SAND2016-8720C

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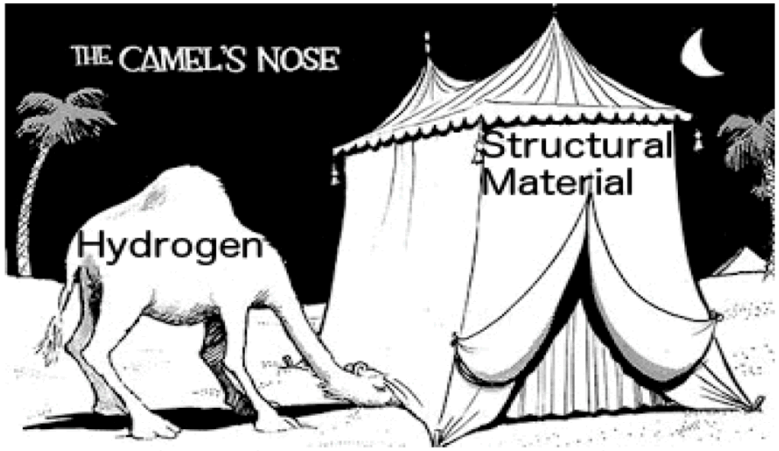
Hydrogen segregation to grain boundaries in nickel



"If the camel (H, He, S) once gets his nose in the tent (engineering materials), his body will soon follow (i.e. performance issues)."

R. Dingreville[1], S. Berbenni[1], C.J. O'Brien[1], S. Foiles[1], R. Karnesky[3]

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SAND2016-XX

International Hydrogen Conference 2016
Modeling and Simulation I session
9/13/2016

Are material optimized microstructure designs mitigating H-assisted aging in our future?

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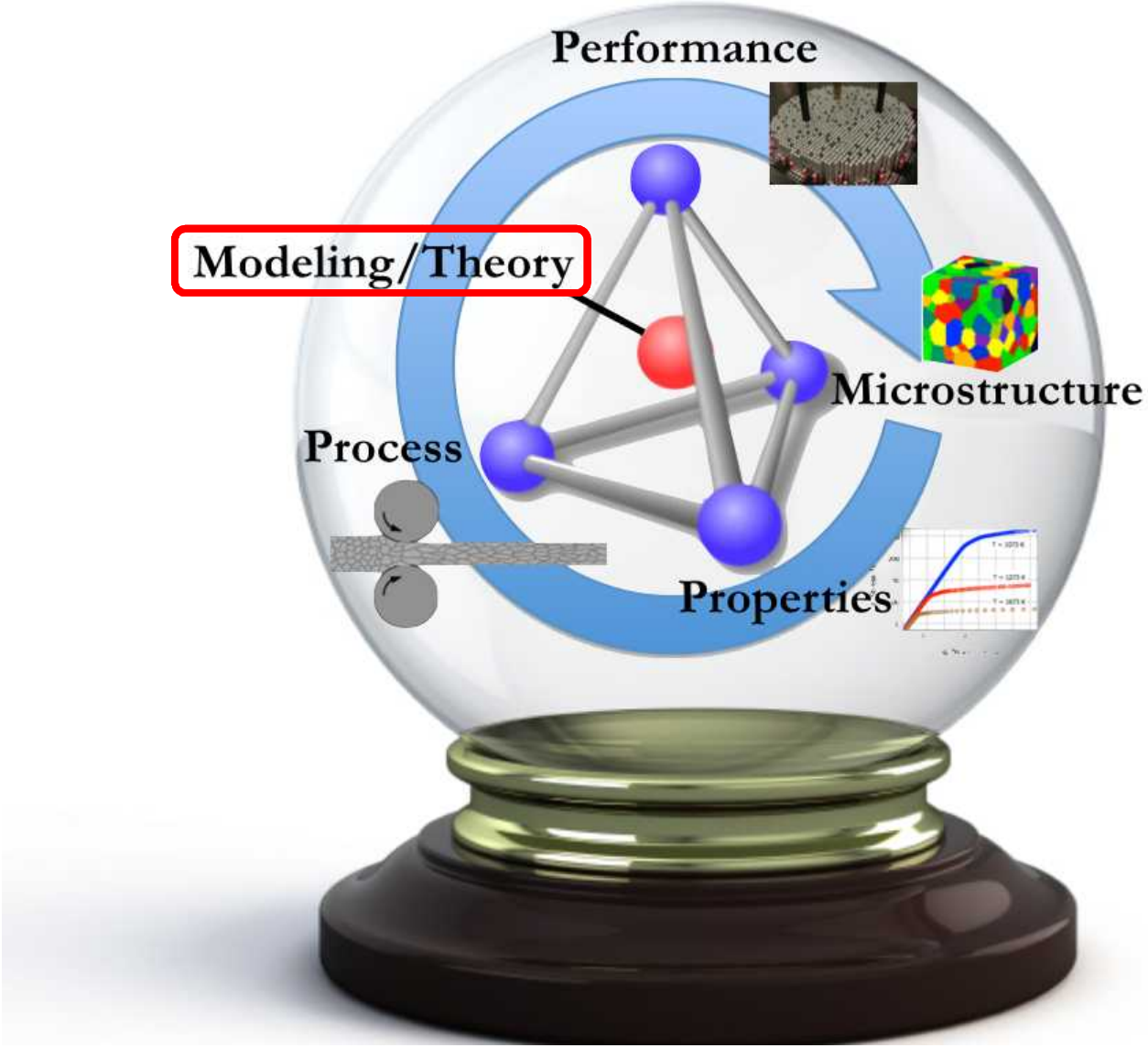

