Carbon diffusion in supersaturated ferrite

Insights from atomistic simulations

[Bridging-Time Scale Techniques and their Applications in Atomistic Computational Science]

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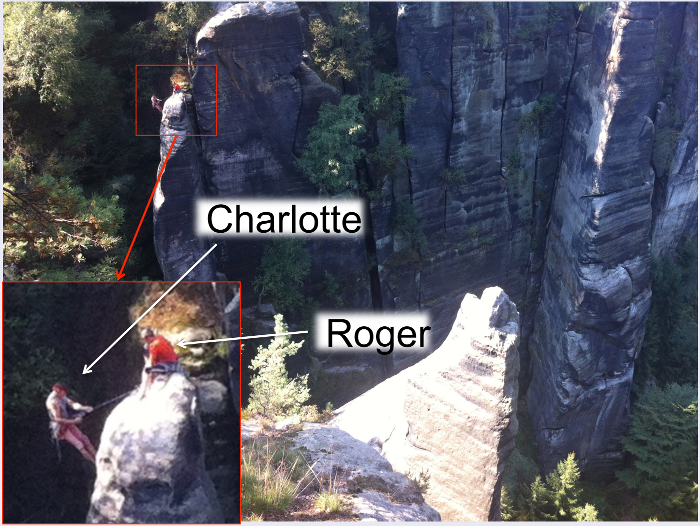
Many thanks to the organisers!

Simulation: a thrilling experience!



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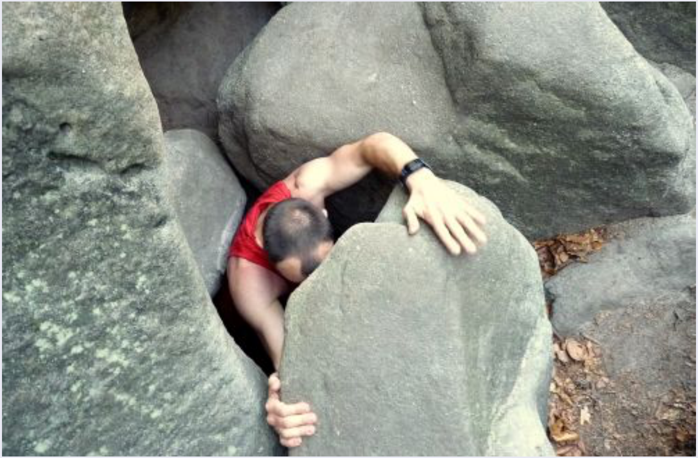
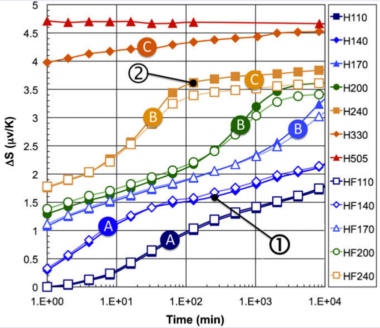
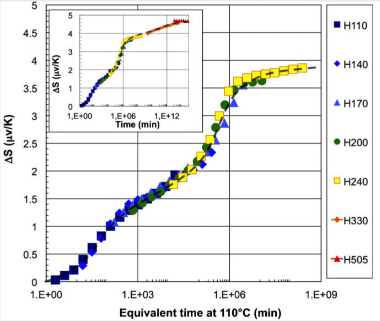


Why does C diffuse so slowly in martensite ?

