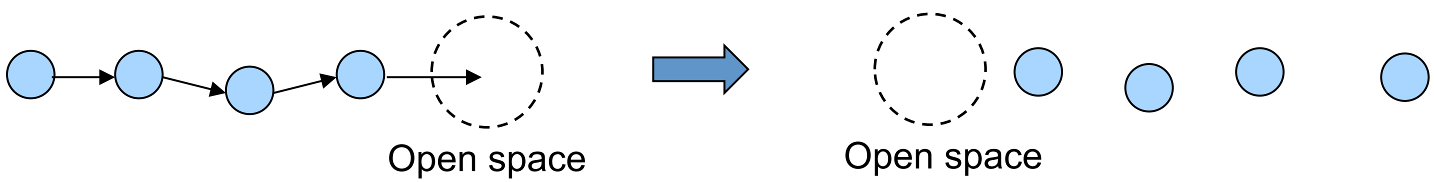
Lattice diffusion

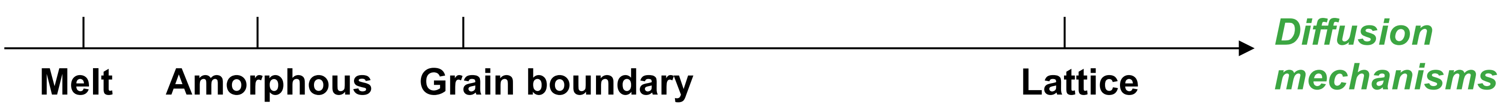
- Vacancies dominate
- Vacancies move by single-atom exchanges

GB diffusion

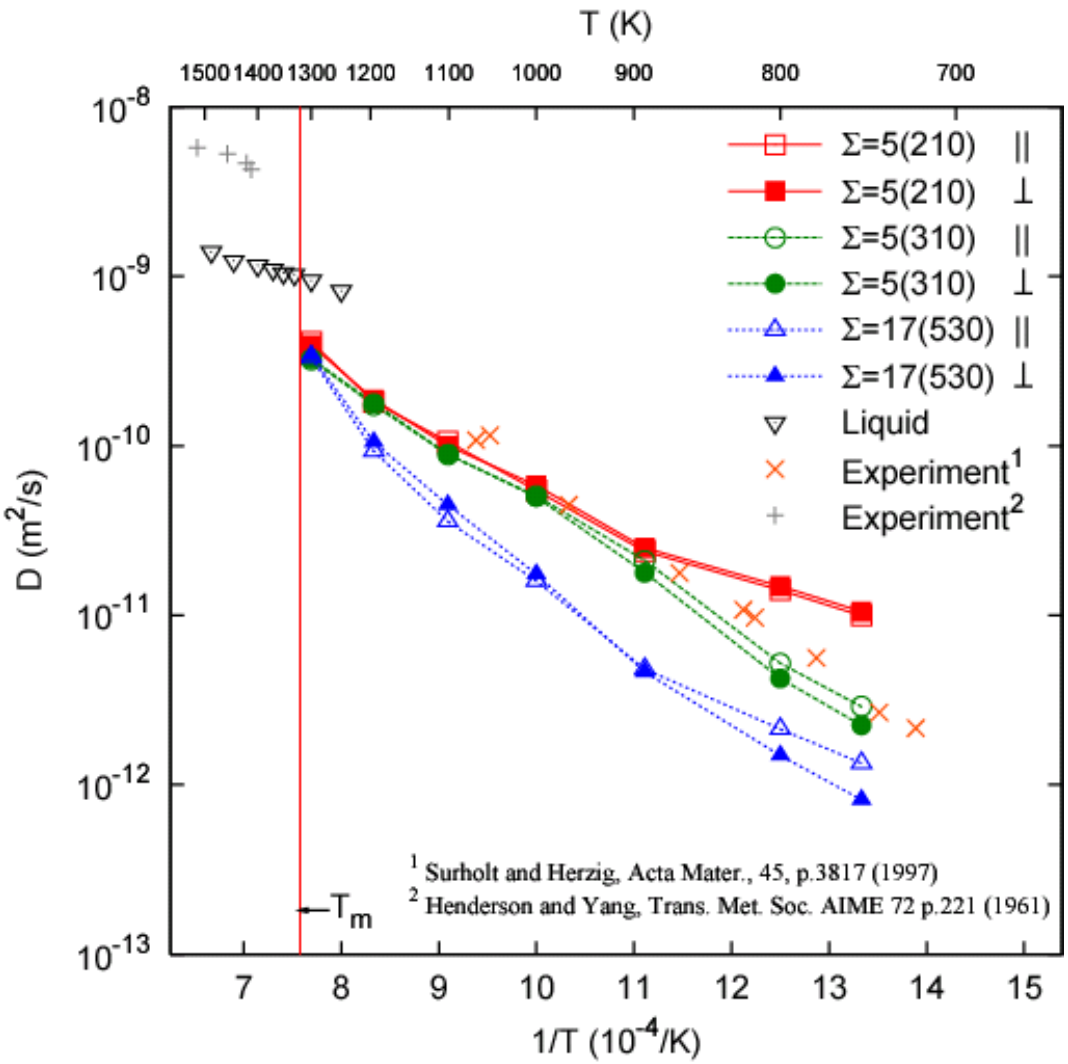
- Vacancies and interstitials are equally important
- Variety of point-defect structures
- Variety of diffusion mechanisms
- Most diffusive events are collective

Typical diffusive event in GBs





GB diffusion in Cu: MD calculations



- Agreement with experiment
- Continuous "premelting" ~100K before T_m
- The Σ5's merge at high temperatures. Universal diffusion mechanism? "Liquid-like" structure? [Keblinski et al, 1997, 1999]

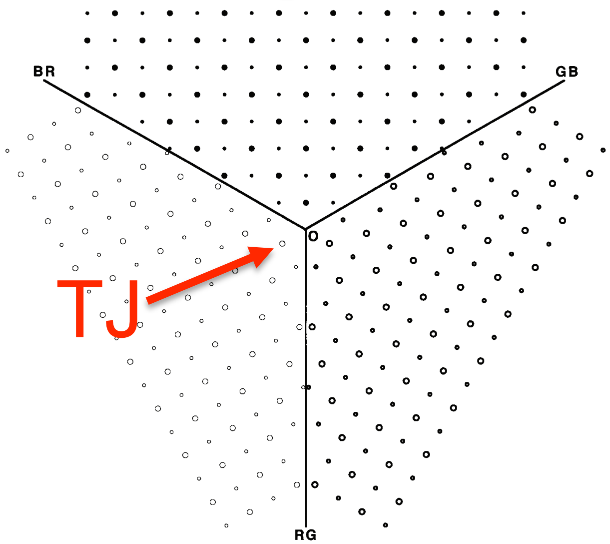
High-temperature mechanisms remain unknown !

A. Suzuki and Y. Mishin, *Journal of Materials Science* **40**, 3155 (2005)

Diffusion along GBs and triple junctions (TJ) in Cu

Tim Frolov

Triple junction (TJ) is a line where three grain boundaries (GBs) meet together



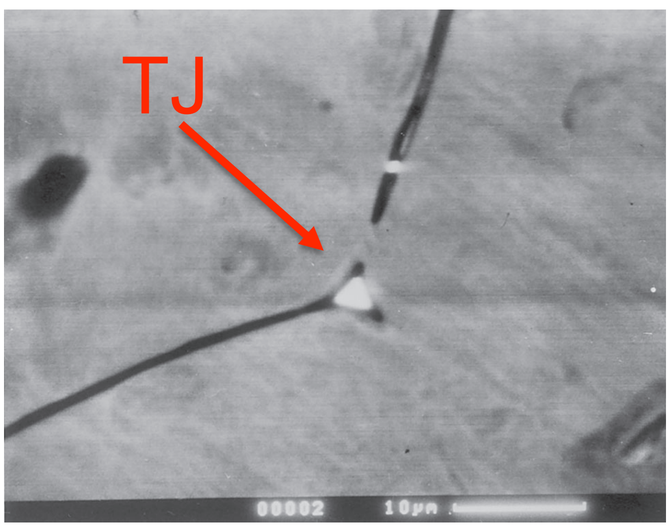


Fig. 1. Electron microphotography (BEI) of sockets for the accelerated penetration Bi in Cu along triple junctions.