Today's reflection and overview

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- **Where hydrogen segregation matters…Cottrell atmospheres**
- **Segregation susceptibility using continuum mechanics:**
  - **GB construct:** Disclination mechanics
  - **Solute trapping at GB:** Fermi-Dirac statistics of site occupancy
  - **The importance of GB character**
- **Comparison to the atomic scale:**
  - Atomistic model for H segregation
- **Perspective and summary:**
  - Reality check

Cottrell atmosphere: Solute atoms can segregate to elastically deformed regions around defects

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Dislocation Theory of Yielding and Strain Ageing of Iron

By A. H. COTTRELL and B. A. BILBY
Metallurgy Department, University of Birmingham

Communicated by N. F. Mott ; MS. received 10th August 1948

ABSTRACT. A theory of yielding and strain ageing of iron, based on the segregation of carbon atoms to form atmospheres round dislocations, is developed. The form of an atmosphere is discussed and the force needed to release a dislocation from its atmosphere is roughly estimated and found to be reasonable. The dependence on temperature of the yield point is explained on the assumption that thermal fluctuations enable small dislocation loops to break away ; these loops subsequently extend and cause yielding to develop catastrophically by helping other dislocations to break away. The predicted form of the relation between yield point and temperature agrees closely with experiment.

Strain ageing is interpreted as the migration of carbon atoms to free dislocations. The rate of ageing depends upon the concentration of carbon in solution and the estimated initial rate agrees with experiment on the assumption that about 0·003% by weight of carbon is present in solution.

[Cottrell and Bilby, Proc Phys Soc Lond, 1948]

$$\frac{c}{c_0} = \exp\left(\frac{p\Delta V}{k_B T}\right)$$

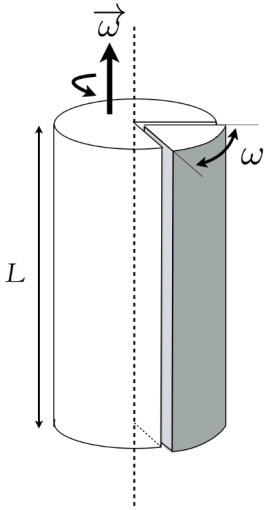
p : hydrostatic pressure

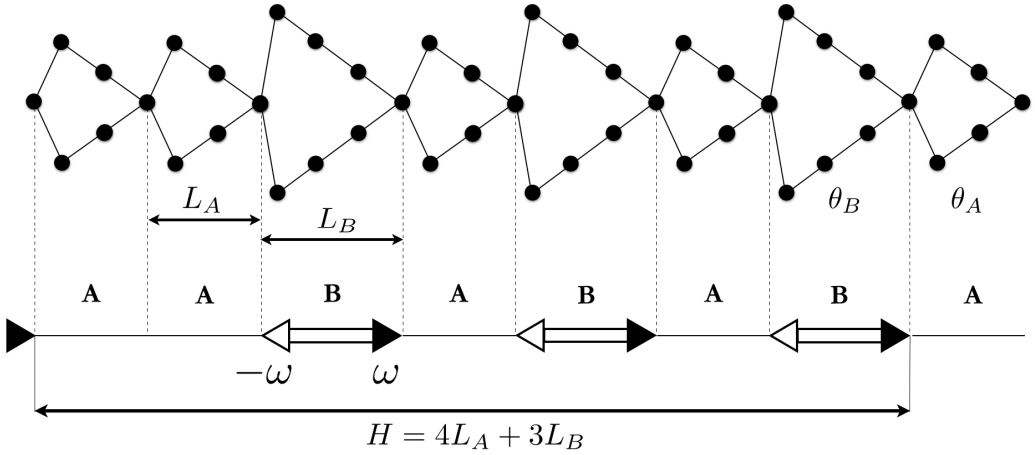
ΔV : solute volume change

- **Solute equilibrium depends on:**
  - Intrinsic character of defect considered
    - Models based on dislocation theory: core effects
  - Screening effects (stress relief)
  - Chemical interaction

- **Scientific questions to be addressed:**
  - What are the characteristics scales of importance?
  - What are the microstructural features (in the sense of GB engineering) impacting H segregation?

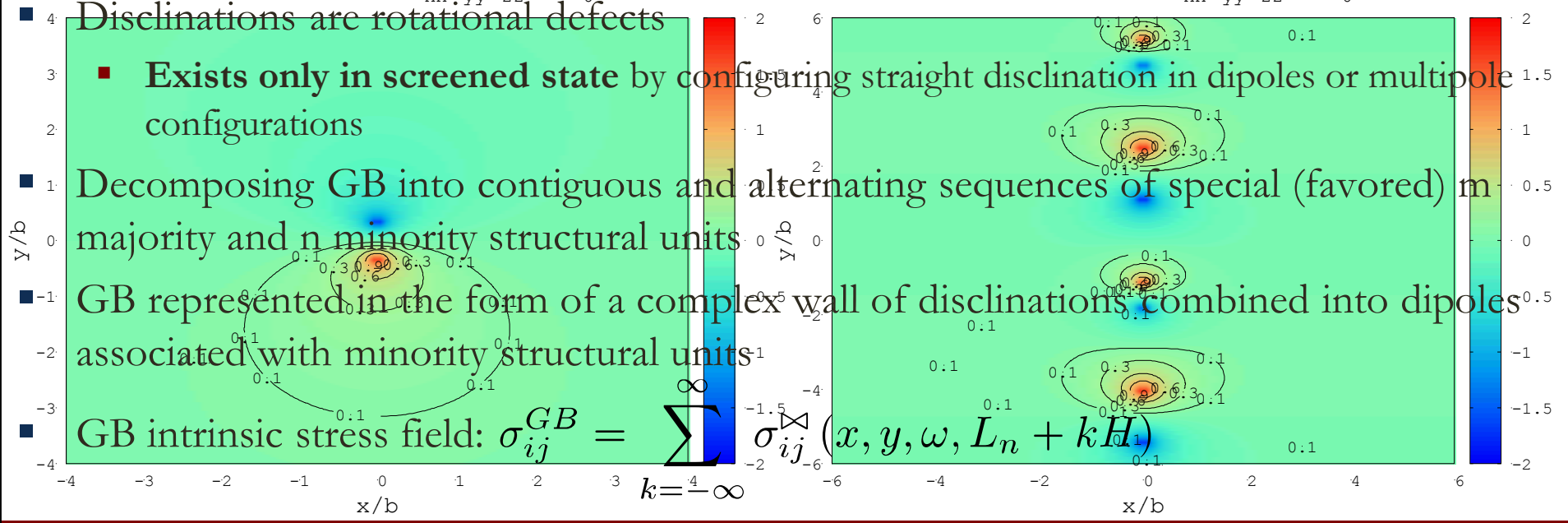
Construction of grain boundaries using disclination structural unit model (DSUM): nuts & bolts





