~~Hot~~ ~~Cool~~ Selected Problems of GB diffusion

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Importance of GB diffusion

GB diffusion is much faster than lattice diffusion

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

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Processes controlled/influenced by GB diffusion:

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

Diffusion is a structure-sensitive property

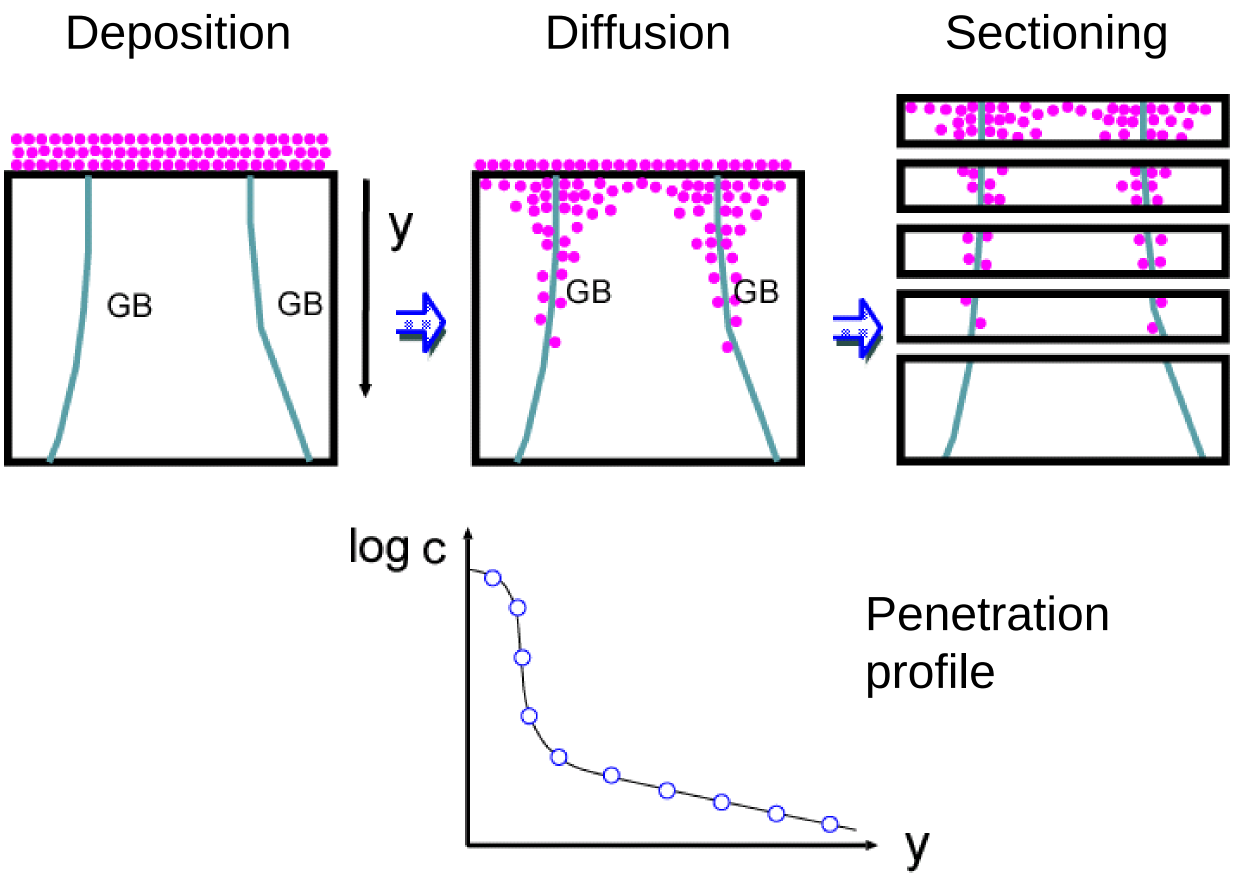
Can we neglect GB diffusion?

- Copper: $D_0 = 1.3 \times 10^{-6}$ m^2/s, $Q = 0.82$ eV
- $T = 700$ K, $t = 1$ min $\Rightarrow L \approx 20$ μm
- $T = 300$ K, $t = 1$ min $\Rightarrow L \approx 2.3$ nm
- $T = 300$ K, $t = 30$ min $\Rightarrow L \approx 12.3$ nm

Experimental methods in GB diffusion

- Radiotracer serial sectioning
  - Mechanical sectioning
  - Sectioning by sputtering
- Non-radioactive methods
  - SIMS
  - AES
  - ESCA

Radiotracer sectioning method



Need many GBs to achieve a high accuracy

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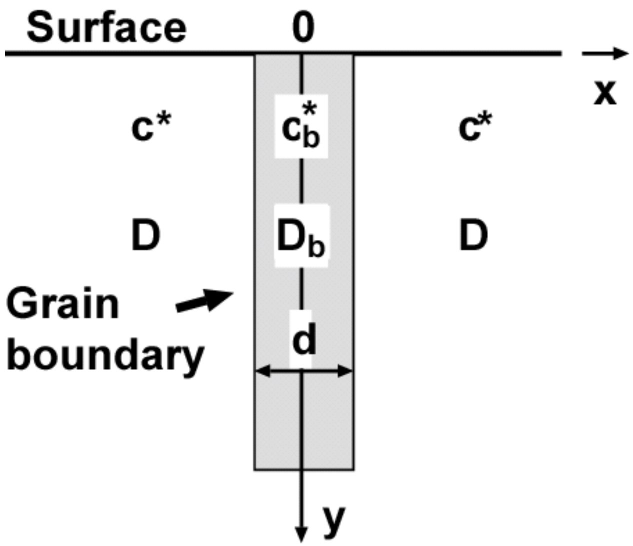
Fisher model of GB diffusion



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

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

<u>Coupling conditions</u>:

Self-diffusion A* $\rightarrow$ A: $c^*_b = c^*$

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

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

Solution of the Fisher model

Under typical experimental conditions

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

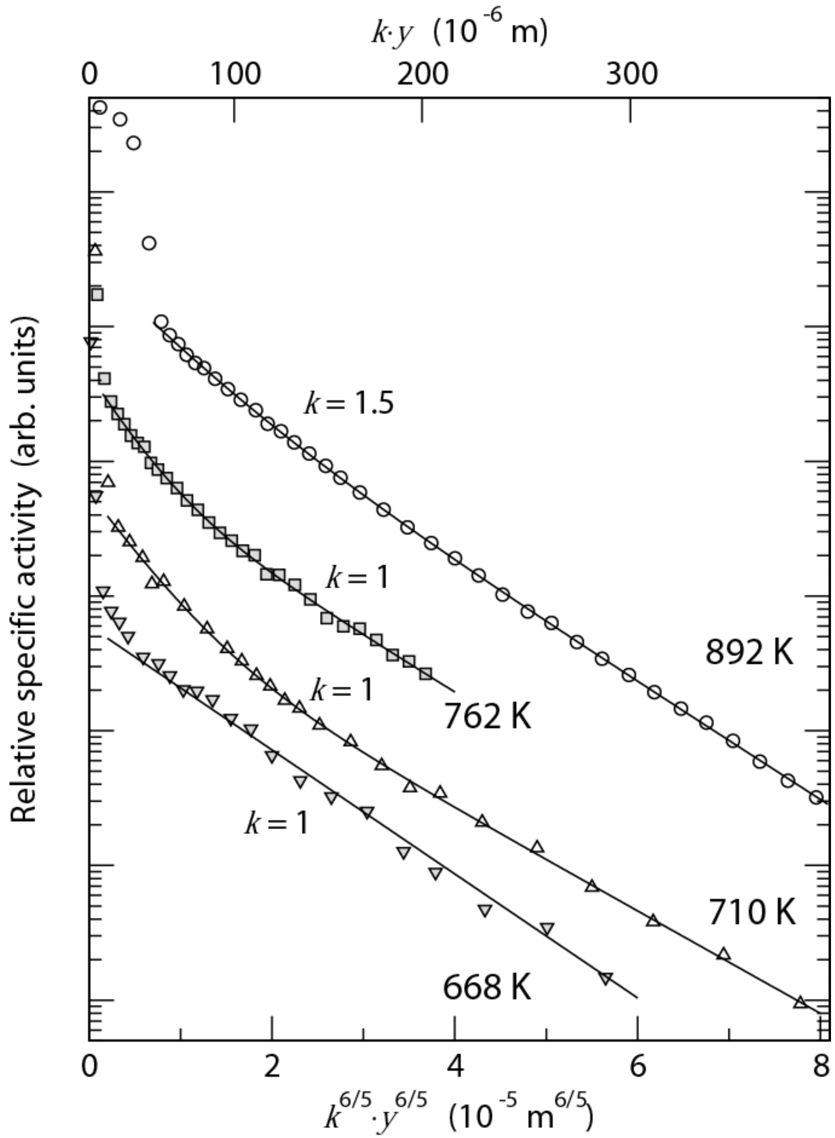
⇓

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

q – numerical factor depending on the surface condition

Must know D from independent measurements

Examples of GB diffusion profiles

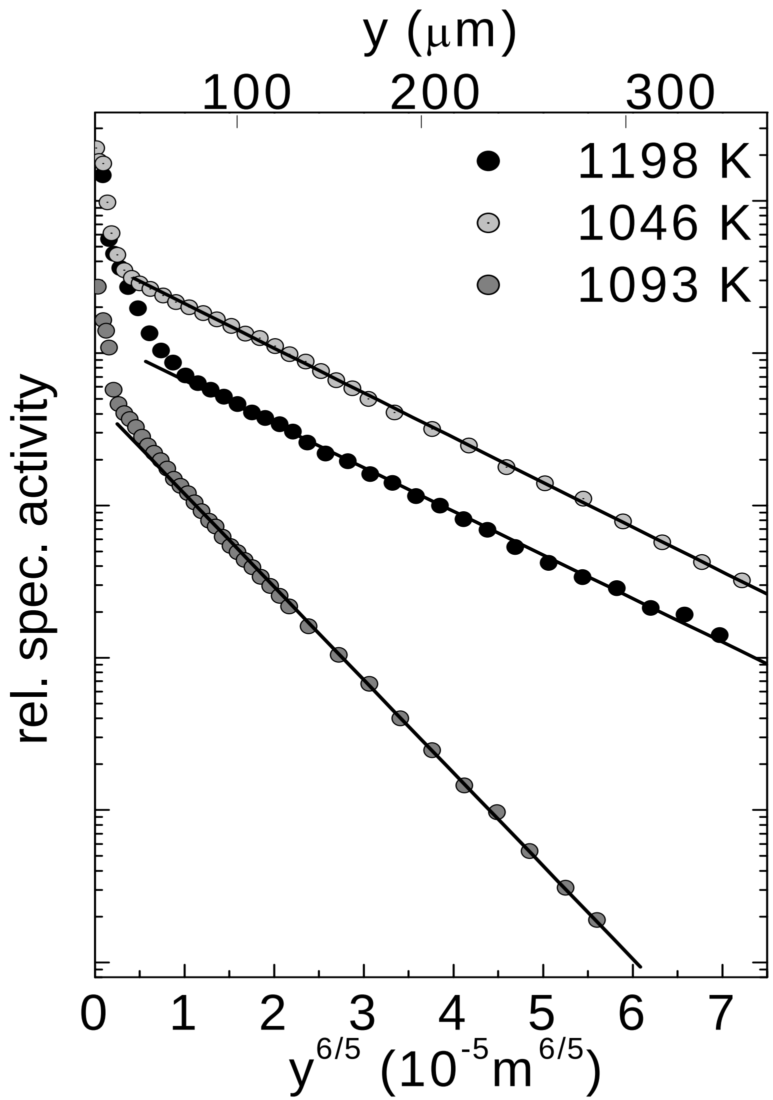


Ag in Cu-0.2at%Ag

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

Examples of GB diffusion profiles

Bi GB diffusion in Cu



Divinski, Herzig, et al Acta Mater (2004)

Topic I: Combined B and C regime measurements

Regime B (high temperatures)

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

Regime C (low temperatures – extremely difficult measurements!)