- TJs may play a role in behavior of nano-crystalline materials
  V.B. Rabukhin et al (1986), B. Bokstein et al (2001)
- Enhanced diffusivity of nano-crystalline materials
  - Plastic deformation
    L.M. Klinger et al (1997), A.A. Fedorov et al (2002), Ovid'ko et al (2004), H. Wang et al (2005) Y. Chen et al (2007)
  - Diffusional creep
- Sites of enhanced segregation
  K. M. Yin et al (1997)
- Can limit GB mobility during recrystallization
- Preferable sites of nano-cracks and corrosion
  G. Palumbo et al (1989), W.M. Kane et al (2008), L.S. Kumar et al (2003)

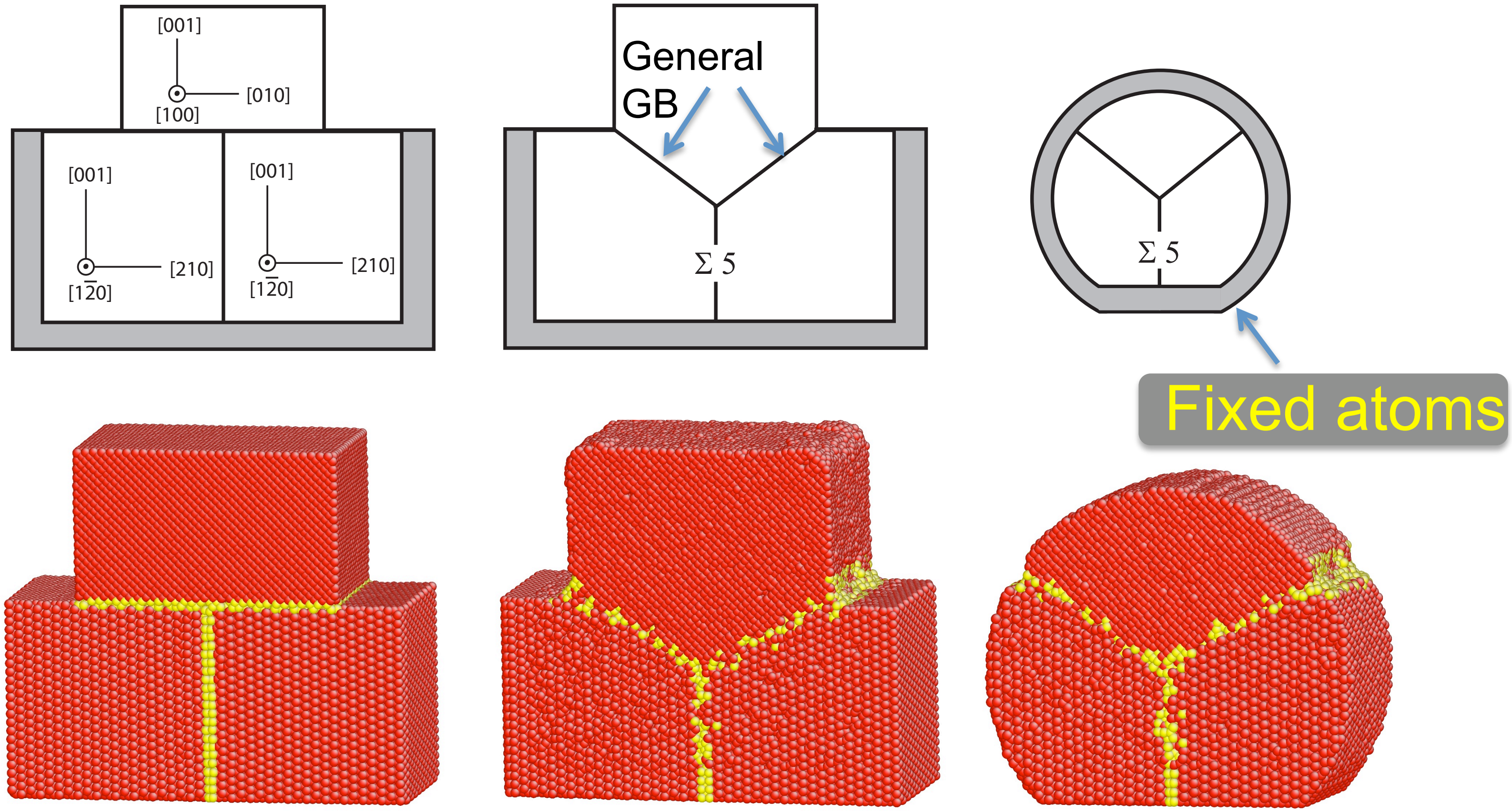
Simulation Methodology

- Copper as a model material
- EAM potential for copper

(lattice parameter, cohesive energy, elastic constants, phonon frequencies, thermal expansion, lattice-defect energies, predicted melting point 1327K)

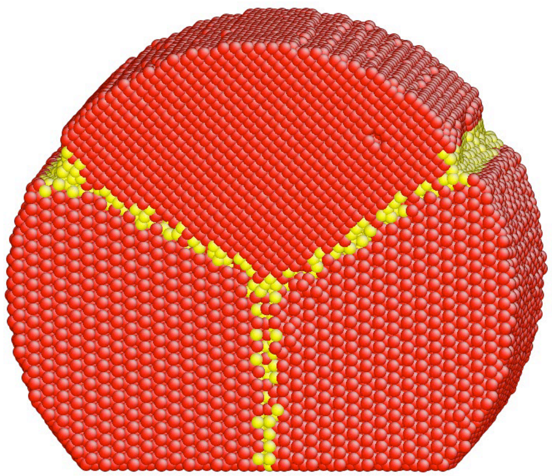
- Simulation method
  - Molecular Dynamics (MD) (IMD, Stuttgart, Germany)
  - Nose-Hoover thermostat
  - 81,137 atoms
  - Temperature range 700K to 1315K
- Visualization
  - Atomeye (J. Li, Modelling Simul. Mater. Sci. Eng. 11 (2003) 173)

Creation of a triple junction

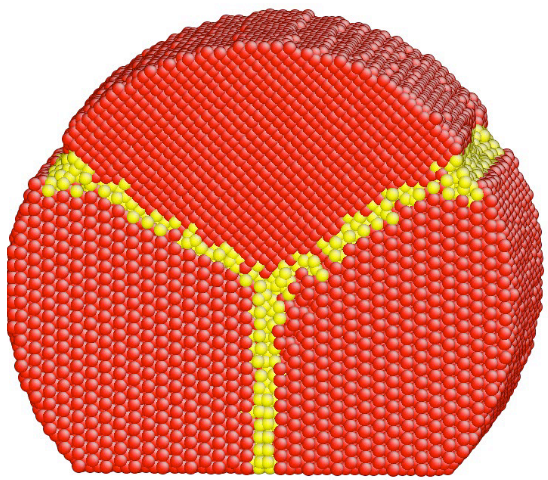


- Three grains with known orientation are brought together
- The structure equilibrates during MD run
- Cylindrical region is cut out from the original block
- Boundary conditions are periodic in the direction parallel to TJ

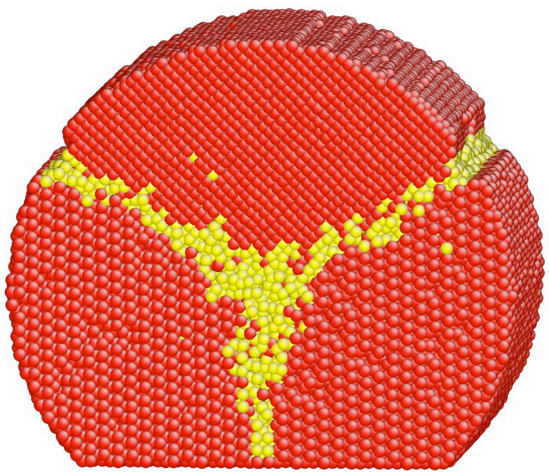
Simulation block at different temperatures