Experiment: ageing of martensite

- Ageing monitored by thermoelectric power (*i.e.* resistivity)





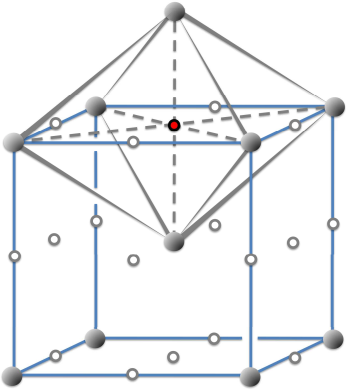
- Time-temperature equivalency: $t = t_0 \exp\left[\frac{Q}{k_B T}\right]$
- $Q = 120$ kJ/mol =1.25 eV (0.85 eV for C in iron)

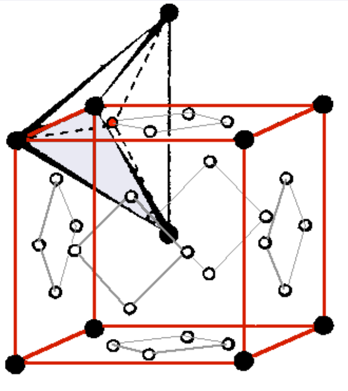
Why is the activation energy higher in martensite?

Why does C diffuse so slowly in martensite ?

Carbon diffusion: how?

- From octahedral to octahedral site
- Through tetrahedral site

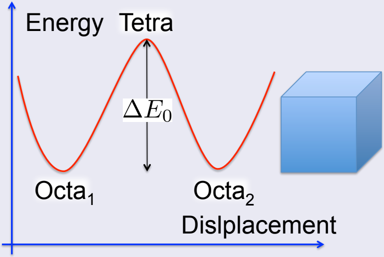




Why does C diffuse so slowly in martensite ?

The solution?

- [C. Zener, *Elast. Anelast. Metals.* **Univ. Chigago Press** (1948)]



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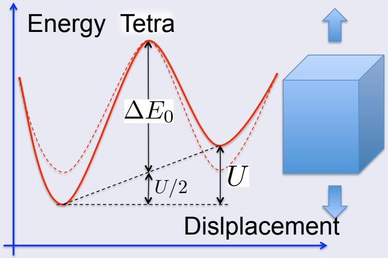


- [M. Hillerts, *Acta Metall.* **7** (1959)]

approximately $\frac{1}{2}U$. As a consequence, the jump frequency will decrease by a factor exp $(-NU/2RT)$, where $NU/2R = 1700c$ deg. Since long range diffusion is dominated by the highest energy barrier, the diffusion coefficient in martensite can be estimated as $D^{\text{martensite}} = D^{\text{ferrite}} \cdot \exp(-NU/2RT)$.

Outline...

Methods

Iron-carbon EAM potential

- [Becquart *el al*, *Comp. Mat. Sc.* **40** (2007)]
- based on Mendelev Fe potential
- fitted from C-Va and C-C interaction energies from DFT
- reproduce tetragonality of Fe-C martensite

Simulation box for MD

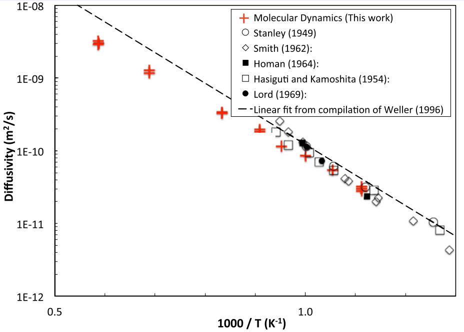
- 2000 Fe atoms and 1, 174 or 250 C atoms (small system)!
- Metropolis Monte-Carlo to relax the box
  - C is forced to remain ordered !
- MD simulation within the NVE ensembles at zero pressure
- 50 ns MD runs

C diffusion in pure Fe

MD results

- Diffusivity from Mean Square Displacements

$$\left\langle \left[\vec{r}_i(t_n) - \vec{r}_i(0)\right]^2 \right\rangle_{t,i} = \frac{\sum_i \sum_{j=1}^{n_{\max}-n} \left[\vec{r}_i((n+j)\,\delta t) - \vec{r}_i(j\,\delta t)\right]^2}{n_C(n_{\max}-n)} \qquad D = \frac{\left\langle \left[\vec{r}_i(t_n) - \vec{r}_i(0)\right]^2 \right\rangle_{t,i}}{6t_n}$$



- Agreement with experiments (high temperature ?).