$\Sigma 397$ $(\theta = 78.58^\circ)$: $(\sigma^{\ddagger}_{xx} + \sigma^{\ddagger}_{yy} + \sigma^{\ddagger}_{zz})/3D_0$

$\Sigma 17$ $(\theta = 61.93^\circ)$: $(\sigma^{\ddagger}_{xx} + \sigma^{\ddagger}_{yy} + \sigma^{\ddagger}_{zz})/3D_0$



- Disclinations are rotational defects
  - **Exists only in screened state** by configuring straight disclination in dipoles or multipole configurations
- Decomposing GB into contiguous and alternating sequences of special (favored) m majority and n minority structural units
- GB represented in the form of a complex wall of disclinations combined into dipoles associated with minority structural units
- GB intrinsic stress field: $\sigma_{ij}^{GB} = \sum_{k=-\infty}^{\infty} \sigma_{ij}^{\bowtie}(x, y, \omega, L_n + kH)$

Symmetric tilt GBs about [001] axis: Structural character

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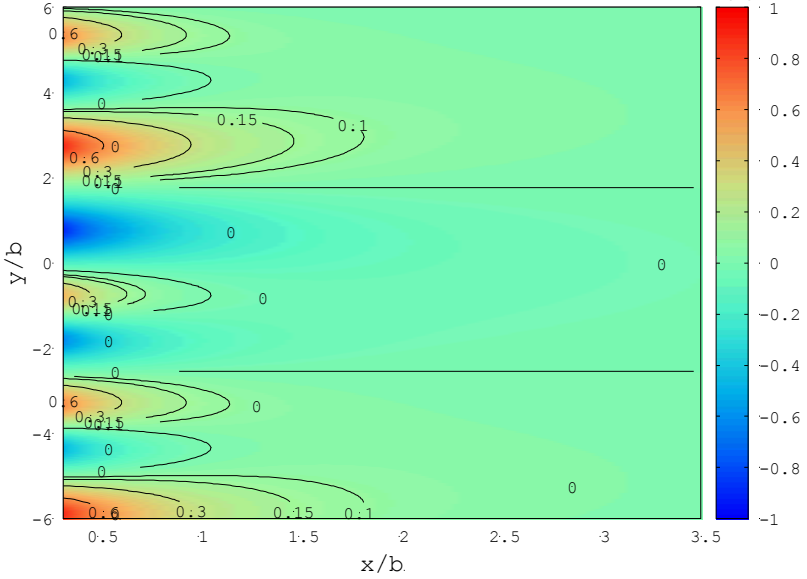
θ [°]	GB plane	Σ	Structural decomposition of the period	
0.00	(1 1 0)	1	|A|	← Perfect lattice
16.26	(4 3 0)	25	|AAB.AAB|	
20.02	(10 7 0)	149	|AABABAB.AABABAB|	
22.62	(3 2 0)	13	|AB.AB|	
25.06	(11 7 0)	85	|ABABABB|	
28.07	(5 3 0)	17	|ABB|	
36.87	(2 1 0)	5	|B.B|	← Σ5 GB
43.60	(7 3 0)	29	|BBC|	
46.40	(5 2 0)	29	|BC.BC|	
53.13	(3 1 0)	5	|C|	← Σ5 GB
58.11	(7 2 0)	53	|CCD.CCD|	
61.93	(4 1 0)	17	|CD.CD|	
64.94	(9 2 0)	85	|CDCDD.CDCDD|	
67.38	(5 1 0)	13	|CDD|	
73.74	(7 1 0)	25	|CDDDD|	
90	(1 0 0)	1	|D|	← Perfect lattice