700 K



1100 K

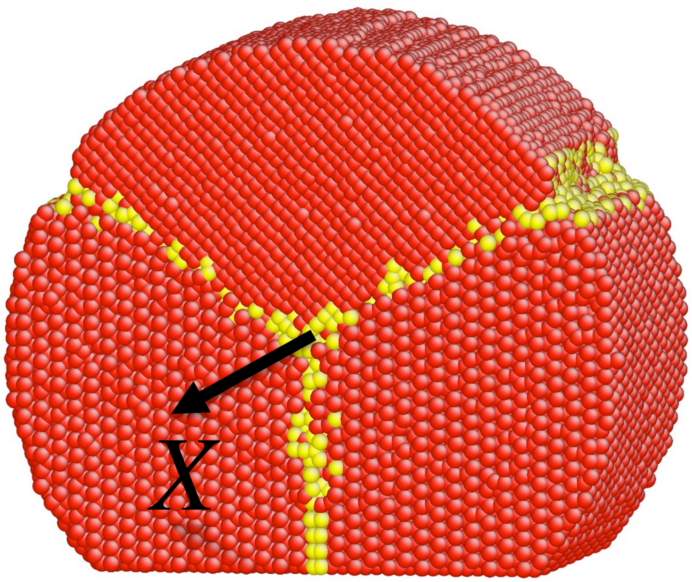


1315 K

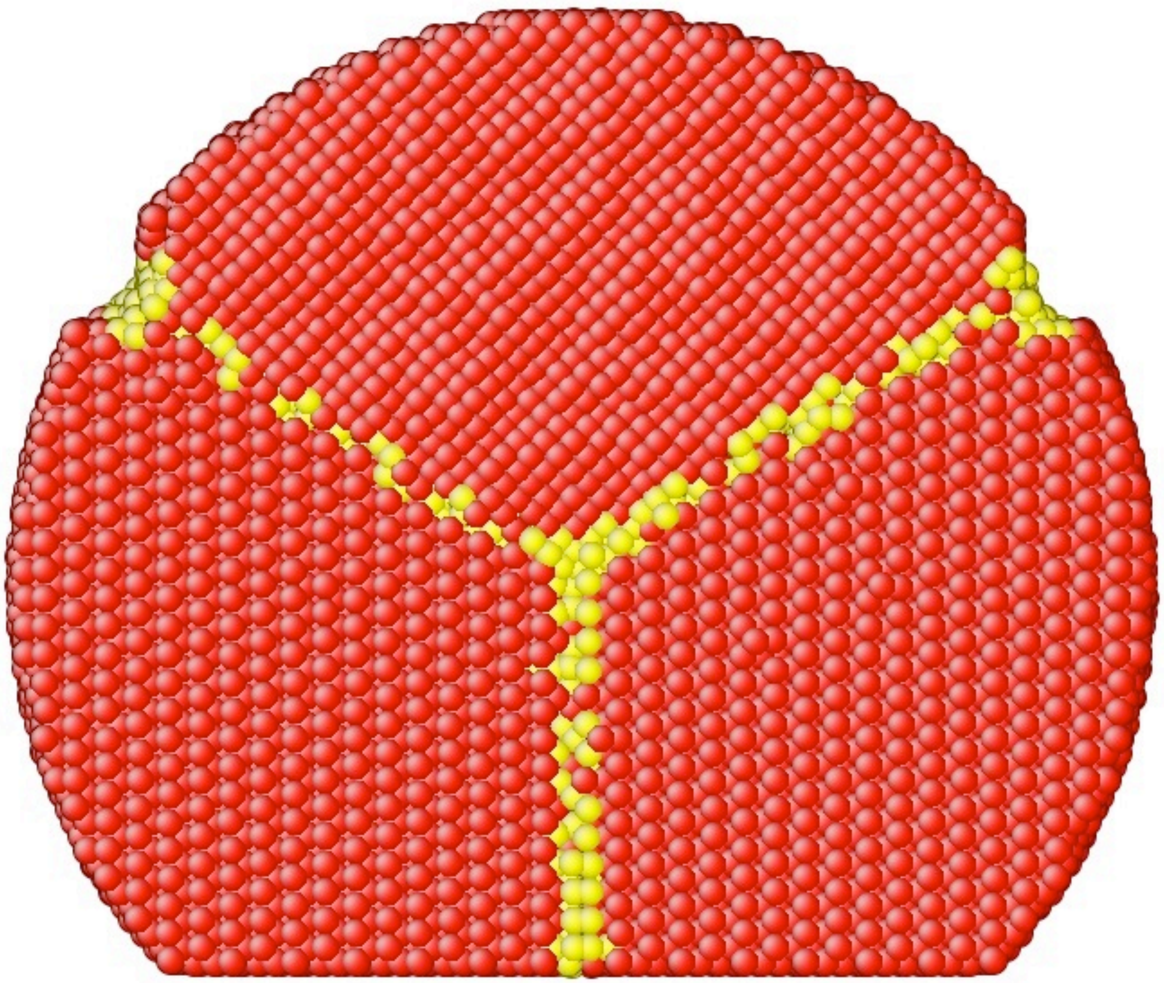
T_m= 1327 K

Diffusion calculations

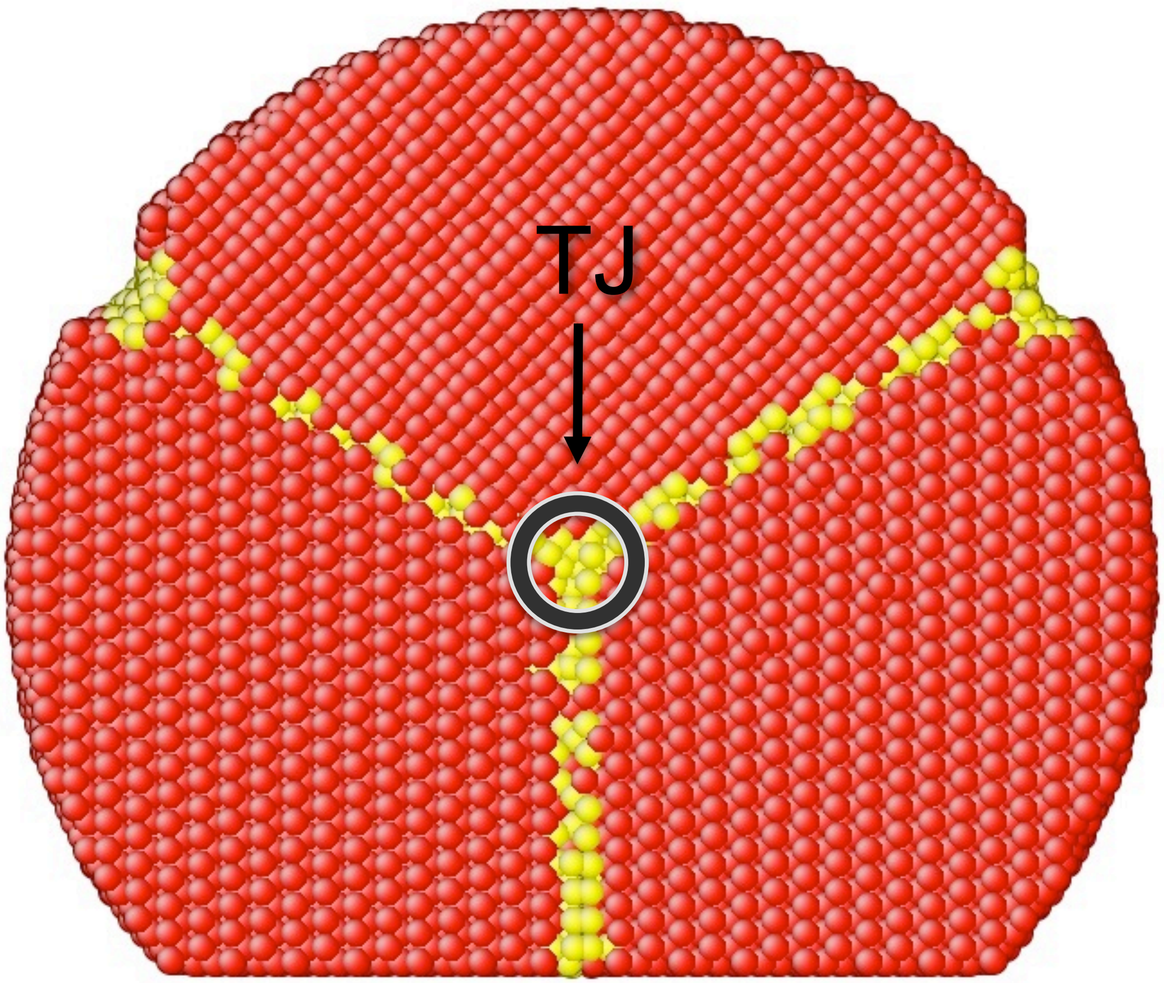
- Einstein relation $\left\langle X^2 \right\rangle = 2Dt$
  - X direction parallel to the TJ
  - *D* diffusion coefficient
  - t time
- Atomic displacements computed for particular regions