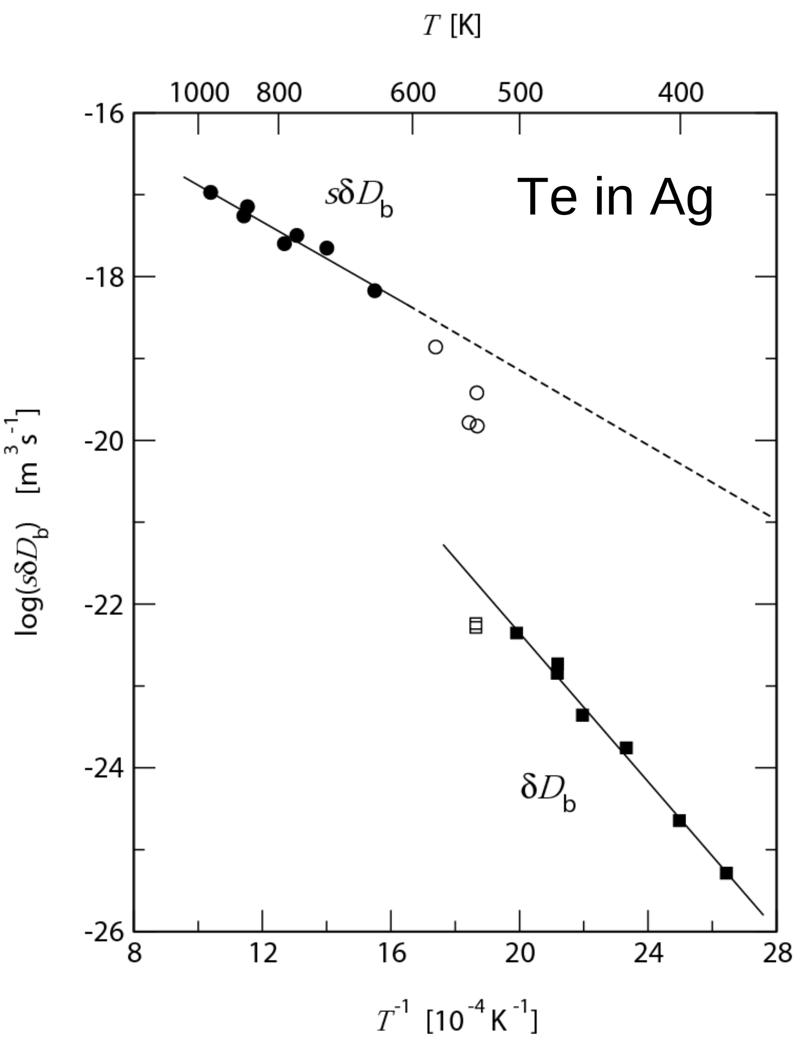
$$(Dt)^{1/2} << s\delta \quad \Rightarrow \quad \bar{c} \propto \exp\left(-\frac{y^2}{4D_b t}\right) \quad \Rightarrow \quad D_b$$

$$\Downarrow$$

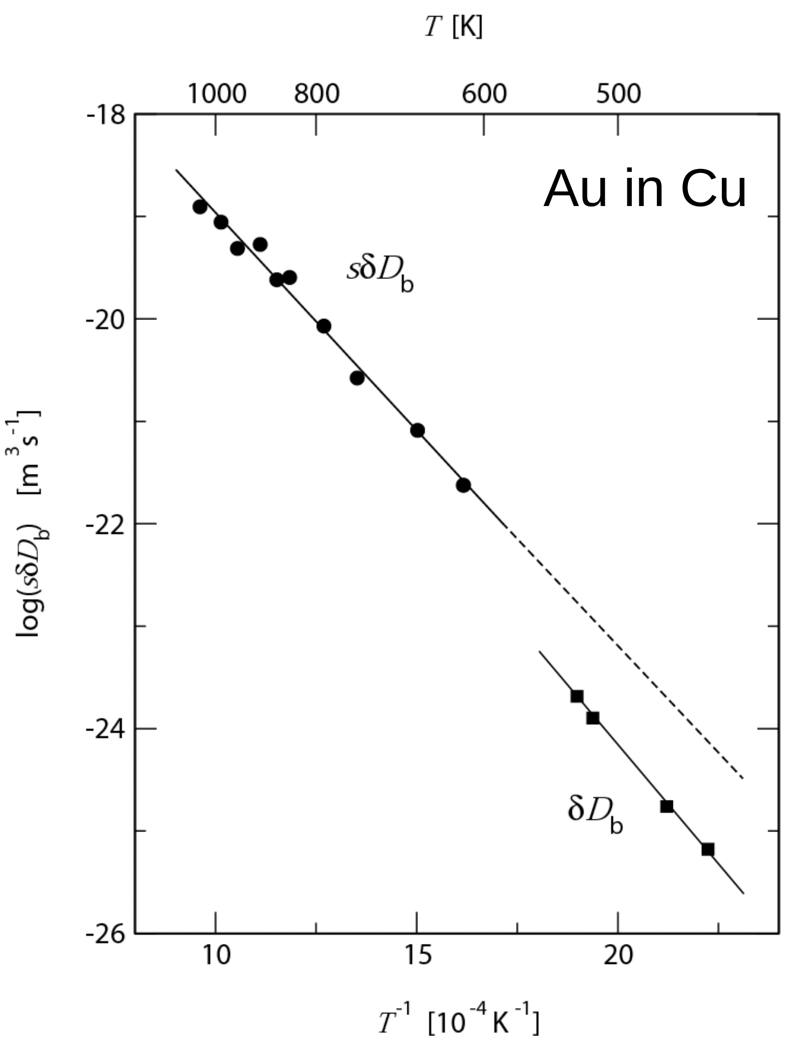
$$s\delta = \frac{(s\delta D_b)_B}{(D_b)_C}$$