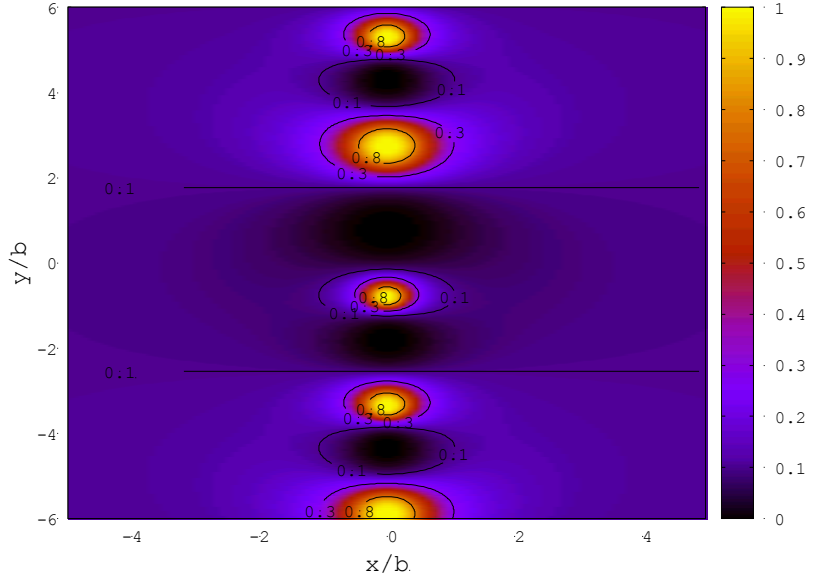
Fermi-Dirac statistics of site occupancy to model solute trapping at GBs

- Interstitial solutes = non-overlapping spherical misfitting inclusions (in the sense of Eshelby's theory) with purely positive dilatational eigenstrain.
- Energetic contribution and work done against pre-existing stresses upon the introduction of solutes.
- Site occupancy field around GB: $\chi(\mathbf{x}) = \dfrac{1}{1 + \dfrac{1-\chi_0}{\chi_0}\exp\left(-\dfrac{1}{3k_BT}\sigma_{ii}^{GB,m/n}\Delta V\right)}$

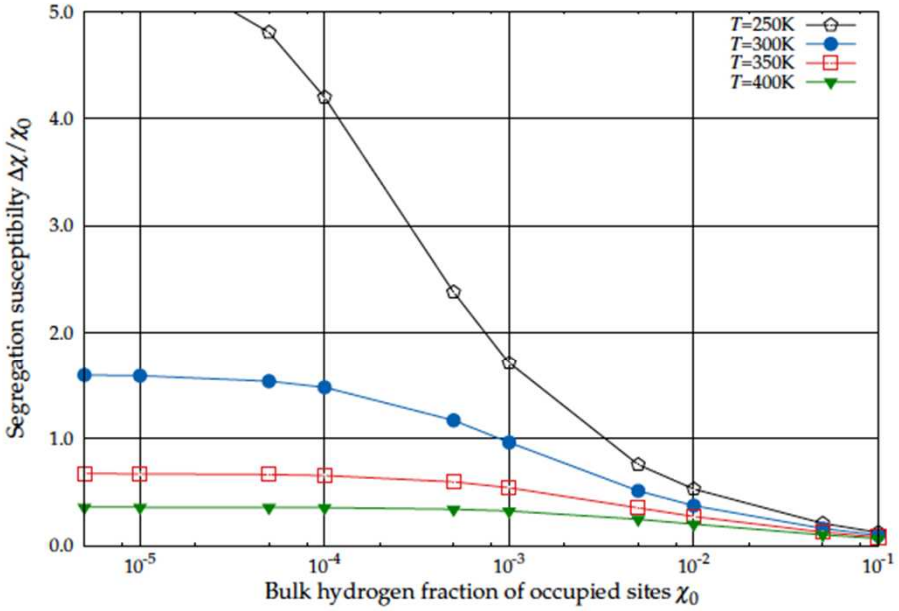
Hydrostatic stress field $\sigma_{ii}^{GB,m/n}$