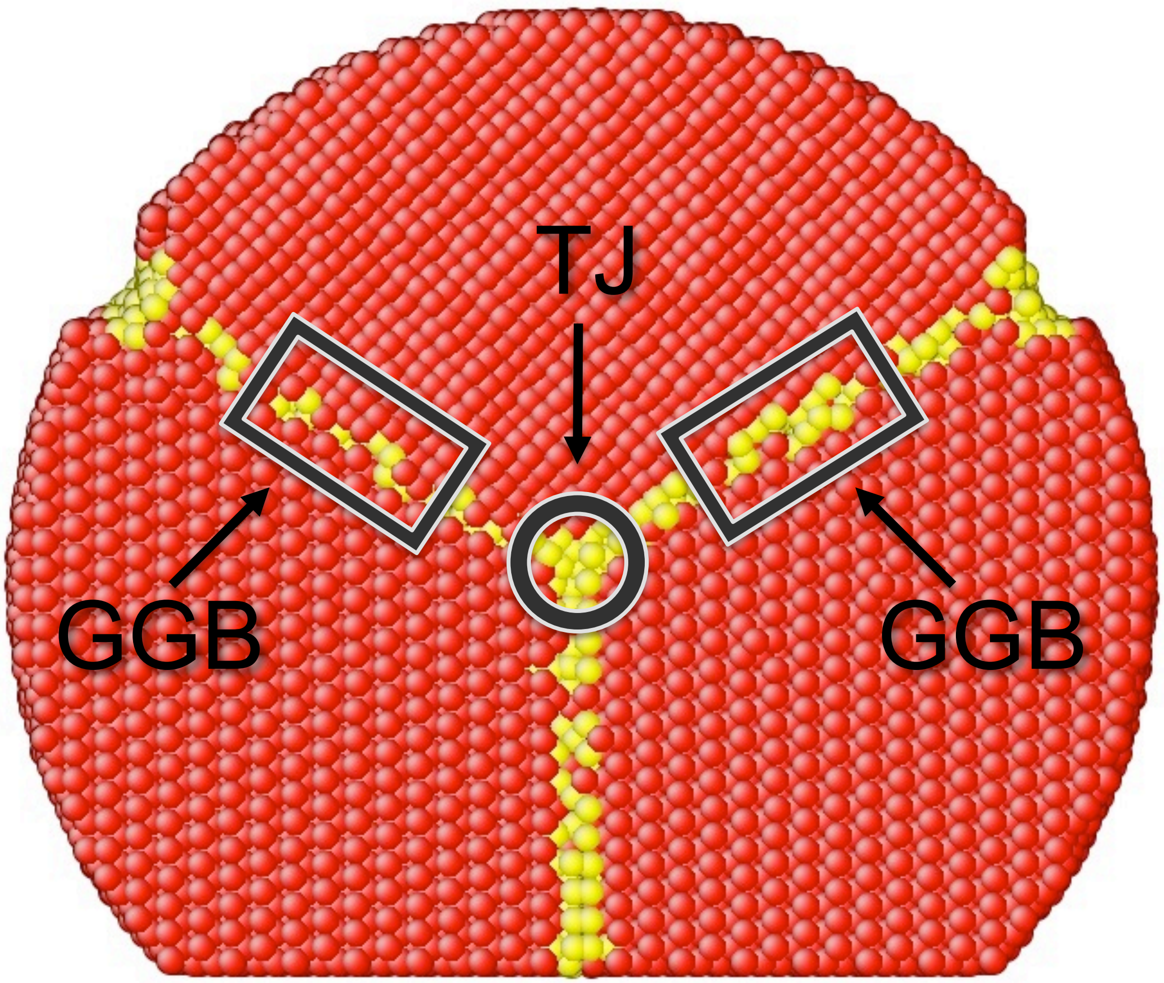
Regions for TJ and GBs diffusion calculation



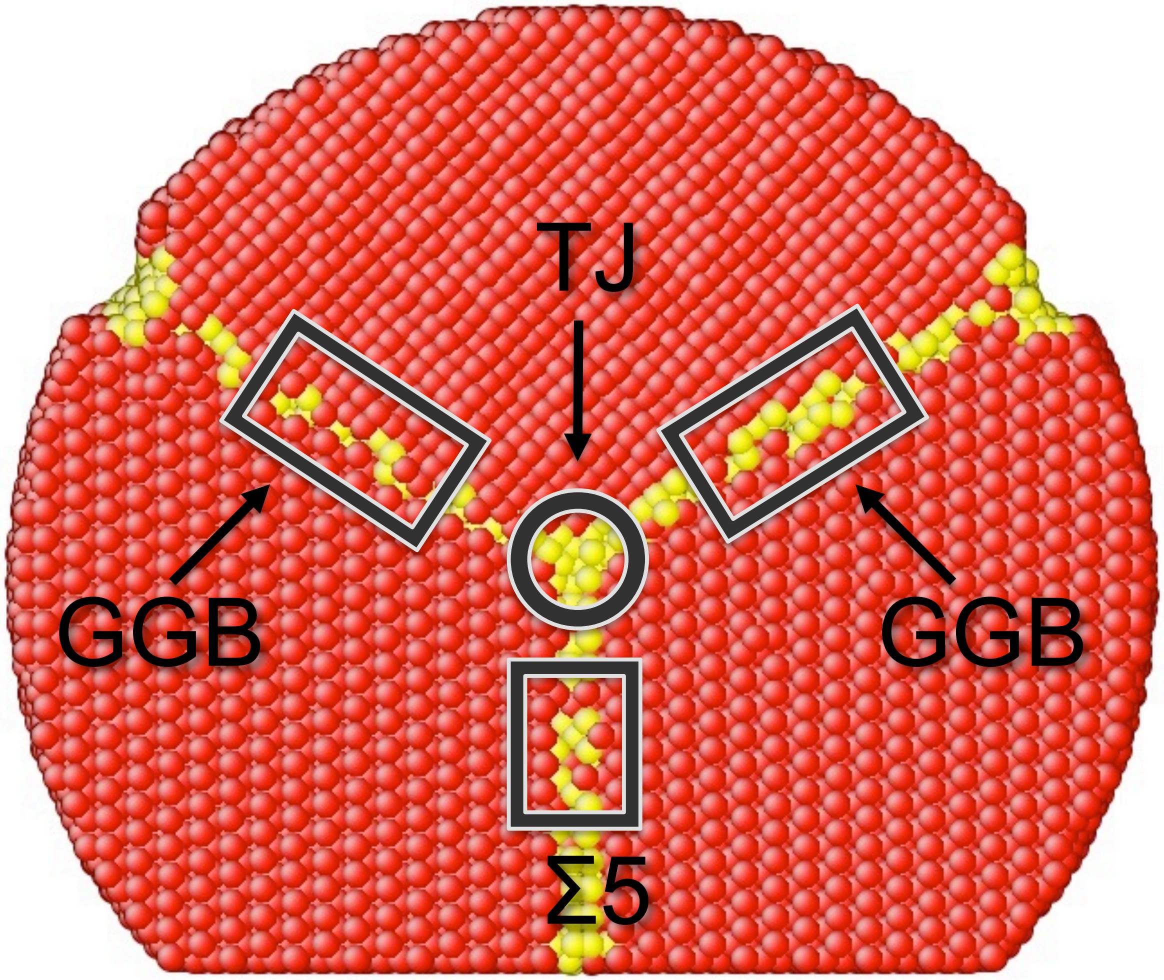
Regions for TJ and GBs diffusion calculation



Regions for TJ and GBs diffusion calculation



Regions for TJ and GBs diffusion calculation



Regions for TJ and GB diffusion calculation

- TJ

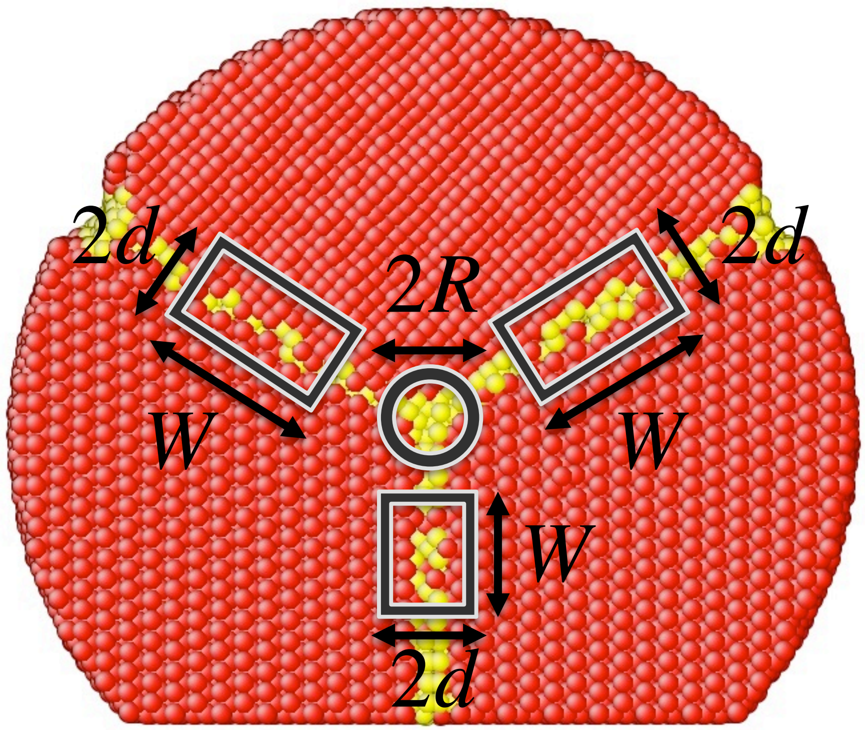
$$2R = 10\overset{o}{A} \quad L = 66\overset{o}{A}$$