Self-diffusion: s = 1 $\Rightarrow$ $\delta \approx 0.5$ 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)

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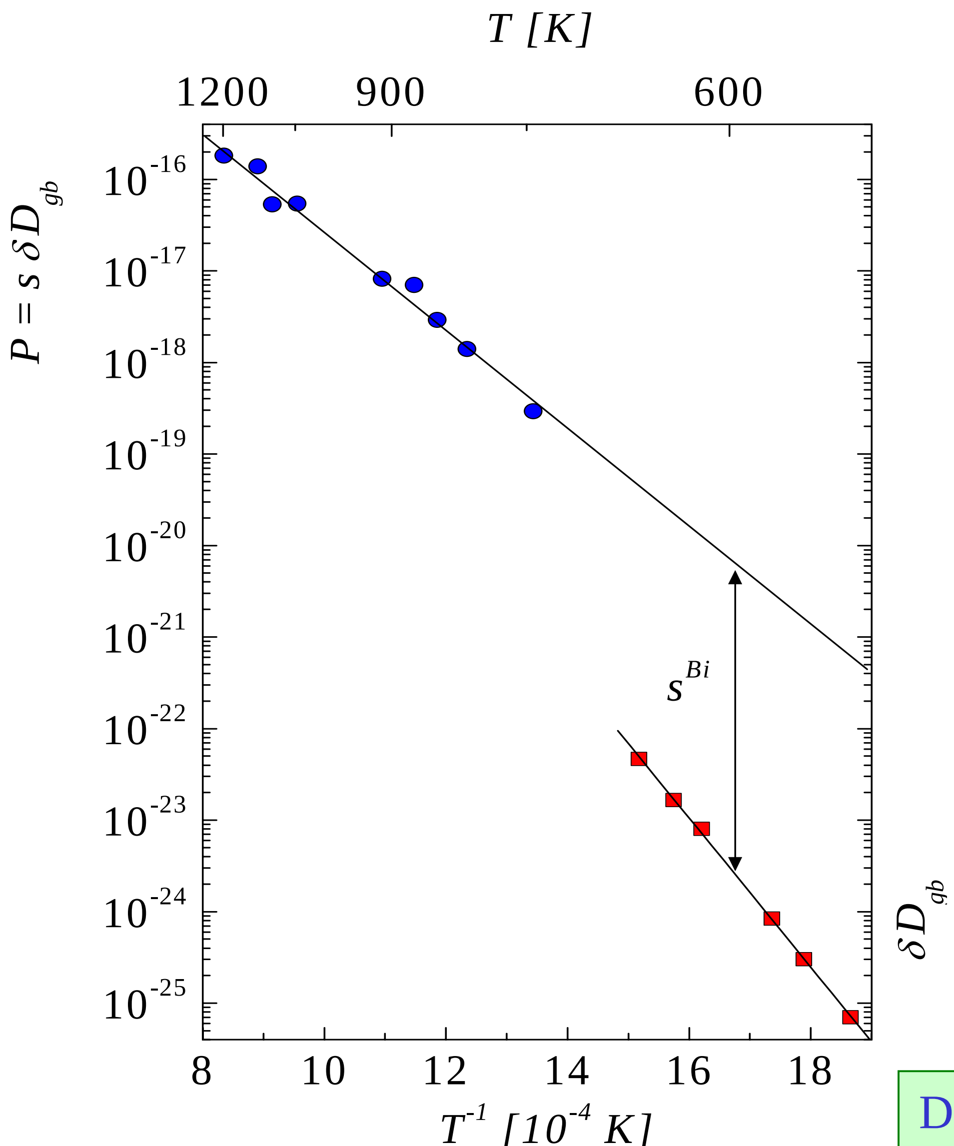
Bi GB diffusion in Cu



Divinski, Herzig, et al Acta Mater (2004)

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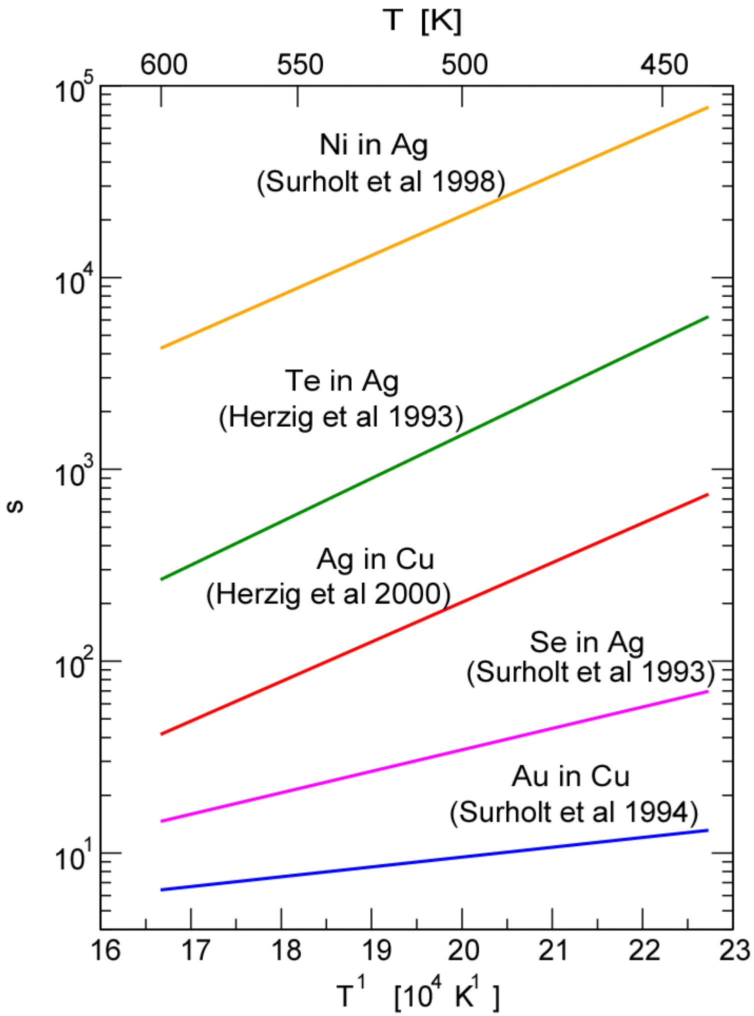
Combined B and C regime measurements

