Energy barriers for carbon diffusion in ferrite under heterogeneous stress

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Context & objectives

➤ The diffusion of carbon in iron controls the kinetics of many transformations in steels (such as, cementite precipitation, martensite ageing, massive austenite↔ferrite transformation and bainite formation).

➤ Diffusion of carbon in **defect-free ferrite** (the body-centred cubic structure of iron): a fairly well known mechanism, extensively studied and characterized.

➤ When **other defects** are present: **both the diffusion mechanism and its kinetics** are affected. Case of **dislocations**: they **create very large and non-uniform stresses**, inducing important effects on the energy barrier of impurities.

➤ Diffusion and segregation of interstitial carbon to dislocations introduced by plastic deformation in ferritic iron: leads to the growth of so-called **Cottrell atmospheres** around the dislocations (**responsible for static strain aging in ferritic steels**).

➤Atomistic simulations provide a good alternative for studying the diffusion processes in the presence of stress:

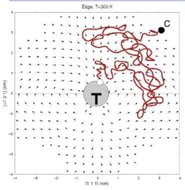
- Molecular dynamics (MD): could serve as a perfect framework if not so limited in simulation time span (typically, a few ns).

- Atomistic Kinetic Monte-Carlo (aKMC) method: very well adapted for studying the diffusion of atomic species, based on knowledge of the different escape pathways and the corresponding escape rates.

➤The impact of the stress field induced by the presence of a defect on the energy barriers cannot be neglected, and need to be quantitatively accounted for.

➤ In this work, the effect of an heterogeneous stress field on diffusion energy barriers is adressed: a novel method, called LinCoSS (Linear Combination of Stress States), which is very fast and easy to implement alternative to existing approaches [1].

KMC trajectory for C diffusion to an edge dislocation in bcc Fe



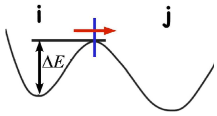
Simulation methods

Atomistic Kinetic Monte-Carlo method:

➤ Residence time algorithm:

time spent in a state *i* before transition to an adjacent state *j*:

$$\tau = -\frac{\ln(r)}{\sum_j R_{i\to j}}$$



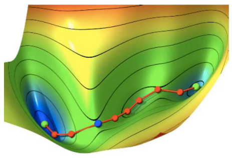
➤ transition rates: $R_{i\to j} = \omega_0 \exp\left(-\frac{\Delta E_{i\to j}}{kT}\right)$ ← *diffusion energy barrier*

➤ Each aKMC time step is associated with a jump (transition i → j)

➤ Accessible time span : minutes, hours ...

➤ Appropriate method for studying diffusion phenomena in the solids

Climbing-Image Nudged Elastic Band (CI-NEB) method:



$$\Delta E_{i\to j} = E^{saddle} - E_i^{min}$$

state-of-the-art method for locating ***saddle points*** on PES knowing the initial and final state configurations; measuring the corresponding energy

Results

Crystallographic structure

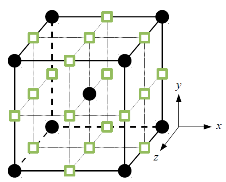
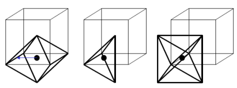


Illustration of the different octahedral site positions (open green squares) in the bcc unit cell. The iron atoms are represented by filled black circles.

Mechanism for C diffusion in stress free bcc Fe:



octahedral ↔ tetrahedral ↔ octahedral
(stable) (saddle) (stable)

Experimental diffusion energy value:

-Resistivity measurements, positron-life time measurements, Snoek relaxation

$$\Delta E = 0.81 - 0.83\ eV$$

Calculated diffusion energy barrier

➤ The CI-NEB method (implemented in LAMMPS [1] software): used as a reference for comparing other methods

- with EAM type Fe-C potential [2], the diffusion barrier for carbon migration in a **stress free ferrite** matrix is:

$$\Delta E(0) = E^{saddle} - E_i^{min} = 0.815\ eV$$

Methods for calculating diffusion energy barriers under stress

➤ Anisotropic elasticity theory:

- total energy of a periodic simulation box with volume V, containing a point defect with elastic dipole P_{ij}, and submitted to a homogeneous strain ε_{ij} is:

$$E^{O,T}(\varepsilon_{ij}) = E^{O,T}(0) - P_{ij}^{O,T}\varepsilon_{ij} + \frac{1}{2}VC_{ijkl}\varepsilon_{ij}\varepsilon_{kl}$$

$$\Delta E(\varepsilon_{ij}) = \Delta E(0) - (P_{ij}^T - P_{ij}^O)\varepsilon_{ij}$$

(P_{ij} is deduced from atomistic simulations)

➤ Linear Combination of Stress States (LinCoSS):

- it is based on the decomposition of a complex stress state into a linear combination of uniaxial and pure shear stress states :