- Σ5

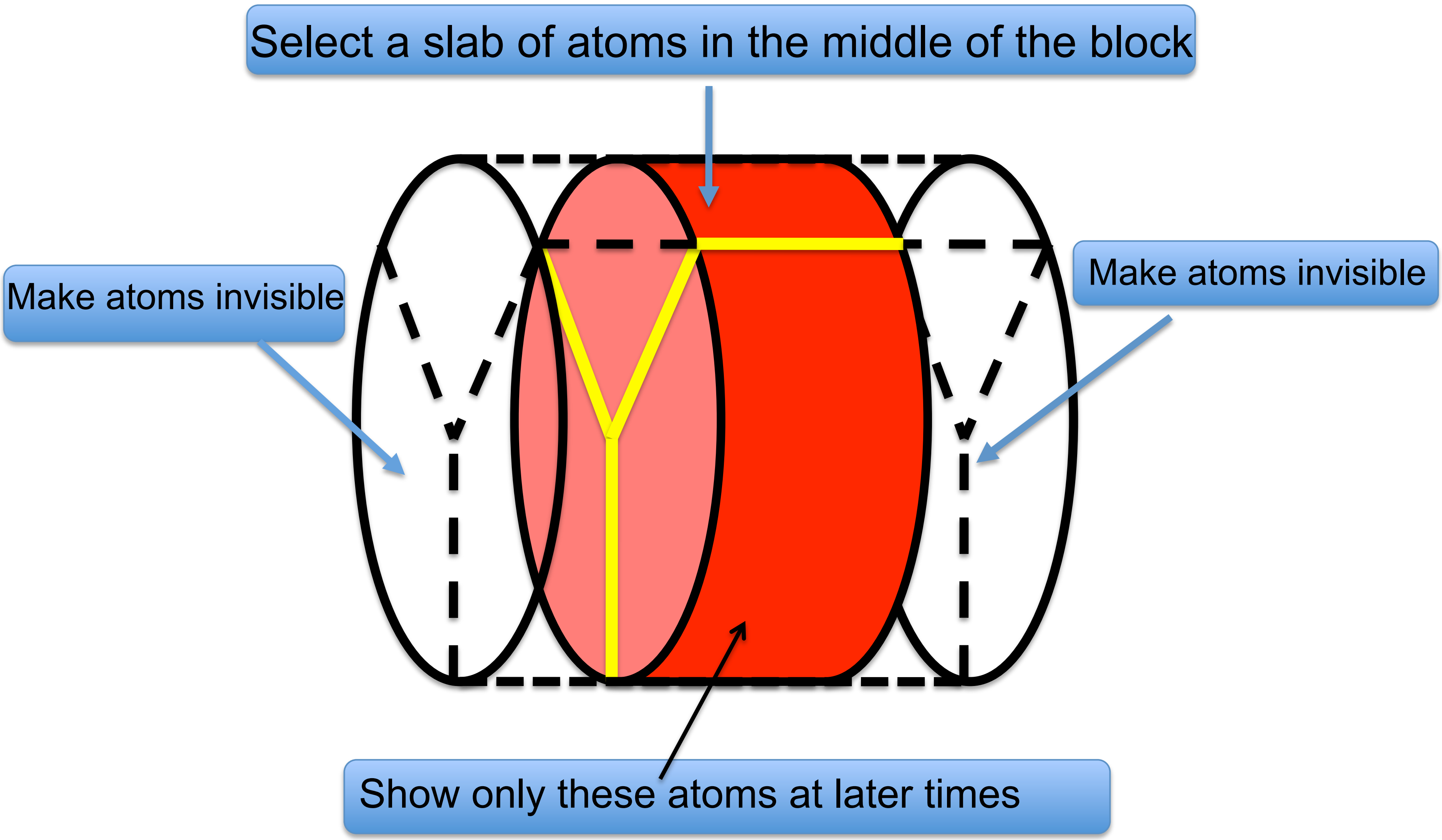
$$2d = 10\overset{o}{A} \quad W = 25\overset{o}{A} \; L = 66\overset{o}{A}$$

- GGBs

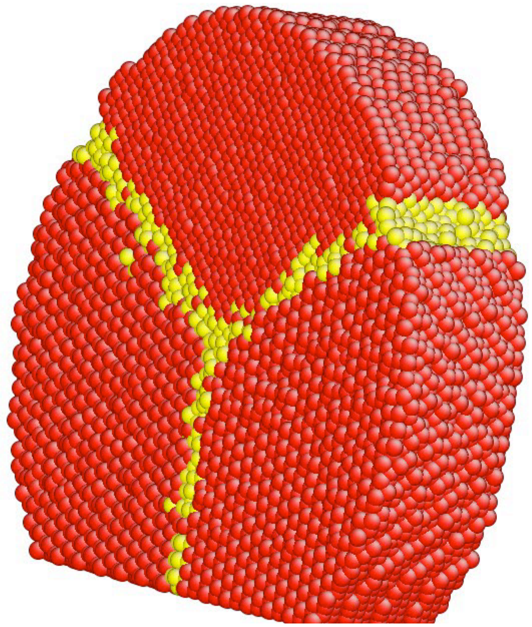
$$2d = 10\overset{o}{A} \quad W = 30\overset{o}{A} \; L = 66\overset{o}{A}$$

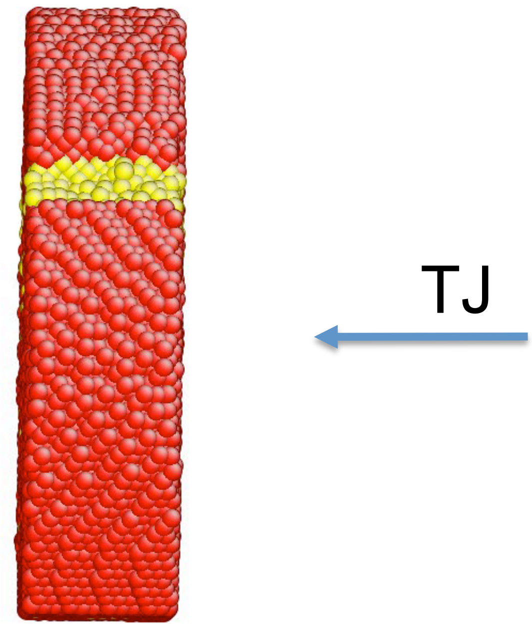


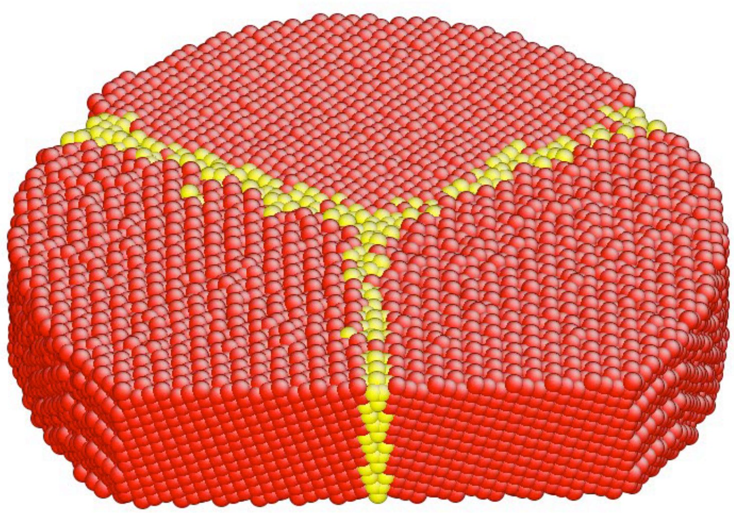
Animation

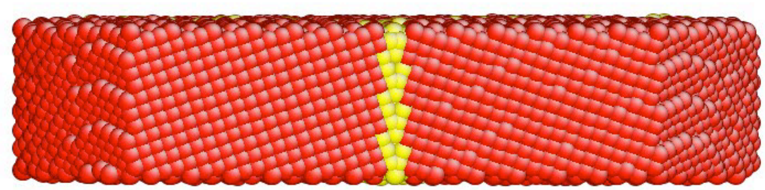

Select a slab of atoms in the middle of the block
Make atoms invisible
Make atoms invisible
Show only these atoms at later times