Segregation factors determined in a number of systems, e.g. Te, Se and Ni in **Ag**; Se, Bi, Fe, Ag and Au in **Cu** [Muenster group, Germany].



Such measurements give access to GB segregation in **ductile** materials. No need to break samples along GBs.

Some measurements have been made on bicrystals !

Courtesy S.V. Divinski

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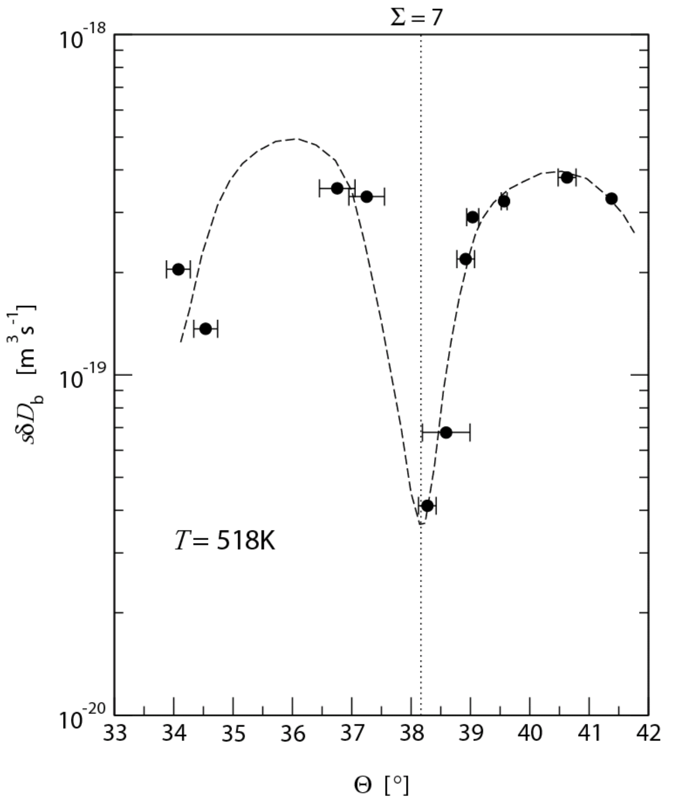
Topic II: GB diffusion measurements as a probe of GB structure and chemistry
(mainly on bicrystals)

- Misorientation dependence D_b (θ)
- Anisotropy of GB diffusion
- "Free volume" of GBs (from the pressure dependence of D_b)
- Probe of phase transitions: melting/premelting, wetting/prewetting

Sharp minimum of GB diffusivity at the exact Σ7 misorientation

Ge diffusion in Al bicrystals with near-Σ7(123)[111] GBs



T. Surholt et al., *Acta Mater*. **46**, 5345 (1998)

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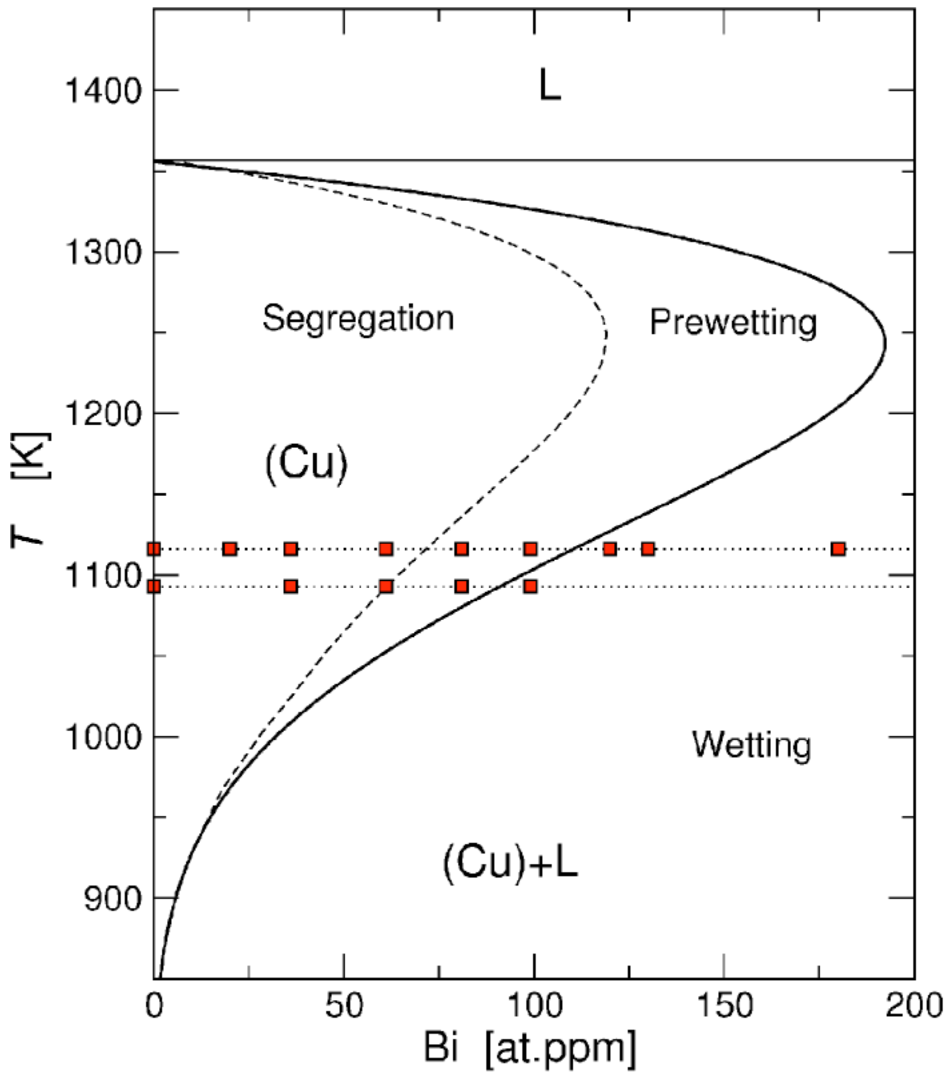
GB diffusion in Cu-Bi alloys*