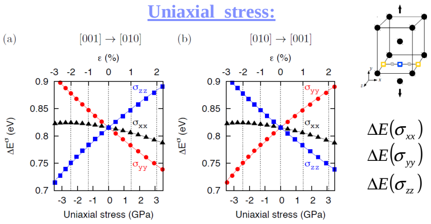
$$\begin{bmatrix}\sigma_{xx} & \sigma_{xy} & \sigma_{xz}\\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz}\\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz}\end{bmatrix} = \begin{bmatrix}\sigma_{xx} & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{bmatrix} + \begin{bmatrix}0 & 0 & 0\\ 0 & \sigma_{yy} & 0\\ 0 & 0 & 0\end{bmatrix} + \begin{bmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & \sigma_{zz}\end{bmatrix} + \begin{bmatrix}0 & \sigma_{xy} & 0\\ \sigma_{yx} & 0 & 0\\ 0 & 0 & 0\end{bmatrix} + \begin{bmatrix}0 & 0 & \sigma_{xz}\\ 0 & 0 & 0\\ \sigma_{zx} & 0 & 0\end{bmatrix} + \begin{bmatrix}0 & 0 & 0\\ 0 & 0 & \sigma_{yz}\\ 0 & \sigma_{zy} & 0\end{bmatrix}$$

⇒ one may assume that the effect of an arbitrary stress field on the energy barriers could be simply evaluated by a linear combination of the effects induced by each stress field component:

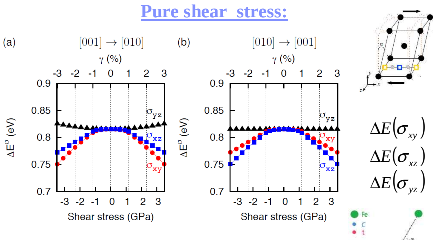
$$\Delta E(\sigma) = \Delta E(\sigma_{xx}) + \Delta E(\sigma_{yy}) + \Delta E(\sigma_{zz}) + \Delta E(\sigma_{xy}) + \Delta E(\sigma_{xz}) + \Delta E(\sigma_{yz}) - 5\Delta E(0)$$

Simple homogeneous stress

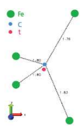
Uniaxial stress:



Pure shear stress:



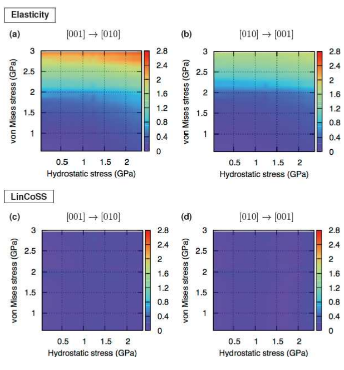
Linear elasticity theory: no variation of the energy barrier with shear stress (error at $\gamma_{xy} \cong 1.5\ \%$ is > 15 meV.



modified saddle point

Complex homogeneous stress

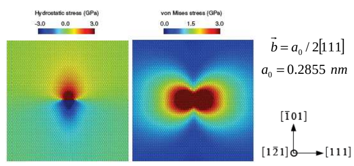
Evolution of diffusion energies under the effect of an arbitrary homogeneous stress field:



Relative errors that one should expect by replacing CI-NEB by linear elasticity theory or by LinCoSS as a function of hydrostatic and von Mises stresses.

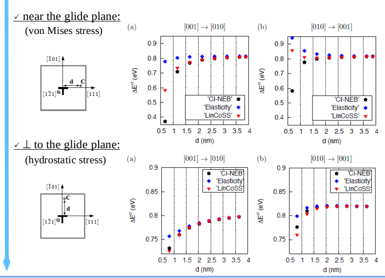
Establishing the validity of LinCoSS model: 2783 combinations of the stress field components were tested.

Heterogeneous stress: edge dislocation in bcc Fe



Atomistic stress distribution of a simulation box (14×14 nm[2]) containing an edge dislocation in its centre.

Carbon atom diffusing towards the core of an edge dislocation:



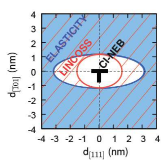
Conclusion

The presence of an imposed stress field modifies the barriers for carbon diffusion in iron because it influences the energy and the atomic configurations of both the stable position (octahedral site) and the saddle point position. We propose a novel method for determining the barriers for carbon diffusion under **heterogeneous stress field**, called **LinCoSS**:

- LinCoSS is very accurate up to relatively high stresses; more accurate than elasticity theory since it provides a better description of the effect of pure shear stress on the energy barriers.

- Coupled to a **KMC algorithm**, it could serve as a good framework for **modelling carbon diffusion in bcc iron in the presence of any kind of defect (dislocation, vacancy, grain boundary, precipitates, *etc.*)**, provided that the stress field induced by the defect does not overpass 3-4 GPa.

- LinCoSS could also be **generalized to the case of vacancy diffusion or to the diffusion of other substitutional atoms**.



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[3] C. S. Becquart, J. M. Raulot, G. Bencteux, C. Domain, M. Perez, S. Garruchet, and H. Nguyen, *Comput. Mater. Sci.*, **40**:119, 2007.