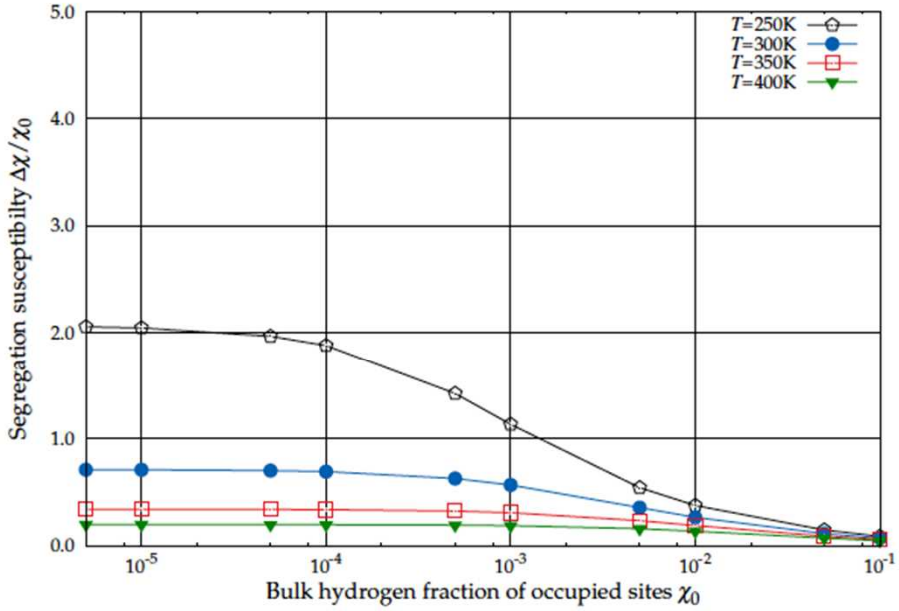
χ-field



On the effect of temperature and prescribed bulk hydrogen fraction



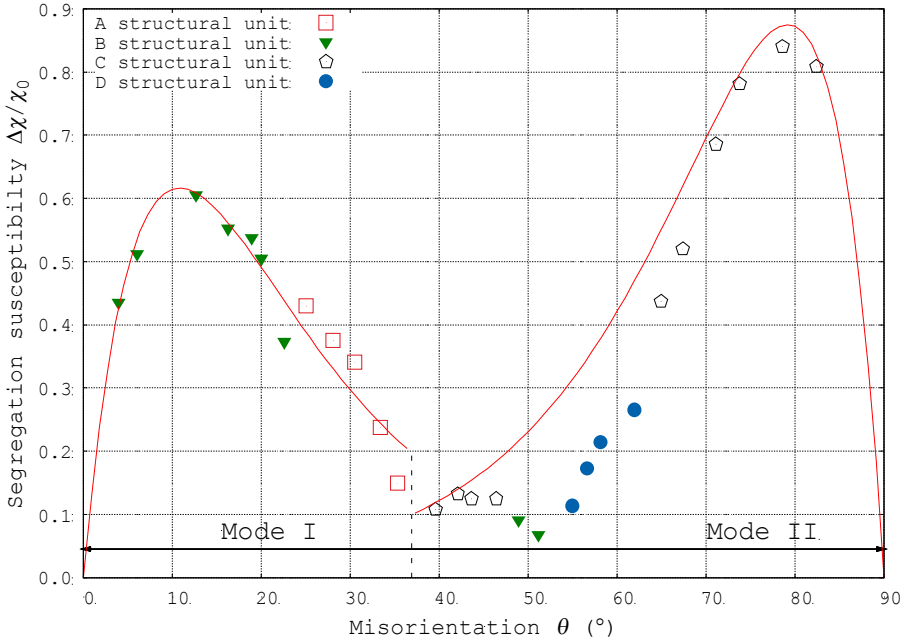
$\Sigma 17/28.07°$ (B structural unit).

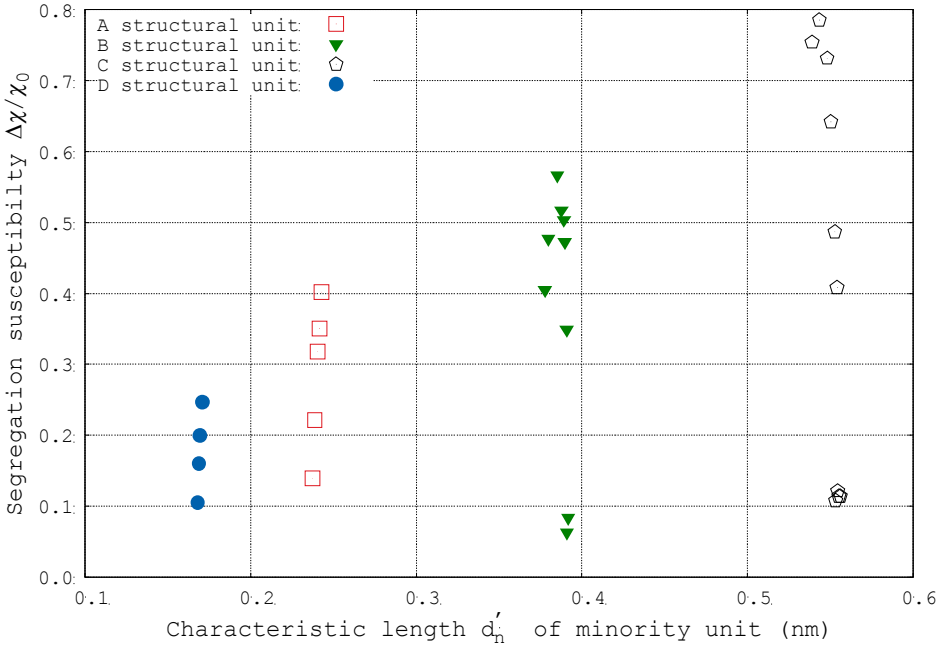


$\Sigma 17/61.93°$ (D structural unit).

- Non-linear dependence on the prescribed bulk hydrogen content.
- Arrhenius-type dependence on temperature.
- Segregation susceptibility less pronounced for GBs with misorientation θ in the range $36^\circ \leq \theta \leq 53^\circ$ (STGBs with only B and C structural units)

Segregation susceptibility variability is impacted by both the minority structural unit & miorientation





- Model consistent with other models using location-based model:
  - GB range extends beyond single GB
  - Core effects spread out
- Cusps corresponding to specific GBs for which structure changes from one minority SU to another
- Three branches corresponding to pairs of structural units (A/B, B/C, C/D)