C diffusion in pure Fe

Accounting for thermal expansion

- MD at various temperature under zero pressure

C diffusion in pure Fe

Accounting for thermal expansion

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$$\epsilon_{therm} = e_1 T + e_2 T^2$$

- Diffusivity equation

C diffusion in pure Fe

Accounting for thermal expansion

- MD at various temperature under zero pressure

$$\epsilon_{therm} = e_1 T + e_2 T^2$$

- Diffusivity equation

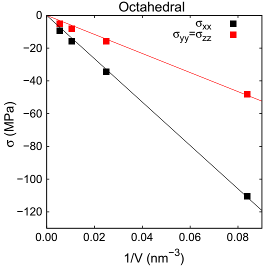
$$\frac{d \ln D}{d(1/T)} = -\frac{\Delta E(T)}{R}$$

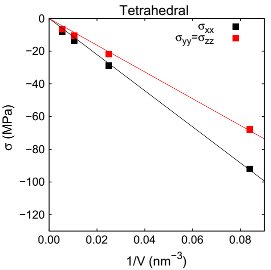
How to dertermine $\Delta E(T)$?

C diffusion in pure Fe

A bit of elasticity theory: (1) dipole moment tensor

- One C atom in a stress free box → dilatation
- One C atom in a fixed volume box → stress field





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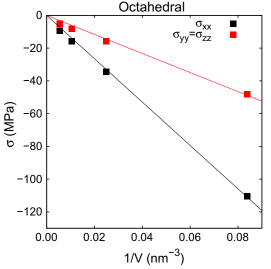

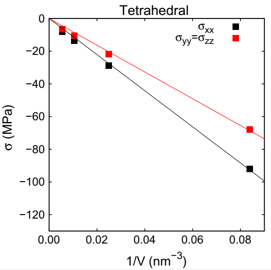

$$\boxed{\sigma^o_{ij} = \frac{1}{V} P^o_{ij}} \qquad P^{o,t}_{ij} = \begin{bmatrix} P^{o,t}_{\otimes} & 0 & 0 \\ 0 & P^{o,t}_{\bullet} & 0 \\ 0 & 0 & P^{o,t}_{\bullet} \end{bmatrix} \qquad \boxed{\sigma^t_{ij} = \frac{1}{V} P^t_{ij}}$$

C diffusion in pure Fe

A bit of elasticity theory: (2) interaction energy

- Interaction energy between a C atom and a far field strain:

C diffusion in pure Fe

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$$E_{inter} = P_{ij}\epsilon_{ij}$$

Back to thermal expansion

- Energy barrier variation with temperature:

C diffusion in pure Fe

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- Energy barrier variation with temperature:

$$\begin{aligned}\Delta E(T) &= \Delta E_0 + \left(P^t_{ij} - P^o_{ij}\right)\mathbb{I}_{ij}\epsilon_{therm} \\ &= \Delta E_0 + \Delta P^{iso}\epsilon_{therm}\end{aligned}$$

- Diffusivity:

C diffusion in pure Fe

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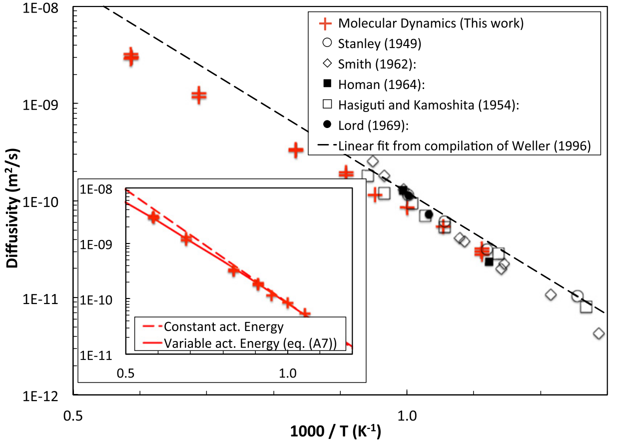
- Diffusivity:

$$\ln D = -\int \frac{\Delta E(T)}{R} d(1/T)$$

C diffusion in pure Fe

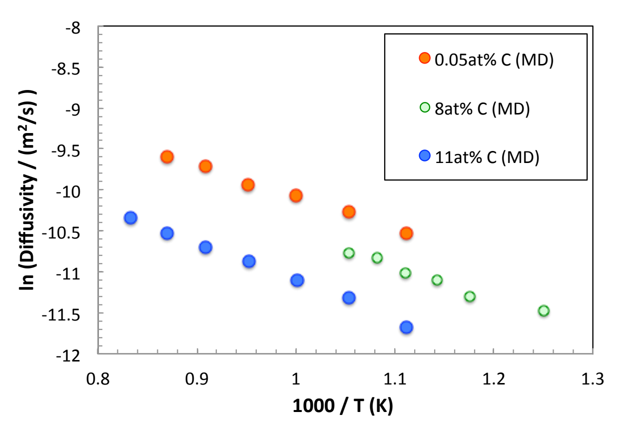
MD results



- Not following experiments...
- ... but we understand MD non linearity!

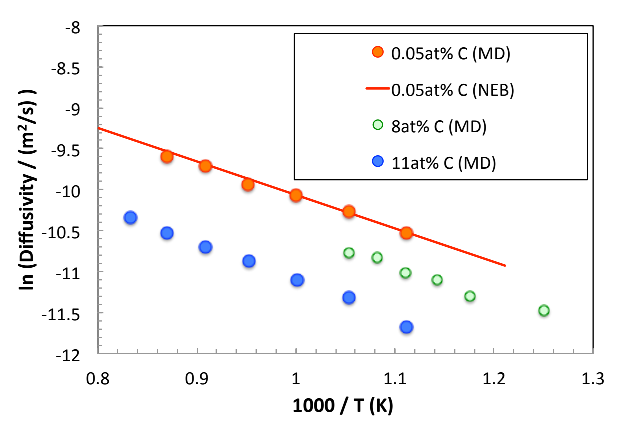
C diffusion in supersaturated Fe

MD results



- If D_0 is constant, why does activation energy varies ?

MD results



- Nice fit, but only for low carbon concentration !

C Diffusion in supersaturated Fe

Introduction
Methodology
Diffusion in pure Fe
Diffusion in supersat. Fe
Conclusions

Another bit of elasticity theory: (3) Effect of C concentration

- Interaction energy:

$$E_{inter} = P_{ij}\epsilon_{ij} \text{ with } P^o_{ij} = \begin{bmatrix} P^o_{\otimes} & 0 & 0 \\ 0 & P^o_{\bullet} & 0 \\ 0 & 0 & P^o_{\bullet} \end{bmatrix}$$

- Ordered C induced elastic distortion :

Another bit of elasticity theory: (3) Effect of C concentration

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- Ordered C induced elastic distortion :

$$\epsilon^{n_C}_{ij} = \frac{n_C}{V} S_{ijkl} P_{kl}$$

- Hillert's idea:

Another bit of elasticity theory: (3) Effect of C concentration

- Interaction energy:

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- Ordered C induced elastic distortion :

