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Diffusion of solute atoms near grain boundaries of nanocrystals

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Outline

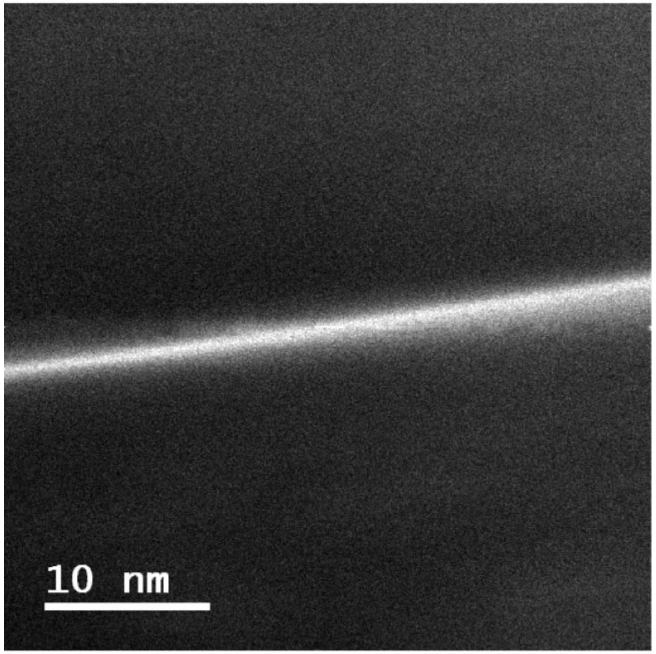
- Introduction
- Mobility along grain boundaries
- Elastic model for grain boundaries
- Approximation of the stress field around a grain boundary
- Diffusion in the stress field of a grain boundary

Introduction

Grain boundary related phenomena in ultra fine grained Al-Zn solid solution processed by high pressure torsion

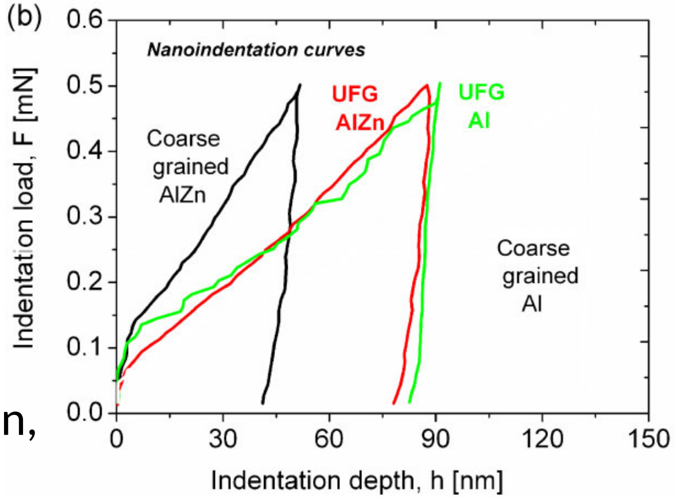
- grain boundary decoration
- Zn-rich layers along Al/Al grain boundaries
- softening in the ultra fine grained Al-Zn solid solution vs. to the same coarse grained solid solution
- enhanced grain boundary sliding at room temperature

(a)



N.Q. Chinh, R.Z. Valiev, X. Sauvage, G. Varga, K. Havancsák, M. Kawasaki, B.B. Straumal and T.G. Langdon, Adv. Eng. Mater. 2014

(b)



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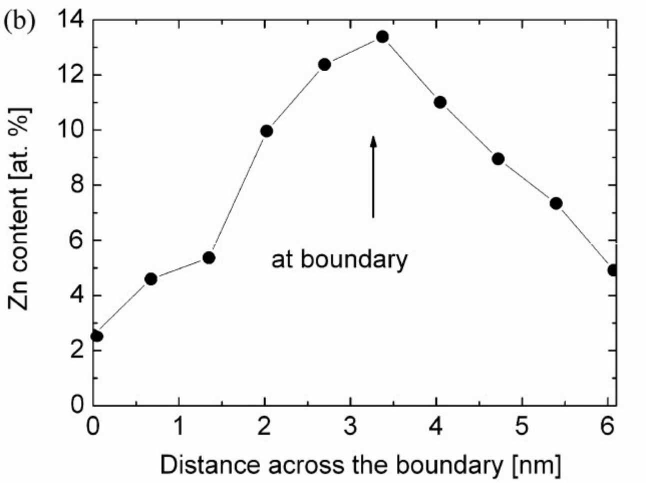
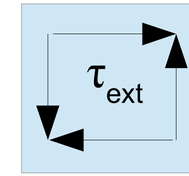