T=1100 K

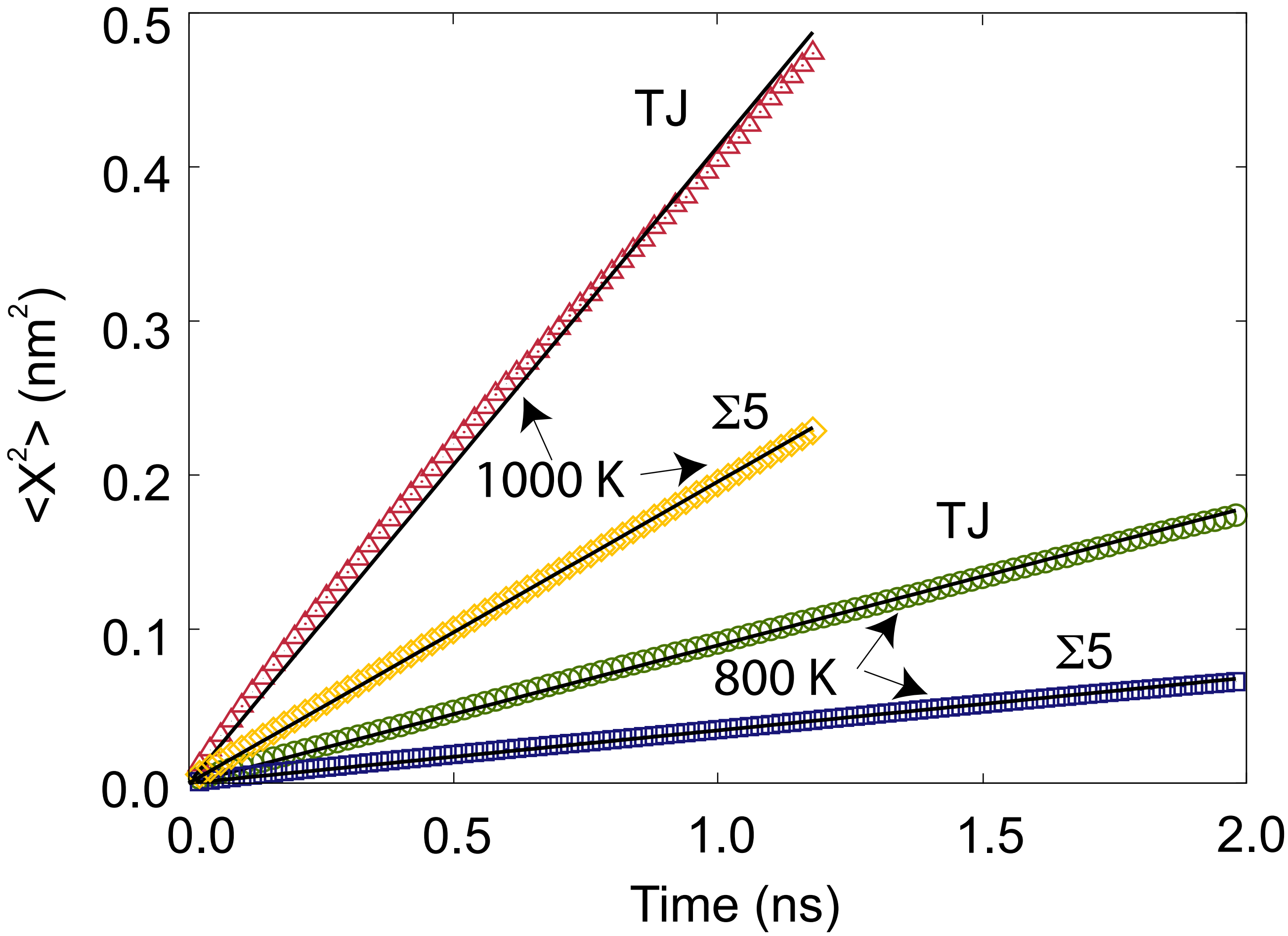






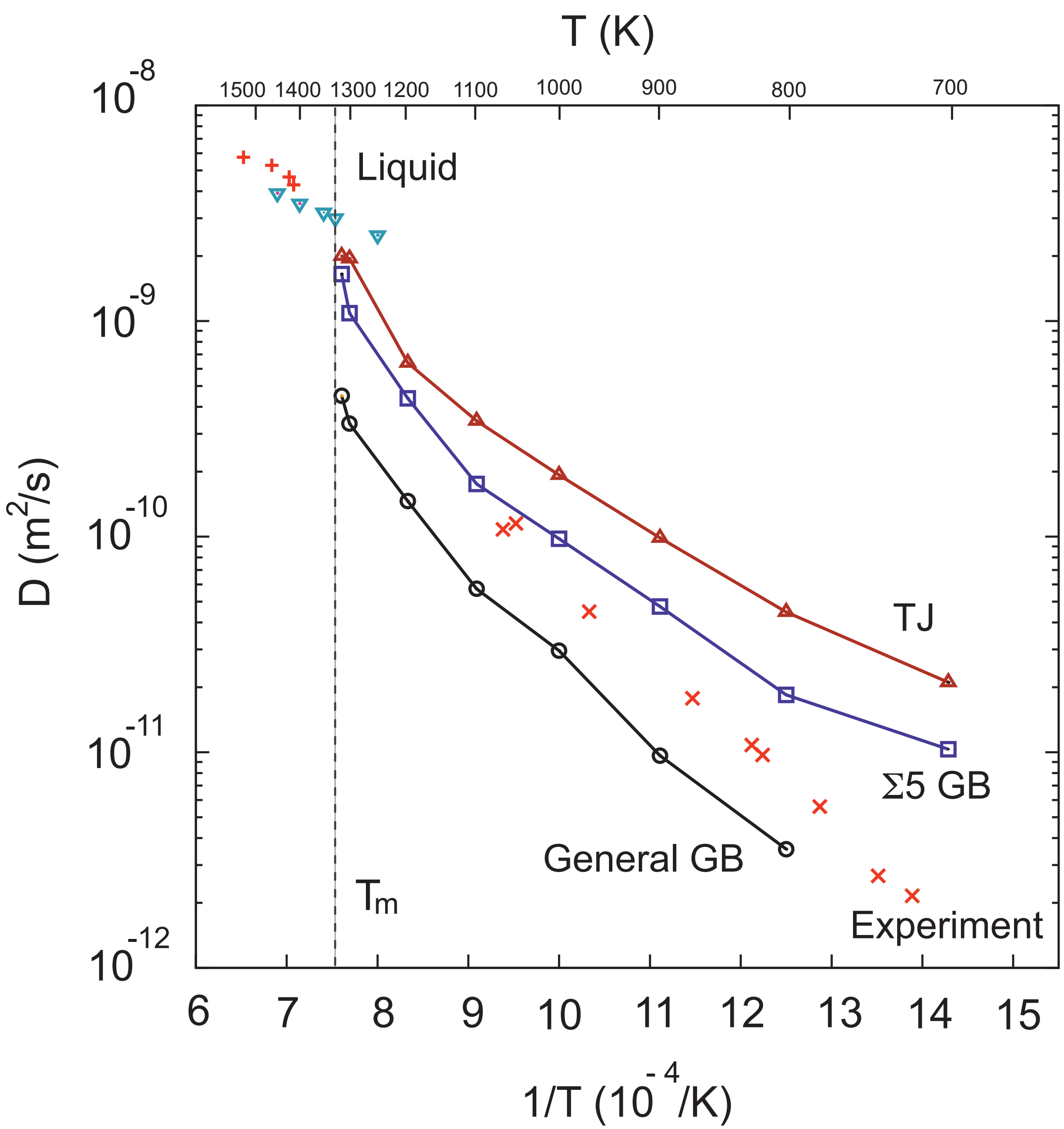


Typical RMS displacement versus time plots for TJ and GBs



- Displacements of atoms follow the Einstein relation

Arrhenius diagram of diffusion



- At all T $D_{TJ} > D_{\Sigma 5} > D_{GGB}$
- Premelting at high T
- Experimental data: polycrystalline copper (average over different GBs and TJs)
  T. Surholt et al (1997)

liquid copper
J. Henderson et al (1961)

Conclusions

- Stable TJs with controlled crystallographic orientations of the grains can be created in computer simulations
- Self-diffusion in the TJ and adjacent GBs was computed over a range of temperatures
- TJ diffusivity is higher than GB diffusivity at all simulated temperatures
- TJ diffusivity only twice large than the diffusivity in Σ5 GB
- Contribution of TJs to diffusivity in nano-crystalline materials is probably overestimated

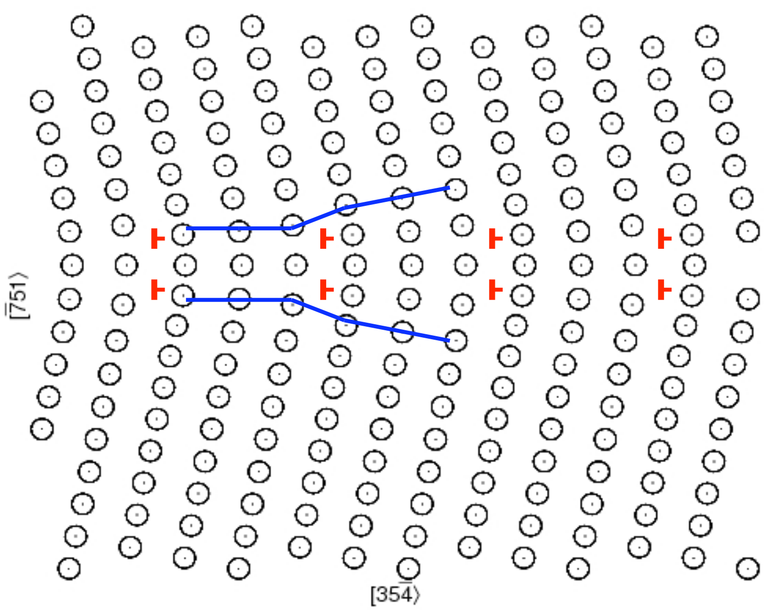
Diffusion along a dislocation grain boundary in Al