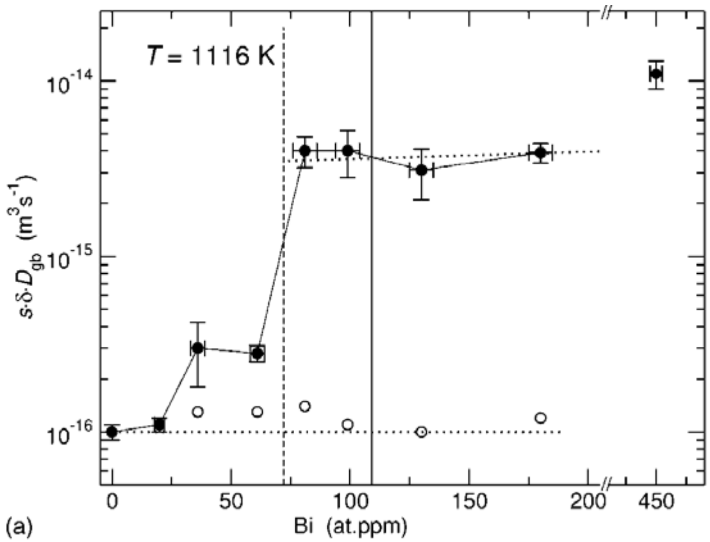
Experimental diagram (AES)

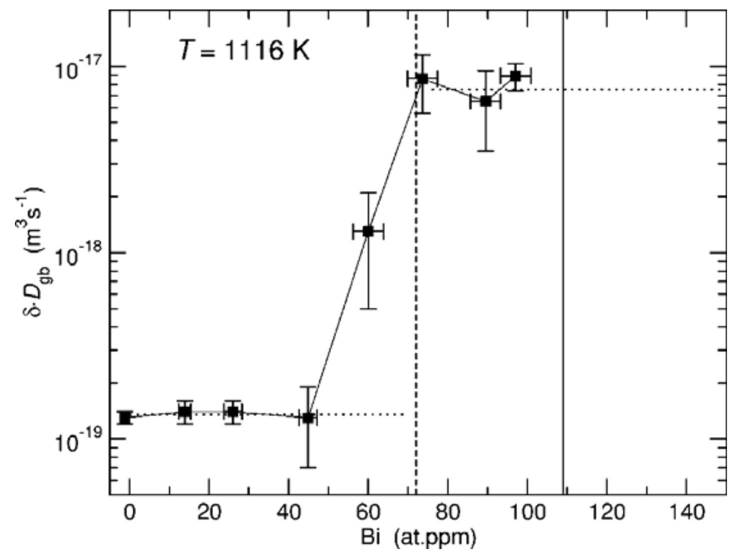
Chang et al, *Acta Mater*. **47**, 4041 (1999)

- The AES experiments involve rapid quenching in the presence of fast Bi diffusion. Are they reliable?
- GB diffusion measurements are made in equilibrium conditions (very long anneals, no quenching, etc.)

* S. Divinski et al., *Phys. Rev*. B **71**, 104104 (2005)

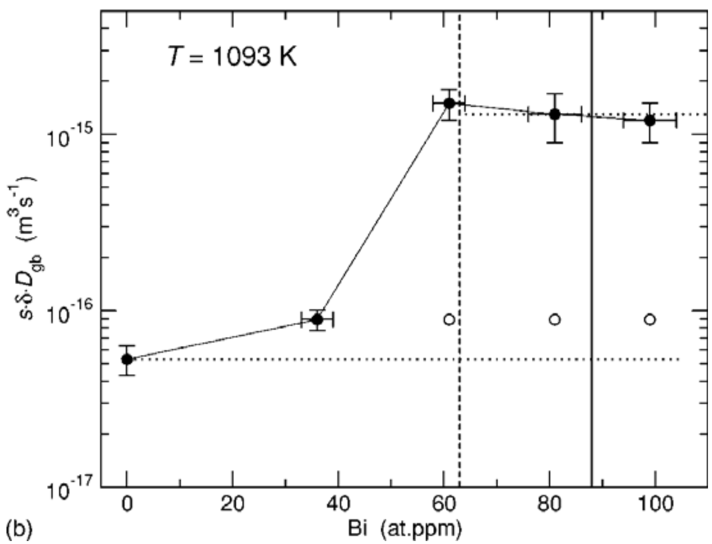
GB diffusion in Cu-Bi alloys*





^{207}Bi in Cu

^{64}Cu in Cu



At the prewetting composition D_b rapidly increases and reaches the liquid value

* S. Divinski et al., *Phys. Rev*. B **71**, 104104 (2005)

Topic III: Atomic mechanisms of GB diffusion

- Which point defects dominate thermal disorder in GBs?
- What are the diffusion mechanisms in GBs?
- What is the relation between GB diffusion and GB structure, energy etc.
- Atomistic calculation of GB diffusion coefficients

Early work (1970s-1980s) suggested the following answers:

- Thermal disorder by vacancies
- Diffusion by single-atom vacancy jumps

Thus, the difference between GB and lattice diffusion was thought to be only quantitative (lower vacancy formation and migration energies).