Introduction



localized grain boundary sliding

without movement of triple junctions

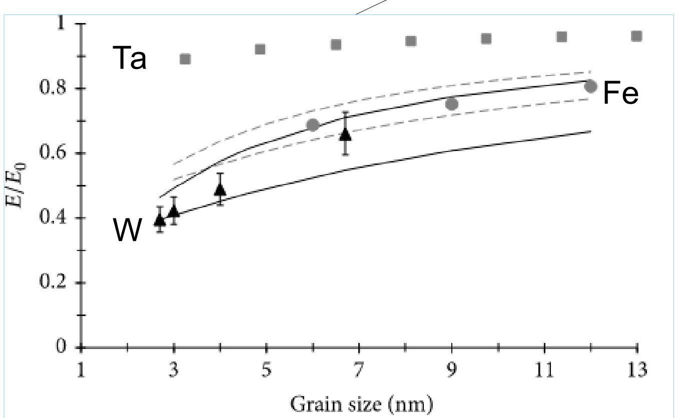
There is always some mobility in grain boundaries

slip within a single grain boundary

it relaxes partially the external stress

it is a reversible effect

it leads to a minor difference in the shear modulus of nanocrystalline materials



Elastic moduli depend on the grain size of nanocrystalline, impurity free metals

P. Valat-Villain, J. Durinck, P.O. Renault, J. Nanomaterials 2017

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Model

Elastic continuum model for localized grain boundary sliding

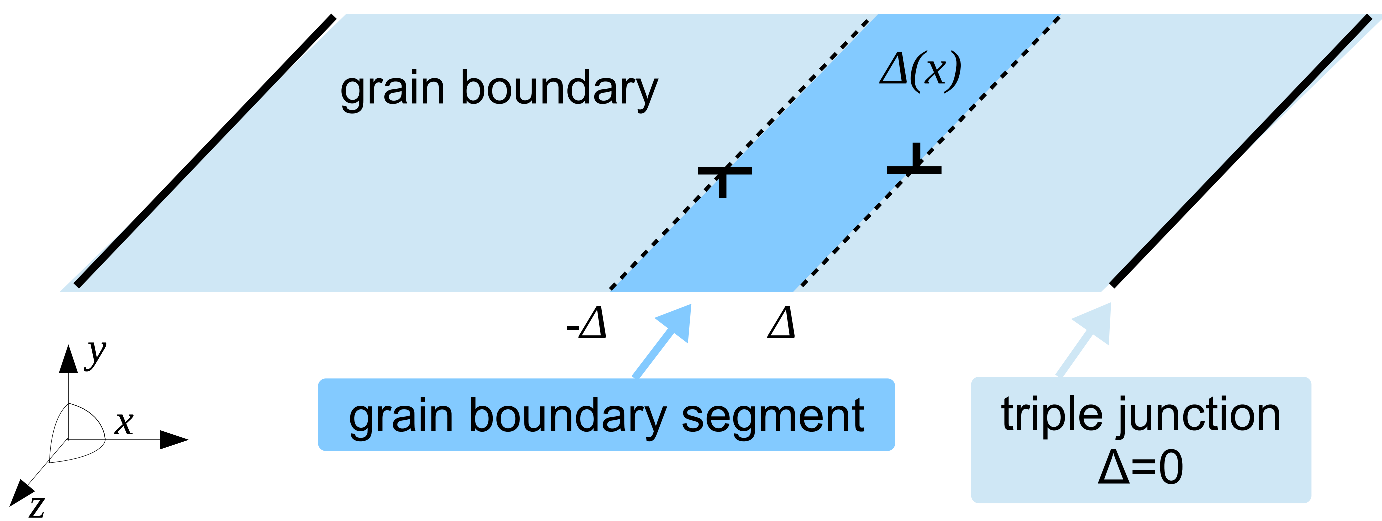
- each segment has a variable Δ(x) local offset
- the offset of the segment is modeled by a pair of edge dislocations
- stress field is the sum of the contributions of the dislocation pairs and the external stress (τ_{ext})
- offset varied to reduce the local shear stress to the strength of the grain boundary (τ_{GB})