Ganga Pun

Symmetrical tilt grain boundary in Al

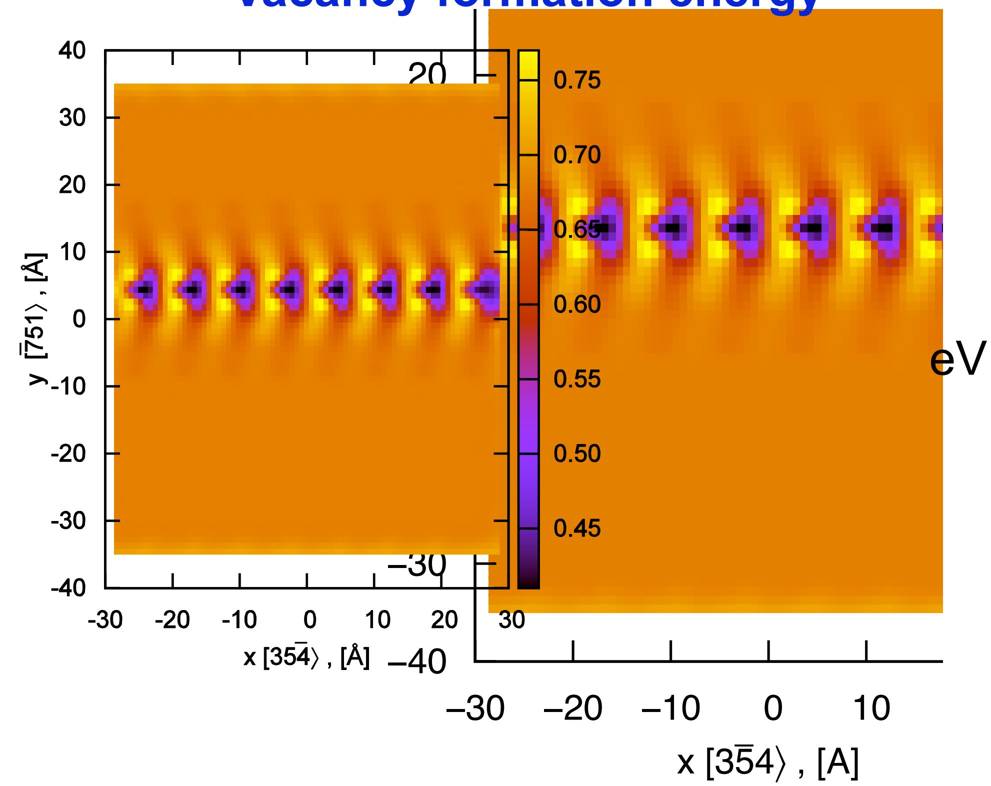
Σ 75 (751) [112], 23.07°

N_{free} = 12,000 atoms
L_x = 58.3Å
L_y = 107.4Å
L_z = 50.4Å



XY view

Vacancy formation energy

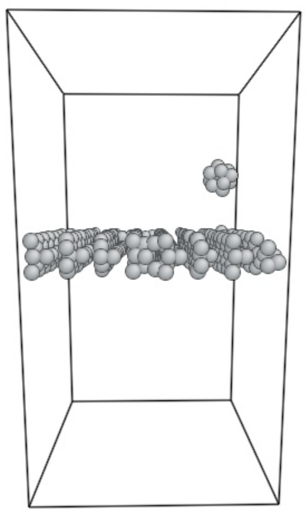


Three types of simulations

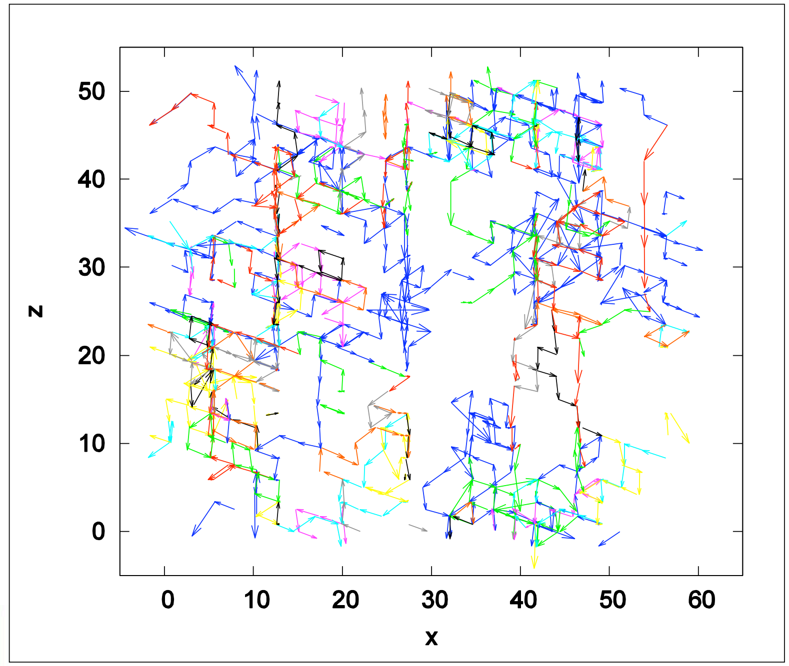
- Pre-existing vacancies
- Pre-existing interstitials
- No pre-existing defect (**intrinsic** mechanism)

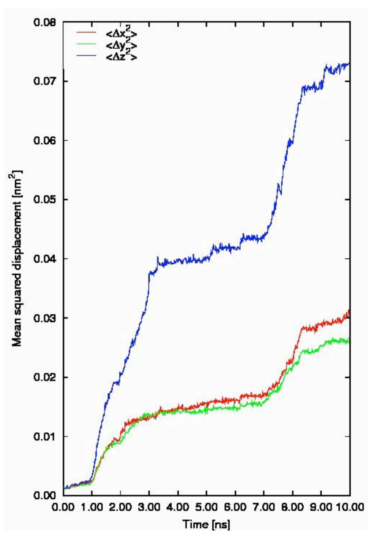
Diffusion along edge dislocations in Σ 75 (751) [112]

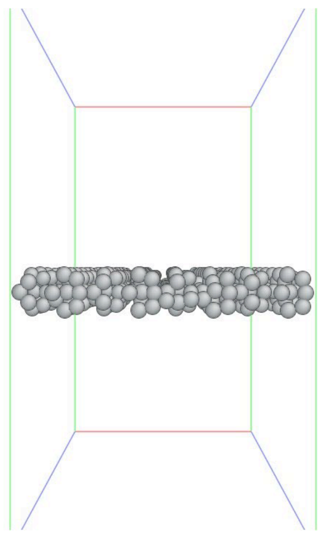
800K (w/vacancy)



Atomic jumps: 900K (with 8 vacancies)







850K (intrinsic)

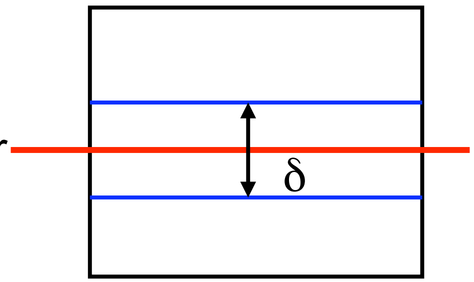
Intrinsic mechanism:

- Frenkel pair forms in the GB
- Vacancy escapes to the lattice
- Interstitial mediates fast diffusion
- The Frenkel pair recombines