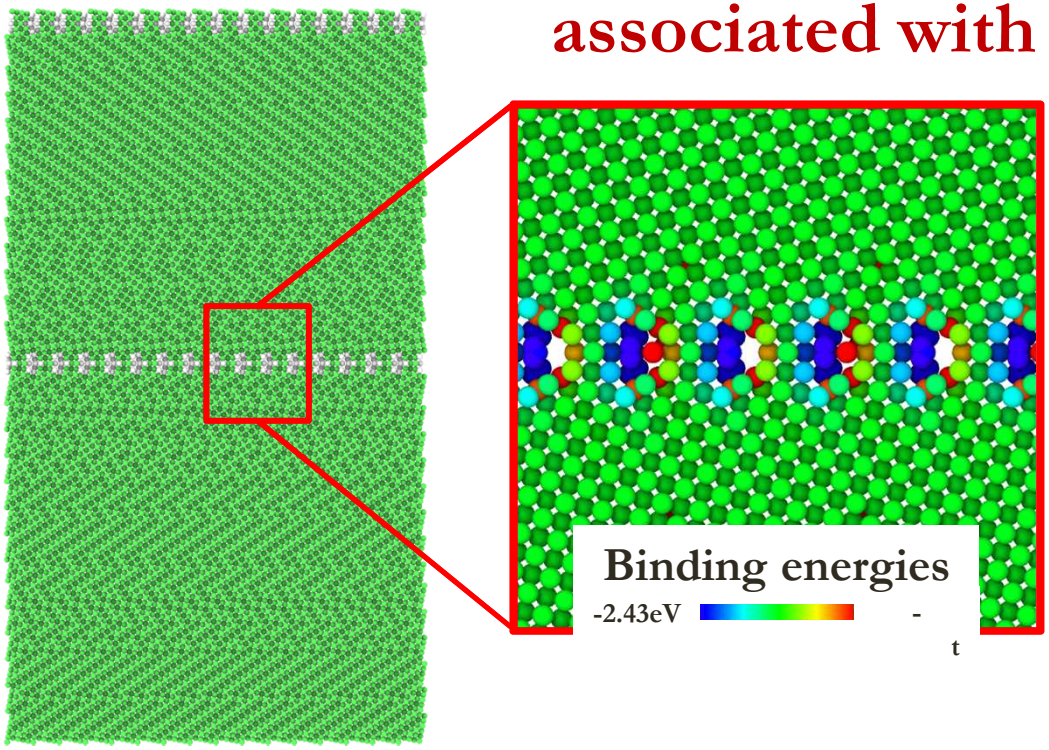
~~Model consistent with other models using location-based model:~~

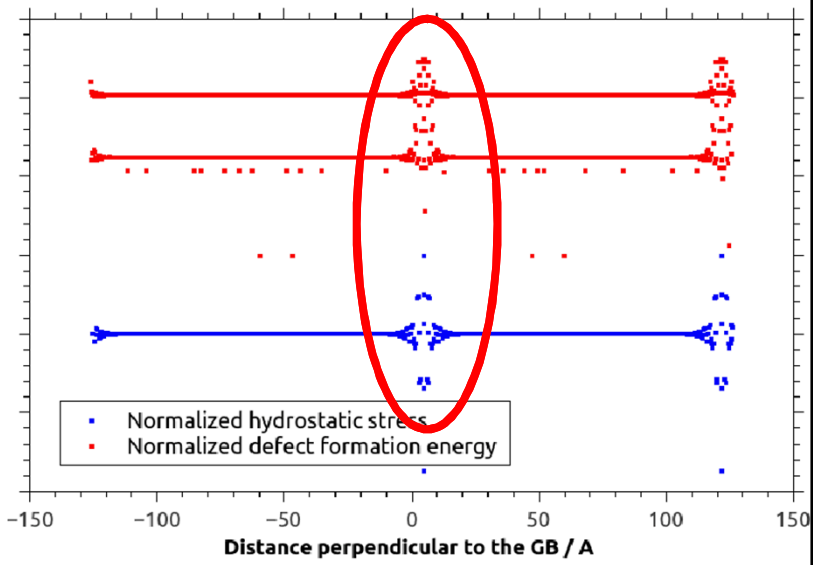
~~GB range extends beyond single GB~~

~~Core effects spread out~~

- Experimental tests that would provide definitive answers appear unfeasible given the limited capabilities of existing experimental techniques in measuring local stresses and compositions in atmospheres on a quantitative level
- Atomistic simulations offer a more viable option. Approximations rest on the reliability in the interatomic potential used

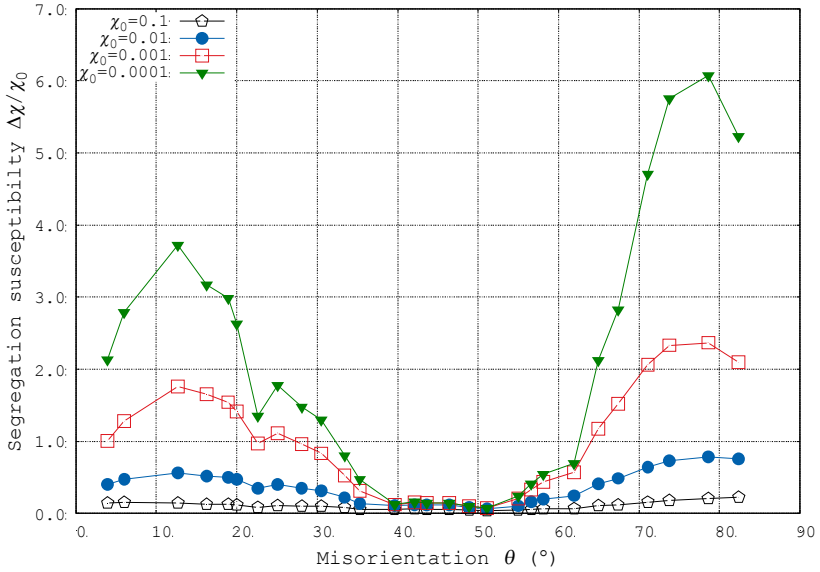
Defect energy formation and hydrostatic stresses associated with GB