stress field of a dislocation

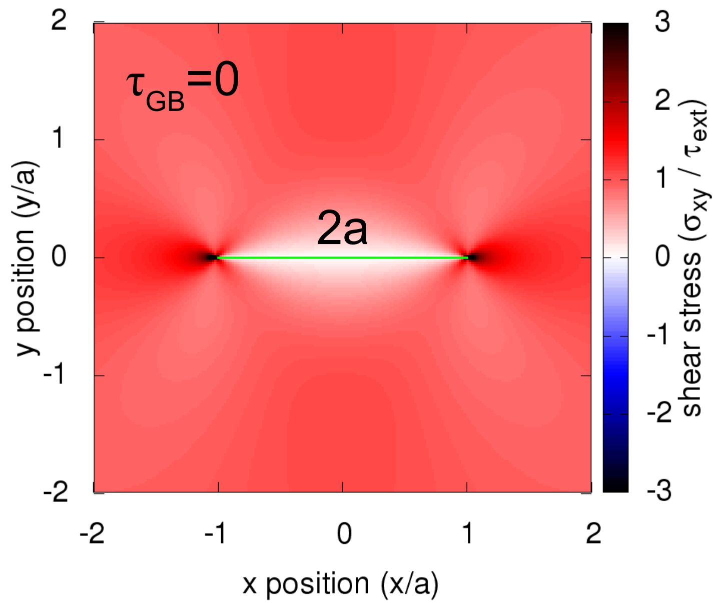
$$\sigma_{xy} = \alpha \frac{x(x^2 - y^2)}{(x^2 + y^2)^2}$$

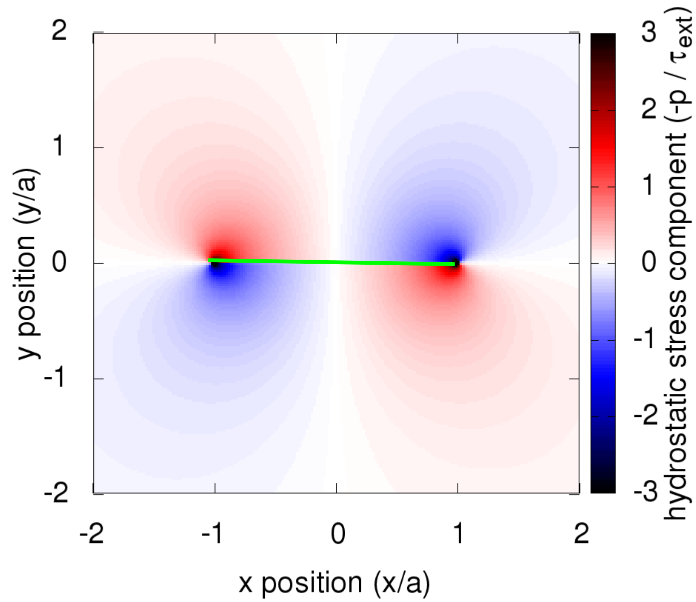
$$\alpha = \frac{G \cdot \Delta}{2\pi(1-\nu)}$$

input parameters: G, ν, a

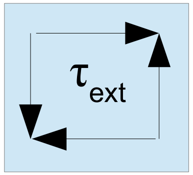


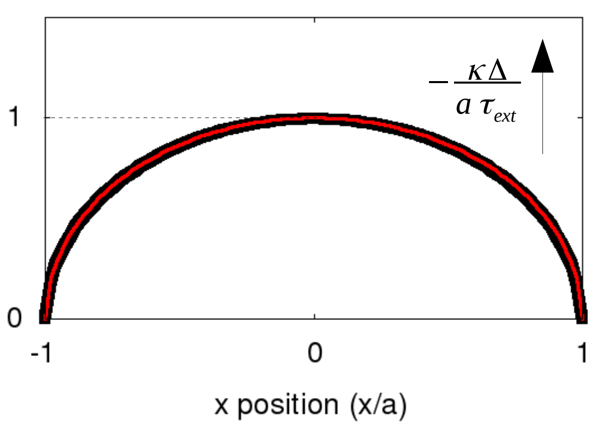
Stress field around a “single” grain boundary under stress