Recent work has shown that GB diffusion is profoundly different from lattice diffusion. And it is much more complex.

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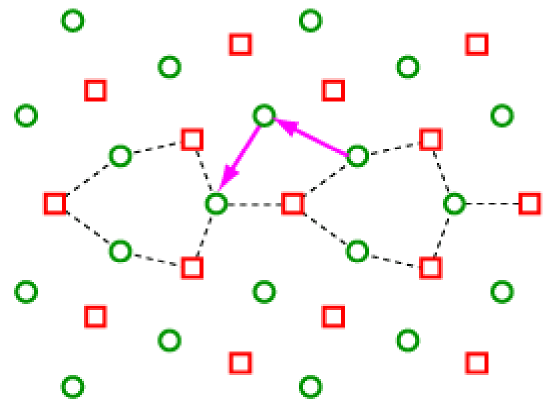
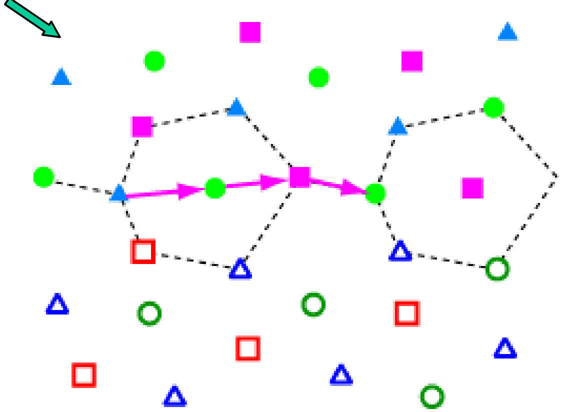
Diffusion mechanisms in GBs

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



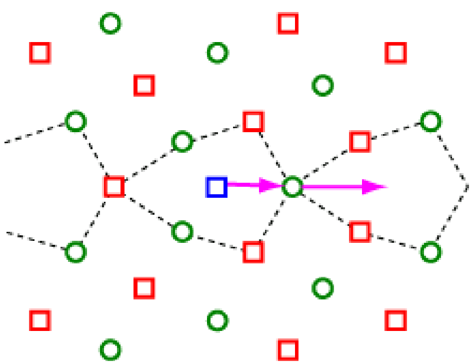
Σ=5(310)[001]

Vacancies

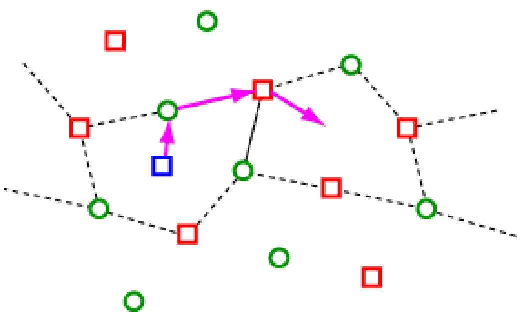


Σ=7(231)[111]

Interstitials



Σ=5(210)[001]



Σ=9(122)[011]

Comparison of GB and lattice diffusion

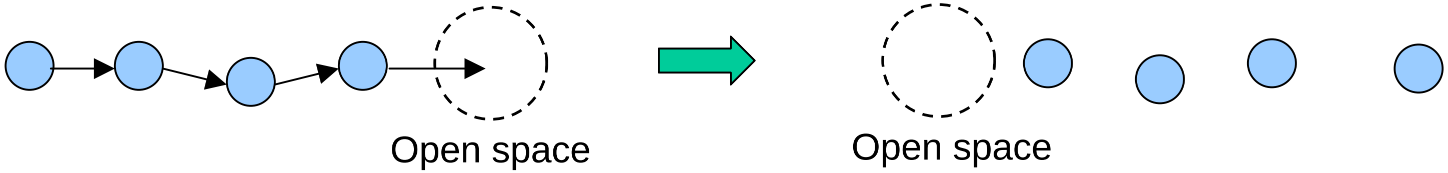
Lattice diffusion

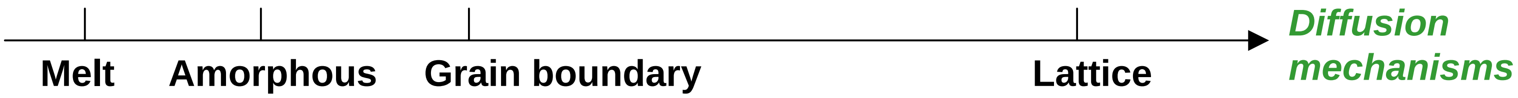
- Vacancies dominate
- Vacancies move by single-atom exchanges