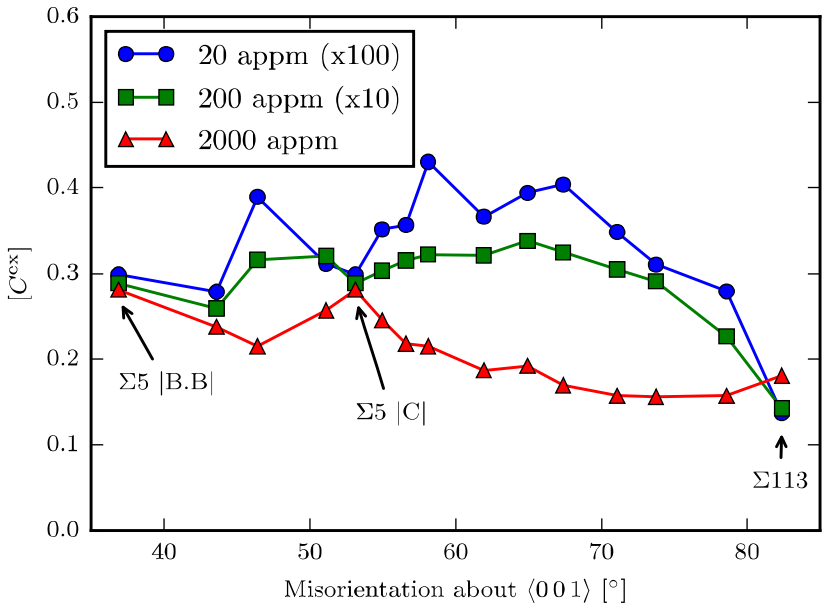




- Trapping sites in the vicinity of the GB have favorable binding energies compared to bulk values
  - Large peaks in distribution to octohedral and tetrahedral sites (bulk)
  - Favored trapping sites in the GB ”interphase”
  - Consistent with Cottrell atmosphere theory
- Defect formation energy and hydrostatic stress are correlated with the boundary structure

How does the continuum model quantitatively compare to the atomistic model?





- The general trends are in "agreement":
  - Susceptibility decreases as concentration increases
  - ``Special" grain boundaries are insensitive w.r.t. H environments: opportunity for GB engineering?
- However some differences persists between the two models:
  - The continuum model cannot assume H-induced microstructural interfacial rearrangement
  - Effect of anisotropy?
  - Dominant chemo-mechanical factor?