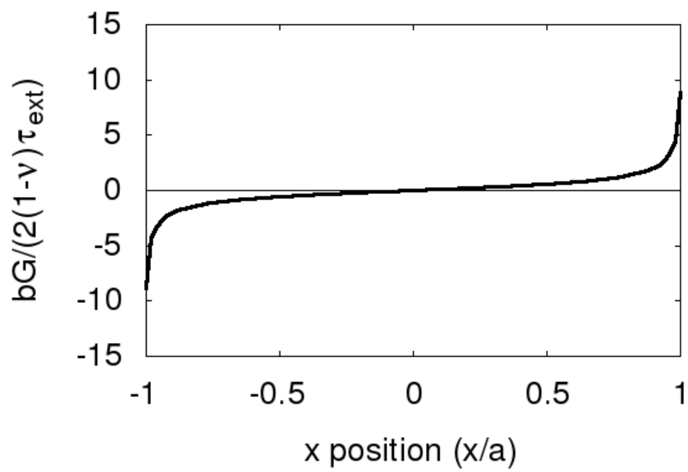




reversible deformation for τ_{GB}=0







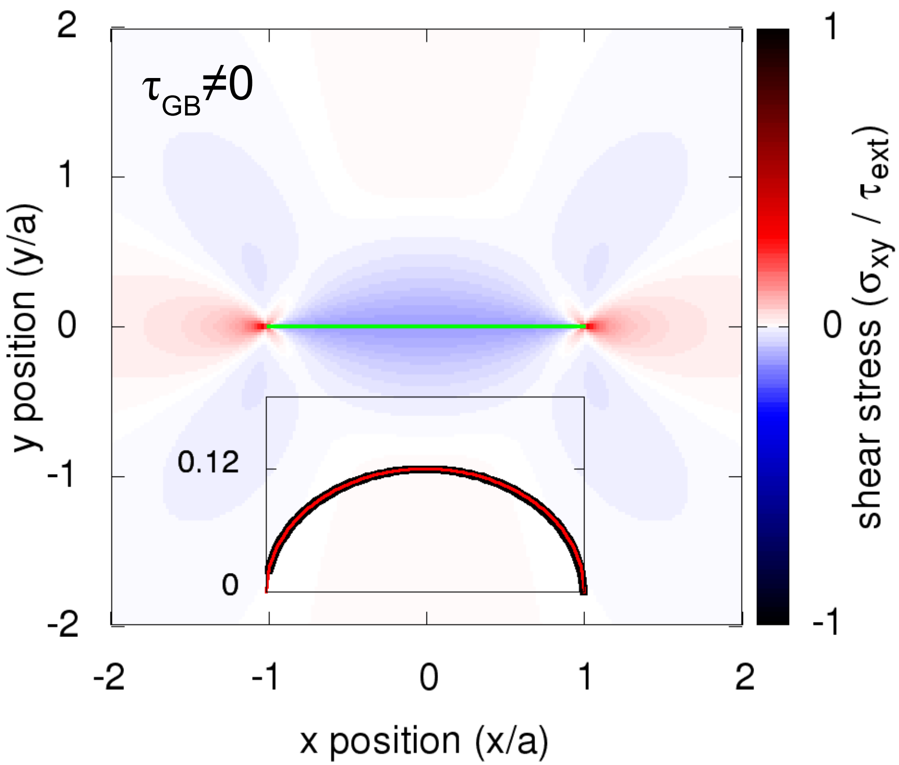
stress field at the triple junctions can be characterized by a stress intensity factor:

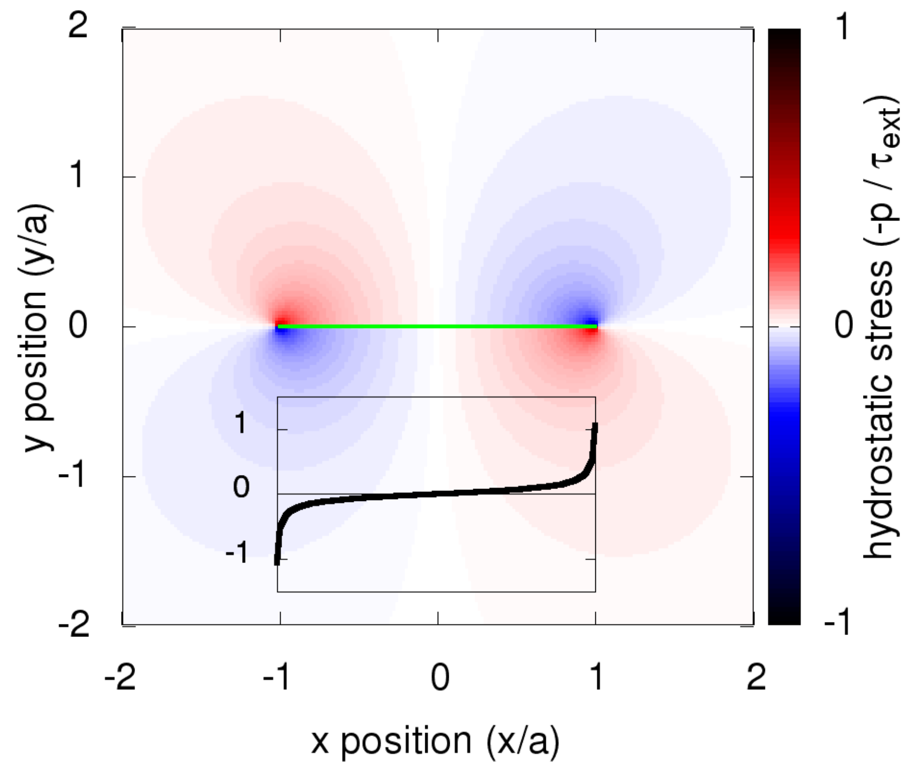
$$K_{II} = \tau_{ext}\sqrt{\pi a}$$

offset distribution:

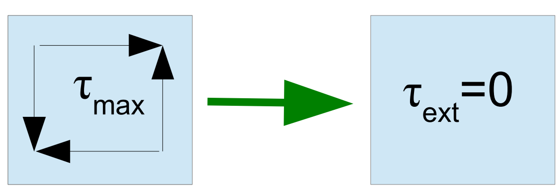
$$\Delta(x) = \frac{a\,\tau_{ext}}{\kappa}\sqrt{1-\left(\frac{x}{a}\right)^2}$$

Residual stress field around a "single" grain boundary





load-unload cycle



irreversible deformation for $\tau_{GB} \neq 0$

$$\Delta(x) = \frac{a(\tau_{max} - \tau_{GB})}{\kappa} \sqrt{1 - \left(\frac{x}{a}\right)^2}$$

$$\Delta_{max} = a(\tau_{max} - \tau_{GB}) / \kappa$$

$$K_{II} = \Delta_{max} \kappa \sqrt{\pi / a}$$

Diffusion in the residual stress field of a grain boundary

Hydrostatic stress component induces diffusion currents in solute atoms and defects with volumetric distortion