GB diffusion

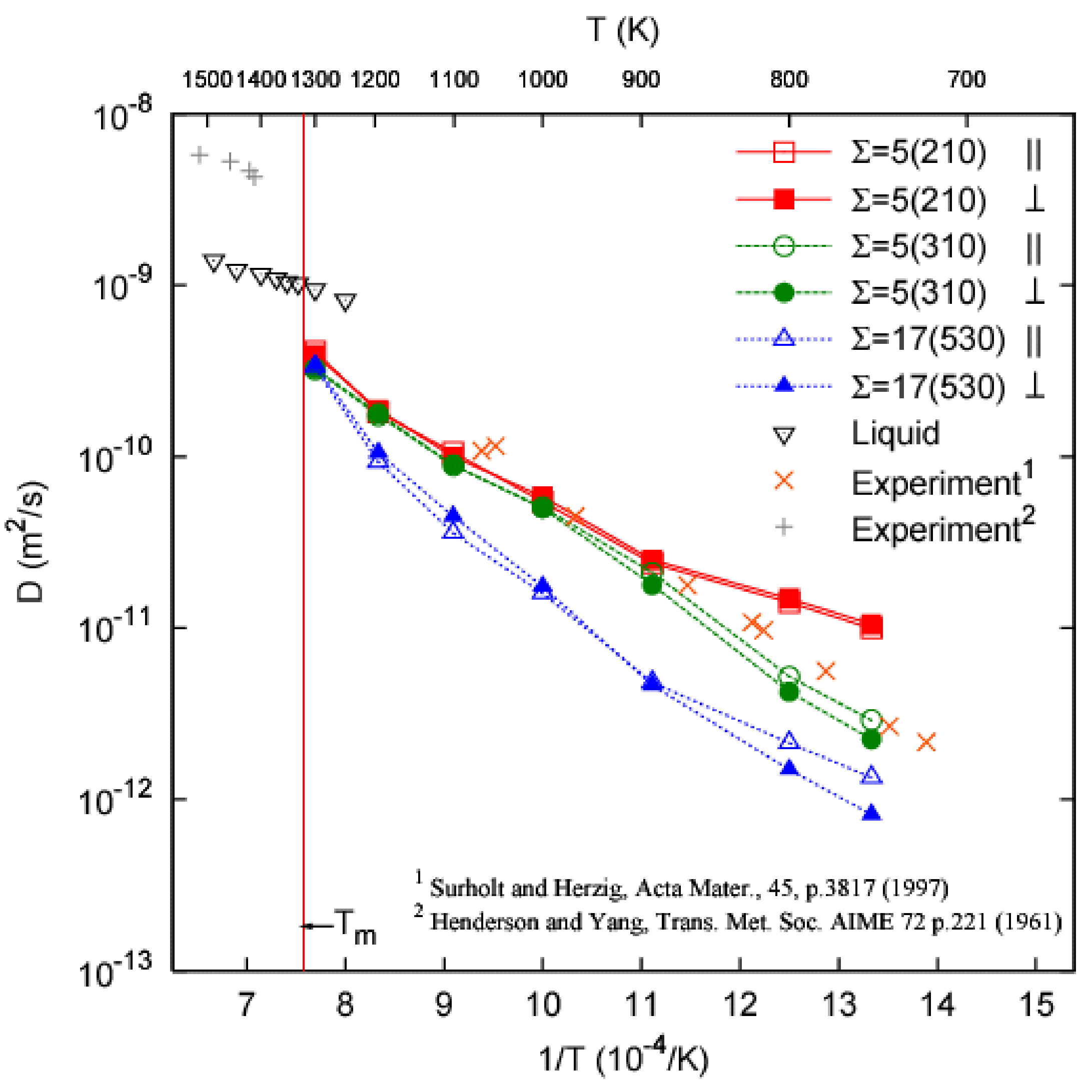
- Vacancies and interstitials are equally important
- Variety of point-defect structures
- Variety of diffusion mechanisms
- Most diffusive events are collective

Typical diffusive event in GBs





GB diffusion in Cu: MD calculations



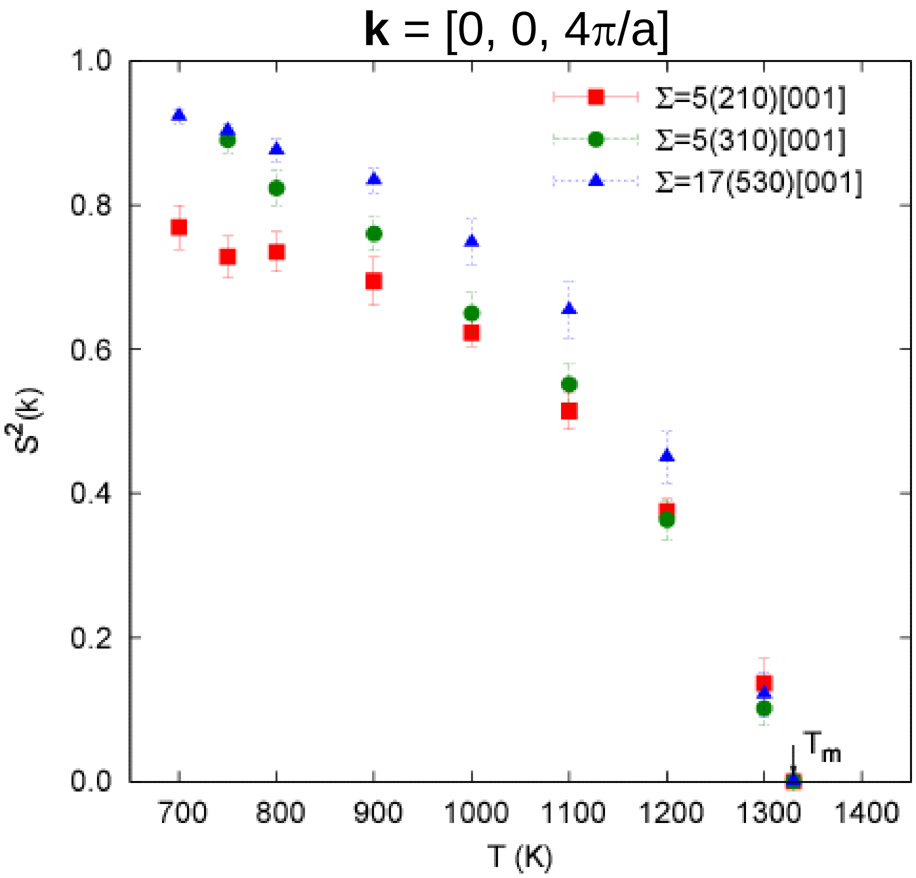
- Agreement with experiment
- Continuous "premelting" ~100K before T_m
- The Σ=5's merge at high temperatures. Universal diffusion mechanism? "Liquid-like" structure? [Keblinski et al, 1997, 1999]

High-temperature mechanisms remain unknown !

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

GB structure factor at high temperatures



- Long-range order in the GB region up to T_m
- S^2 goes to zero continuously
- S^2's of Σ=5's merge near T_m

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