A closer look at the comparison: Σ29 (|2BC|) θ=43.6°

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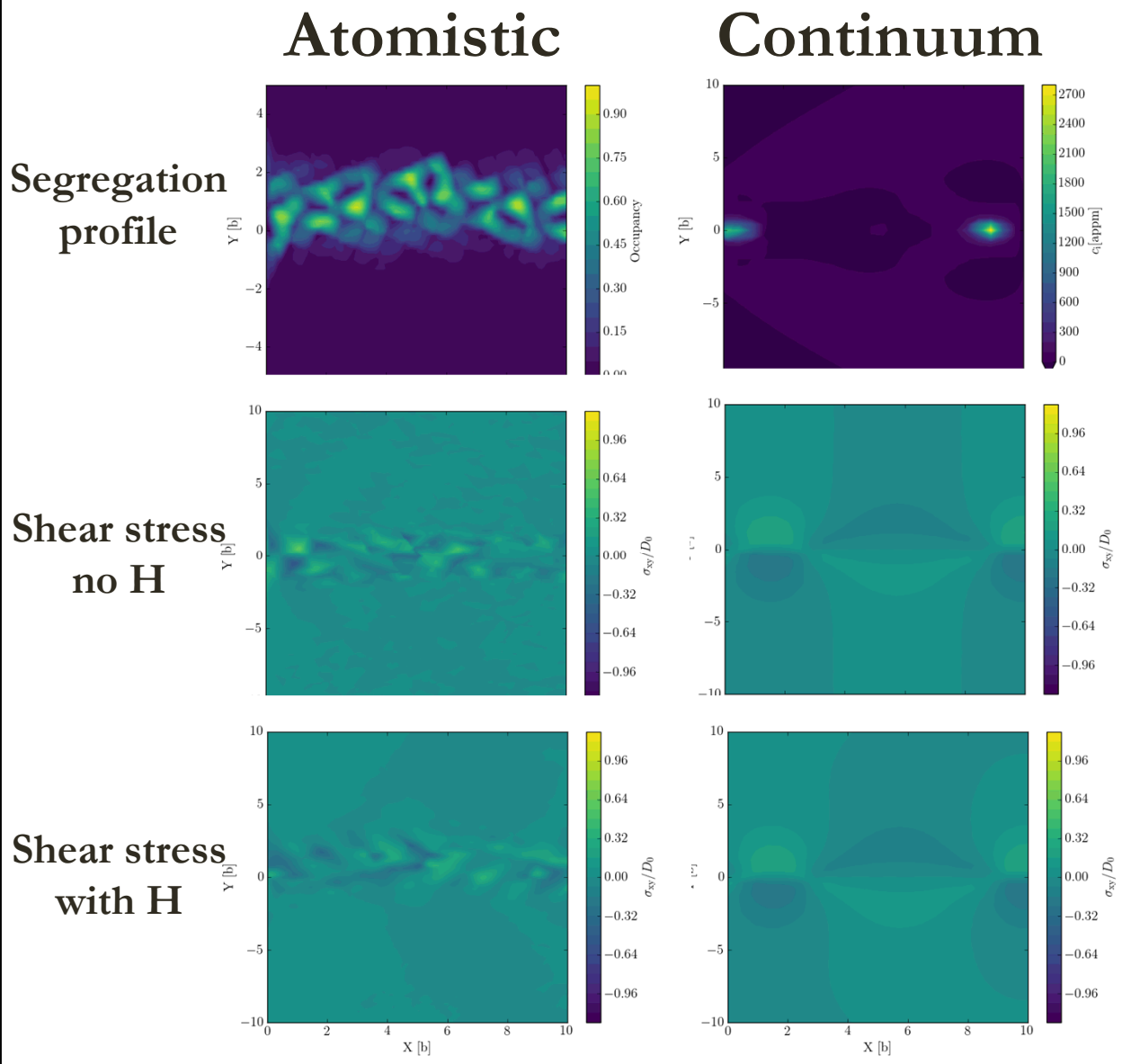
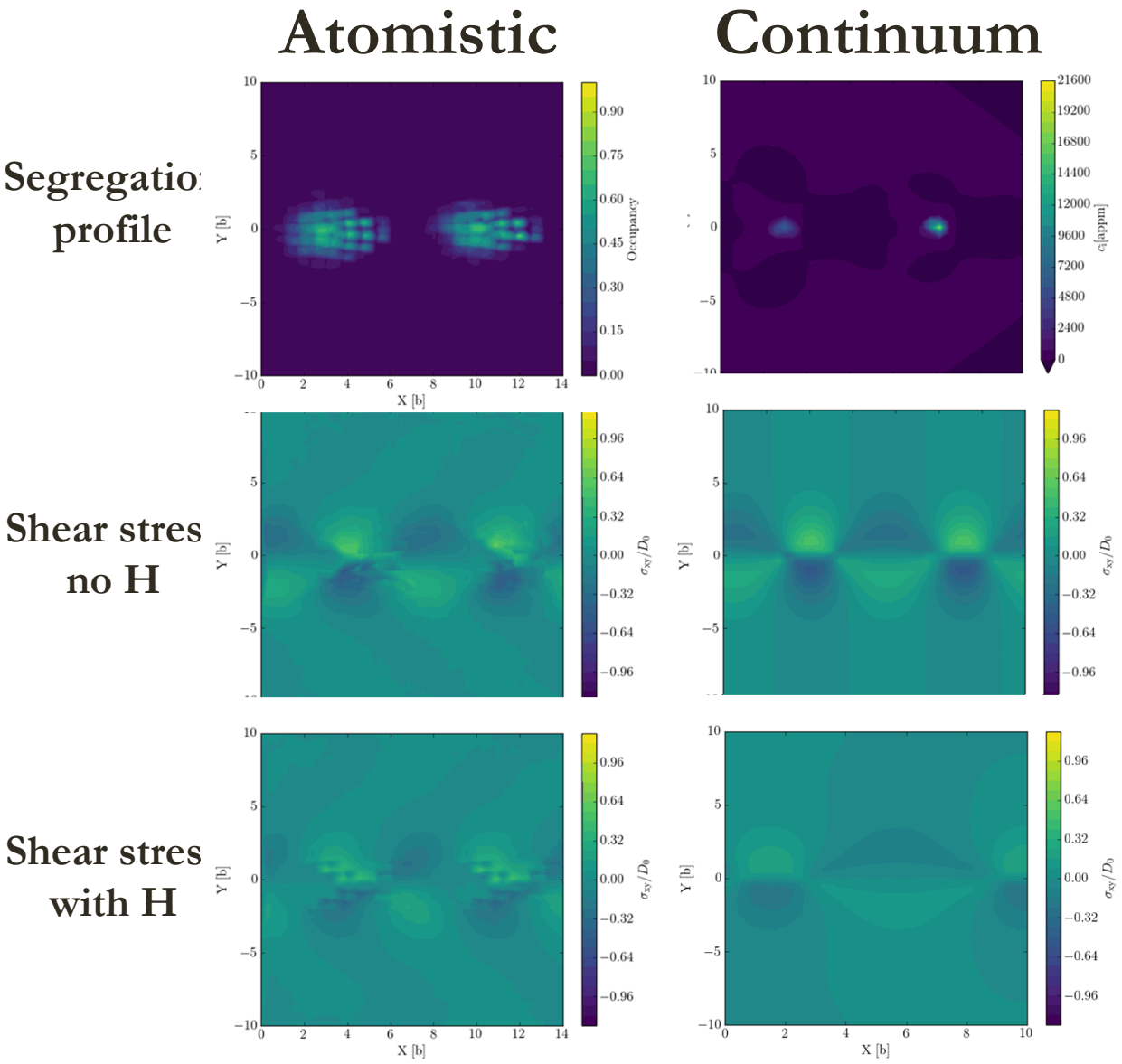


- Overlapping of B structural units separated by a single C structural unit
- **Upon H introduction:**
  - Both approaches predict relaxation of the elastic fields
  - Faceting transition from atomistic model

A closer look at the comparison: Σ101 (|C7D|) θ=78.58°



- C structural units separated by large perfect lattice portions
- **Upon H introduction:**
  - Segregation profiles similar
  - Relaxed elastic fields similar

Food for thoughts:

- **Determination of segregation to a structure of a reasonable general GB is fraught with uncertainty:**
  - **On the atomistic side:**
    - What's 0.1 eV between friends?
      - That level of error is 'good' for empirical potentials. Empirical potentials are often limiting
      - An error of 0.1 eV in a segregation energy can easily translate into an order of magnitude error!
  - **On the continuum side:**
    - GB construct is dependent on the identification of interfacial structure from atomistic
    - Cannot predict surface reconstruction (metastable states)

Conclusion

- **Comparison of Cottrell atmospheres as predicted by continuum theory (Eshelby) against atomistic simulations**
  - Linear defects mechanics (DSUM) offers a simple methodology to study solubility susceptibility
  - Both model provide insight on the correlation between the solubility susceptibility, the grain boundary structural characteristics and the associated misorientation

- **Differences still subsist:**
  - Getting the "right" GB structure upon the H introduction is challenging
    - Metastable of microstructure when interaction with H environments
  - Simultaneous and concurrent effects at interface?

- **Towards grain boundary engineering?:**
  - How 'right' do the calculations have to be in order to be able have faith in the qualitative results?