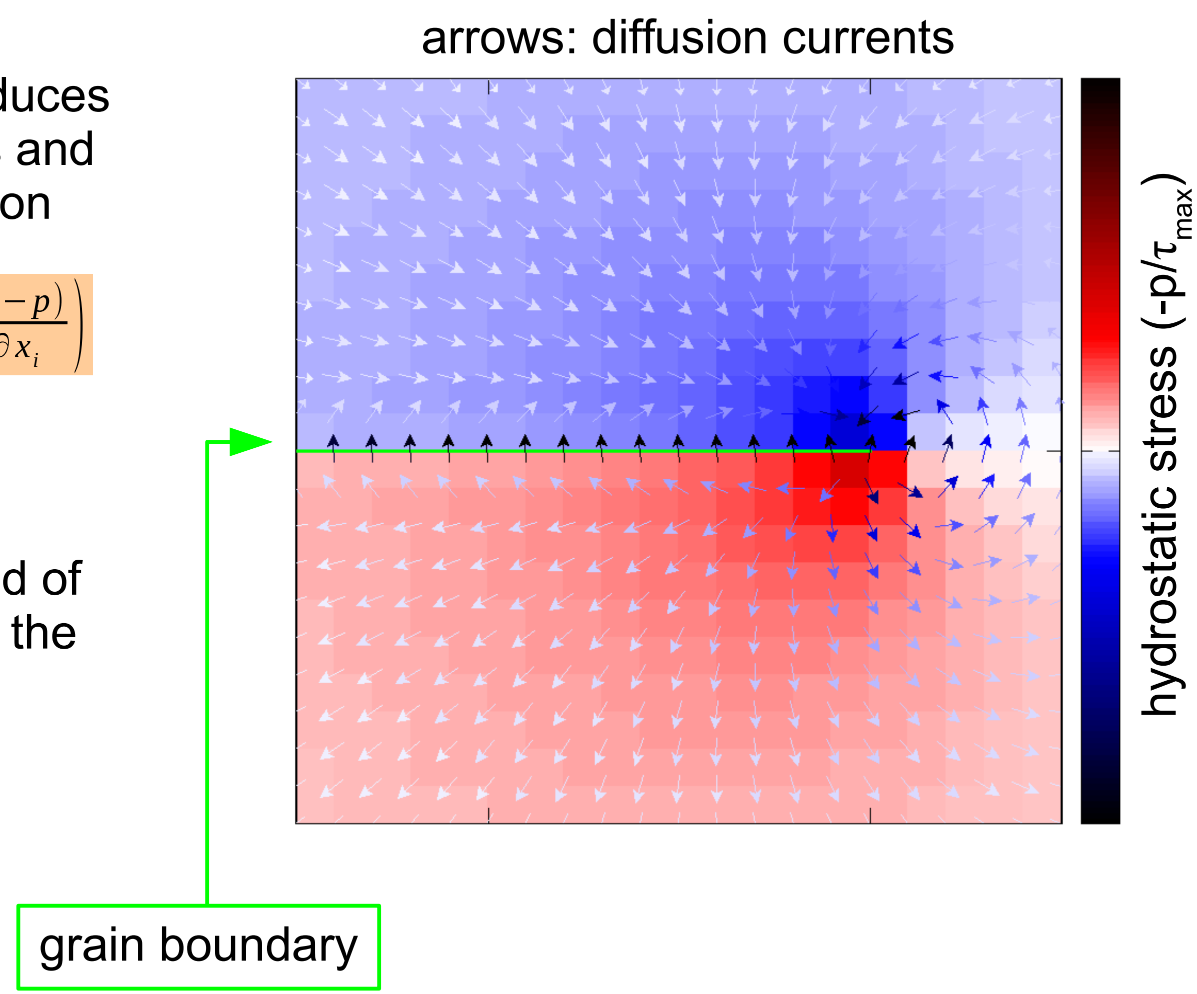
$$j \propto -D \frac{\partial(-p)}{\partial x_i}$$

$$\frac{\partial c}{\partial t} + \frac{\partial j}{\partial x_i} = 0$$

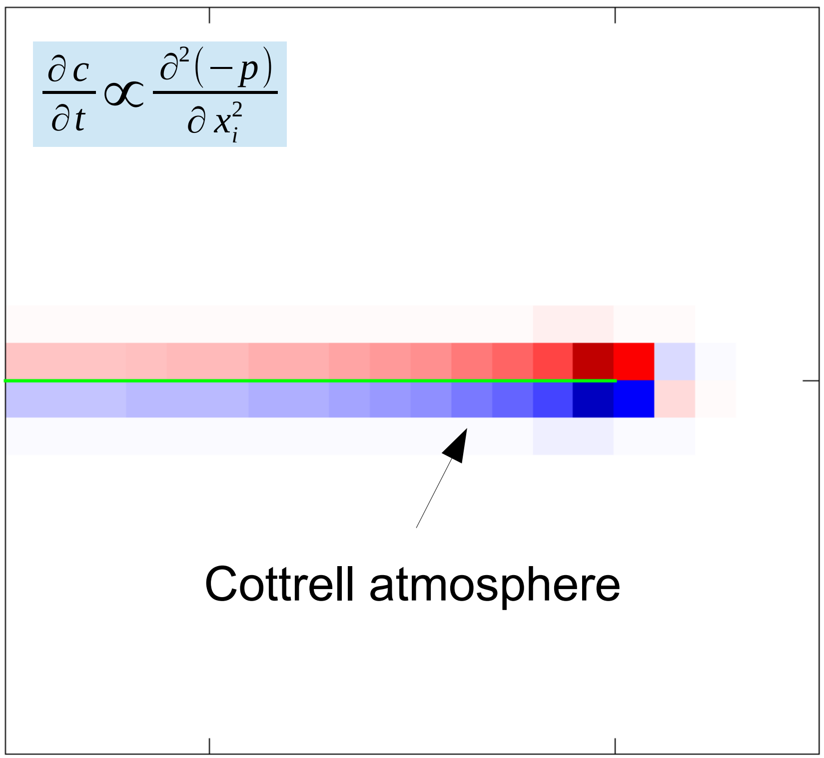
$$\frac{\partial c}{\partial t} \propto \frac{\partial}{\partial x_i}\left(D \frac{\partial(-p)}{\partial x_i}\right)$$

this diffusion effect on solute atoms in the stress field of an edge dislocation is known as the Cottrell atmosphere

A.H. Cottrell, B.A. Bilby, Proc. Phys. Soc. A 62 (1949) 49-62.