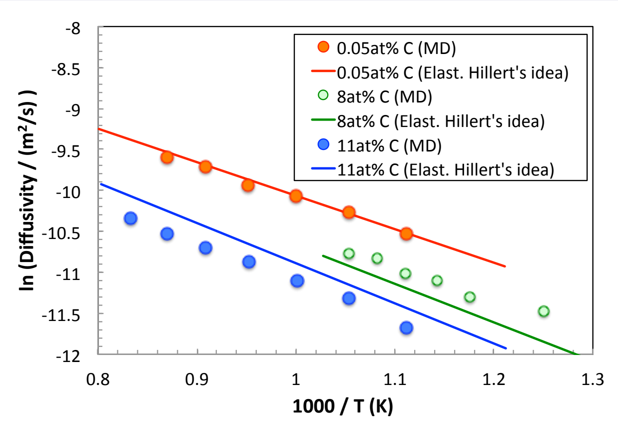
$$\epsilon^{n_C}_{ij} = \frac{n_C}{V} S_{ijkl} P_{kl}$$

- Hillert's idea:

$$\begin{aligned} \Delta E &= \Delta E_0 + \frac{1}{2}(E^{unfav.} - E^{fav.}) \\ &= \Delta E_0 + \frac{1}{2}\left(E^{o,unfav.}_{inter} - E^{o,fav.}_{inter}\right) \\ &= \Delta E_0 + \frac{1}{2}\left(P^{o,unfav.}_{ij} - P^{o,fav.}_{ij}\right)\epsilon^{n_C}_{ij} \end{aligned}$$

C diffusion in supersaturated Fe

MD results *vs* Elasticity theory following Hillert's idea



- Nice fit for low C concentration only !?!

C diffusion in pure Fe

A las bit of elasticity theory: (4) accounting for octa and tetra

- Interaction energy:

$$E_{inter} = P_{ij}\epsilon_{ij} \text{ with } P_{ij}^{o,t} = \begin{bmatrix} P_{\otimes}^{o,t} & 0 & 0 \\ 0 & P_{\bullet}^{o,t} & 0 \\ 0 & 0 & P_{\bullet}^{o,t} \end{bmatrix}$$

- C induced elastic distortion:

$$\epsilon_{ij}^{n_C} = \frac{n_C}{V} S_{ijkl} P_{kl}$$

- Energy barrier:

A las bit of elasticity theory: (4) accounting for octa and tetra

- Interaction energy:

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- C induced elastic distortion:

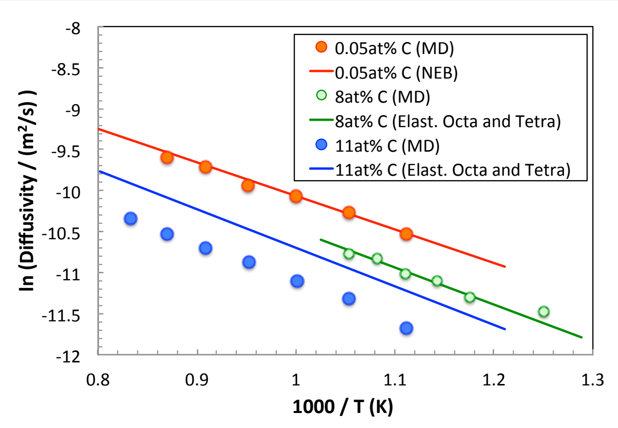
$$\epsilon_{ij}^{n_C} = \frac{n_C}{V} S_{ijkl} P_{kl}$$

- Energy barrier:

$$\begin{aligned} \Delta E &= \Delta E_0 + \left(E_{inter}^{t} - E_{inter}^{o}\right) \\ &= \Delta E_0 + \left(P_{ij}^{t} - P_{ij}^{o}\right)\epsilon_{ij}^{n_C} \end{aligned}$$