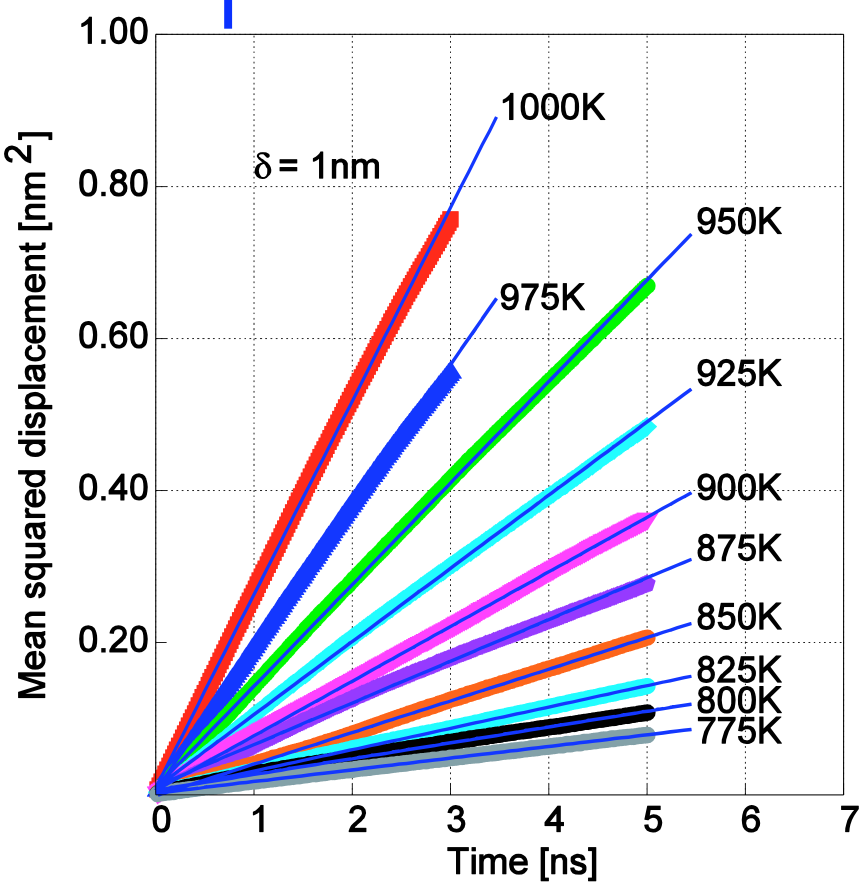
Calculation of “raw” diffusivity

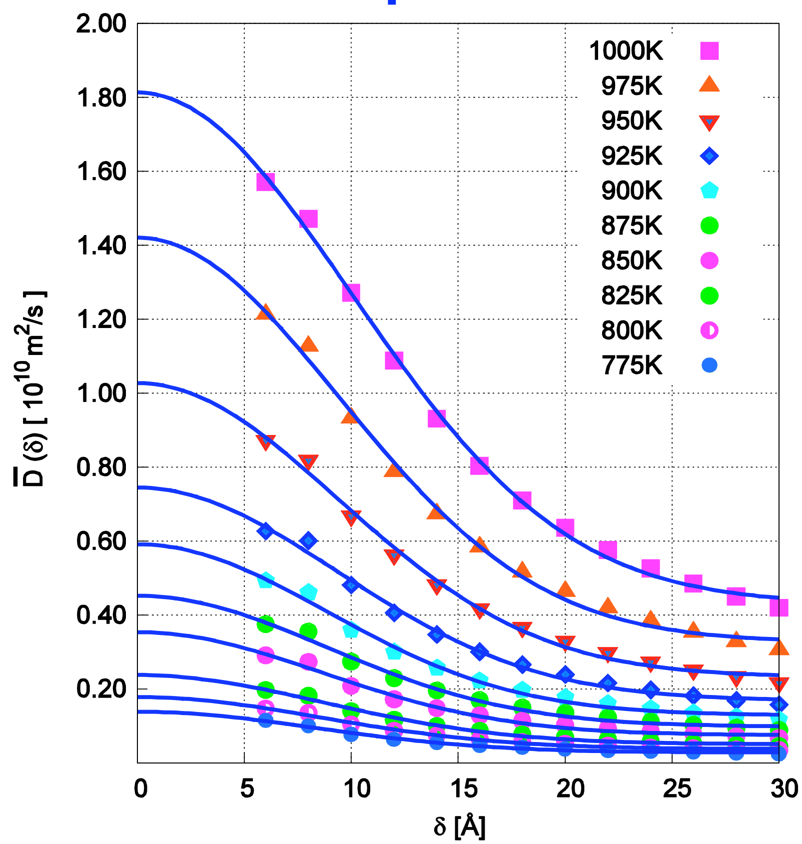
Case with 8 interstitials

$$\overline{D}^{raw}(\delta) = \frac{\langle z^2 \rangle}{2\tau}$$



$$\overline{D}^{raw}(\delta) = A\exp\left(-\frac{\delta^2}{\delta_0^2}\right) + B$$





Calculation of actual diffusivity

$$\overline{D}^{raw}(R) = \frac{\langle z^2 \rangle}{2\tau}$$

↓

$$\overline{D}^{raw}(\delta) = A\exp\left(-\frac{\delta^2}{\delta_0^2}\right) + B$$

↓

$$\overline{D}_{GB}^{raw}(\delta = \delta_0) \approx A/e$$

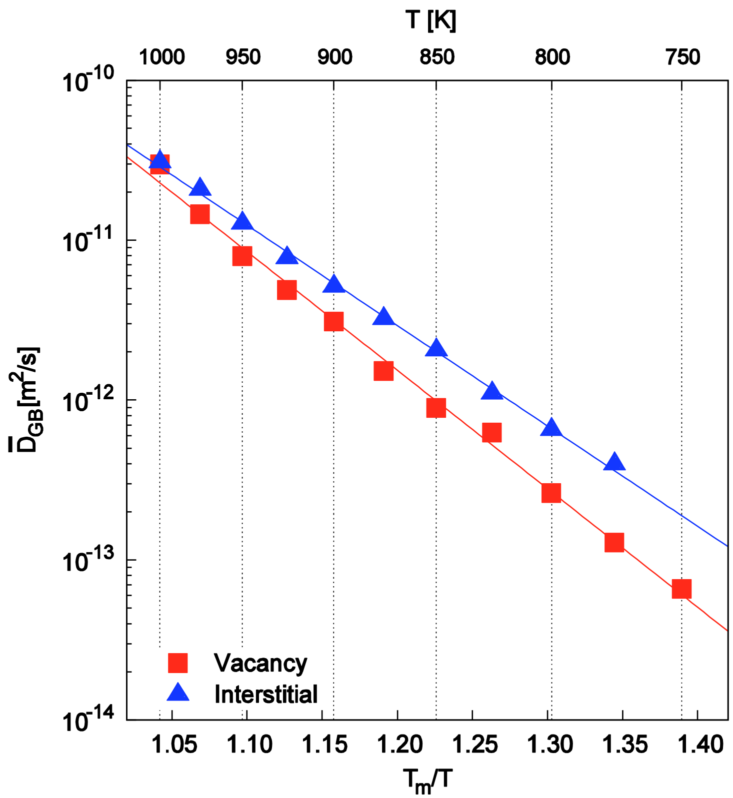
↓

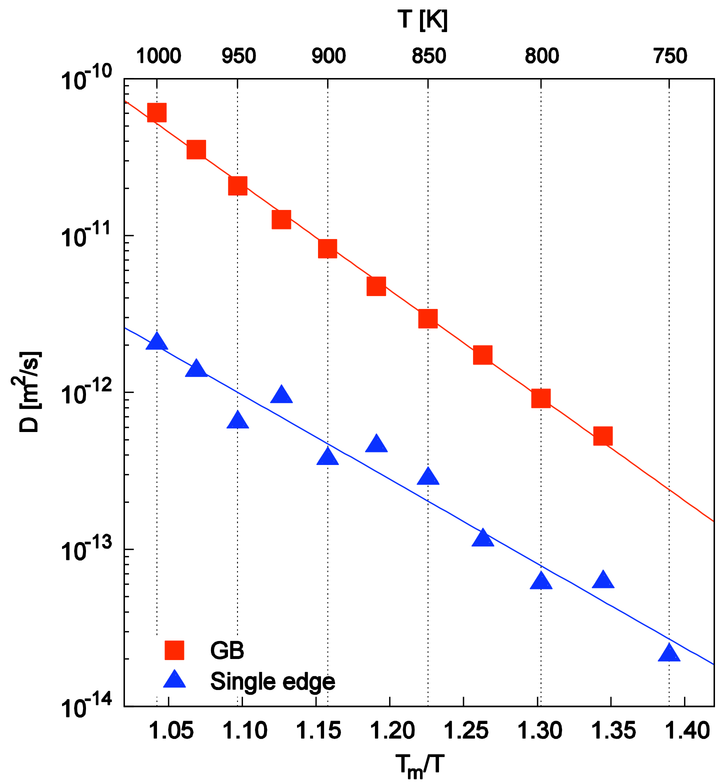
$$\overline{D}_{GB} = \overline{D}_{GB}^{I} + N^{eq}{}_{v}\left(\overline{D}_{GB}^{\mathrm{raw}} - \overline{D}_{GB}^{I}\right)/N_v$$

$\overline{D}_{GB}^{I}$: average intrinsic diffusivity

$$N^{eq}{}_{v} = \sum_{i=1}^{N} \exp\left(-\frac{E_{vi}}{kT}\right)$$

Arrhenius plots





δ_0 = 0.35-0.40 nm

	Vacancy	Interstitial
E_a (eV)	1.53 ± 0.03	1.30 ± 0.02
$Log(D_0)$ (m^2/s)	-2.91 ± 0.20	-4.00 ± 0.11

	Grain boundary	Single edge
E_a (eV)	1.39 ± 0.02	1.11 ± 0.07
$Log(D_0)$ (m^2/s)	-3.29 ± 0.15	-6.10 ± 0.43

Conclusions

- Σ 75 (751) [112], 23.07° symmetrical tilt grain boundary:
  - Interstitial diffusion dominates over vacancies
  - High diffusivity compared to single edge core
- Working on other low angle symmetrical tilt and twist grain boundaries

Last slide of my presentation at this workshop on February 7, 2006:

Conclusions

- Once very fashionable, the area of GB diffusion is not hot anymore. It is **not** considered to be cool enough. It cannot compete with carbon nanotubes and quantum dots
- It is only the Herzig group in Muenster that keeps GB diffusion measurements alive
- Development of GB diffusion theory stopped (June 1, 2005)
- Posterity will not forgive us

Never say never!