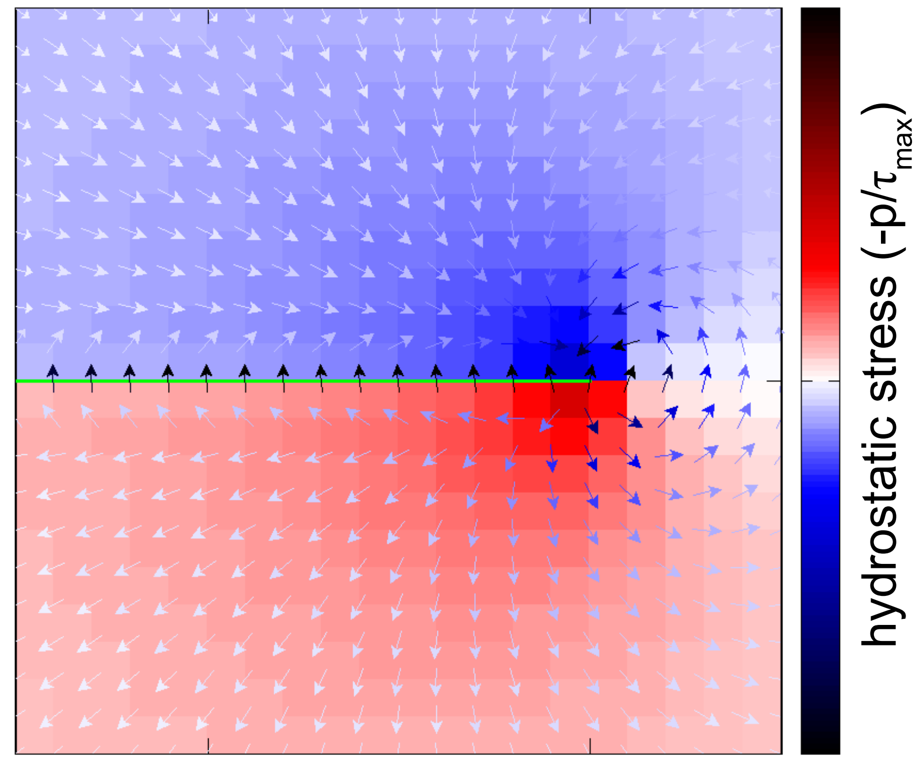


Diffusion in the residual stress field of a grain boundary



accumulation of diffusing objects
(solute atoms and vacancies)
at the divergence of the diffusion currents

arrows: diffusion currents



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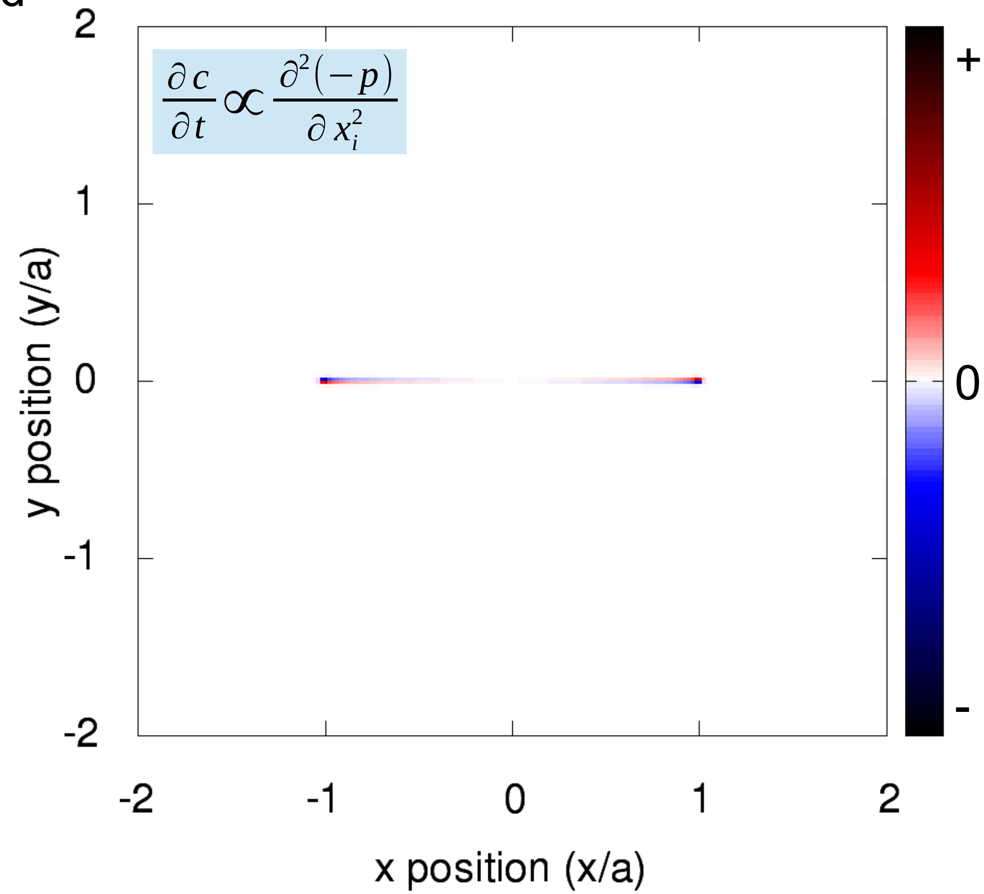
Diffusion in the residual stress field of a grain boundary