C diffusion in supersaturated Fe

MD results *vs* Elasticity theory acounting for Tetra and Octa

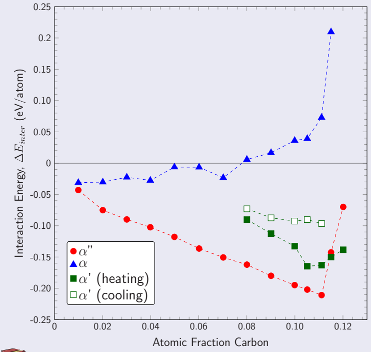


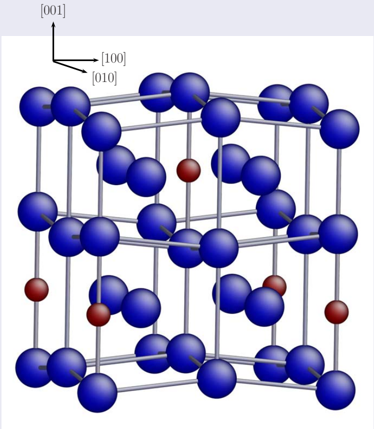
- Still not working for 11% !?!

C diffusion in supersaturated Fe

What happens at 11%C?

- A new phase !?!

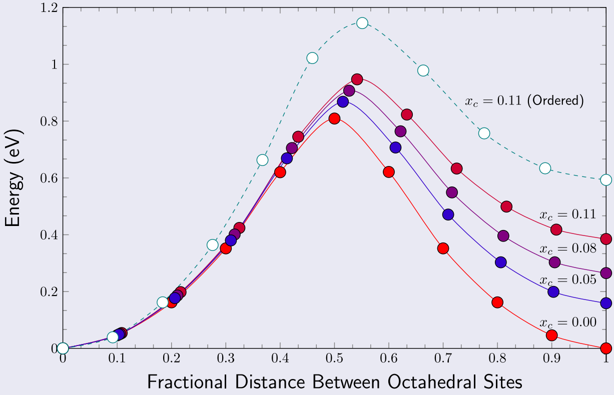




[Sinclair *el al*, *Phys. Rev. B*. **81** (2010)]

How can it change diffusivity?

- NEB on strained simulations boxes:



- $Fe_{16}C_2$ exhibits higher energy barrier

C diffusion in supersaturated Fe

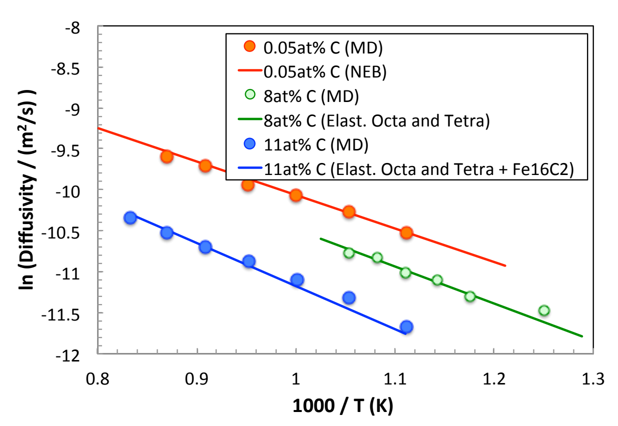
A mixture of fully ordered $Fe_{16}C_2$ and ordred 11%C?

- Order parameter η
  - $\eta = 1$ for $Fe_{16}C_2$
  - $\eta = 0$ for "random" ordered structure

$$\Delta E = k_B \ln\left(\eta \exp\left[\frac{\Delta E^{Fe_{16}C_2}}{k_b T}\right] + (1-\eta)\exp\left[\frac{\Delta E^{Fe11\%C}}{k_b T}\right]\right)$$

C diffusion in supersaturated Fe

Final comparision



- $D_0 = 1.1 \times 6\ \mathrm{m}^2/\mathrm{s}$ in all cases

Conclusions and outlook

C Diffusion in supersaturated Fe

Conclusion

- Ordered C in solid solution modifies diffusivity of C
- Hillert was (almost) right !
- Better to account for octa and tetra variation with C content

[Lawrence *el al*, *Modelling Simul. Mater. Sci. Eng.* **22** (2014)]

Outlook

- Diffusion of C within a Cottrell atmosphere
  - see Charlotte's talk on thursday
- Formation of carbides...