Hydrostatic stress component of the grain boundary induces diffusion in solute atoms and other point defects with volumetric distortion

(Stress field of the GB in the model is formed by finite number of edge dislocations)

- Formation of double layers along GBs
- Diffusion is selective regarding grain boundaries
- Parallel diffusion of solute atoms and vacancies
- Vacancy concentration may increase substantially in the grain boundary



Diffusion in the residual stress field of a grain boundary

Solute atoms have either positive or negative volumetric distortion

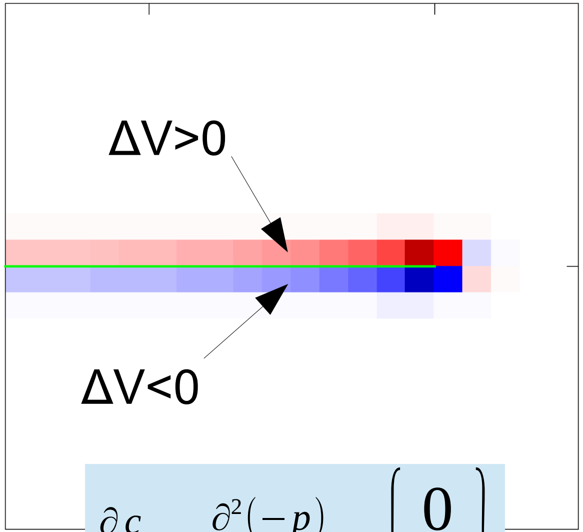
ΔV>0
ΔV<0

ΔV>0

- Solute atoms and vacancies diffuse into the opposite direction
- Solute accumulation may decelerated by the vacancy diffusion

ΔV<0

- Solute atoms and vacancies diffuse into the same direction
- Solute accumulation may accelerated by the vacancy diffusion
- Mobility of the grain boundary increases substantially due to the high vacancy concentration
- It is equivalent to a high temperature grain boundary, but only in case of local grain boundary slip
- Slip process self amplifies itself



$$\frac{\partial c}{\partial t} \propto \frac{\partial^2(-p)}{\partial x_i^2} = \left\{ \begin{matrix} 0 \\ \frac{\partial \delta}{\partial y} \end{matrix} \right\}$$

metallic atomic radii

Al: 143 pm
Zn: 134 pm

Summary

- Mobility in grain boundaries can lead to localized grain boundary sliding
- Localized grain boundary sliding relaxes the external shear stress partially in grain boundary and forms a stress field around the grain boundary.
- Elastic continuum model was constructed
  - to determine the shear offset distribution along the grain boundary
  - to calculate the surrounding stress field
- Hydrostatic component of this stress field induces diffusion currents of vacancies and solute atoms towards the grain boundary
- In Al-Zn solid solution, this process explains the accumulation of Zn atoms in the grain boundaries
- Increased vacancy concentration (compared to the thermal equilibrium) is anticipated in the Zn rich grain boundaries, which explains enhanced grain boundary sliding at room temperature in ultra fine grained Al-Zn

Acknowledgements

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Thank you for your attention!

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