# Diffusion in Energy Materials

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# Outline

Atomic scale simulations can be valuable to guide engineering practice:

- Improving the Performance of Energy Materials
- Understanding Microstructural Degradation in Nuclear Fuels
- Structural Integrity of Nuclear Pressure Vessels Steels

# Modelling Methodology

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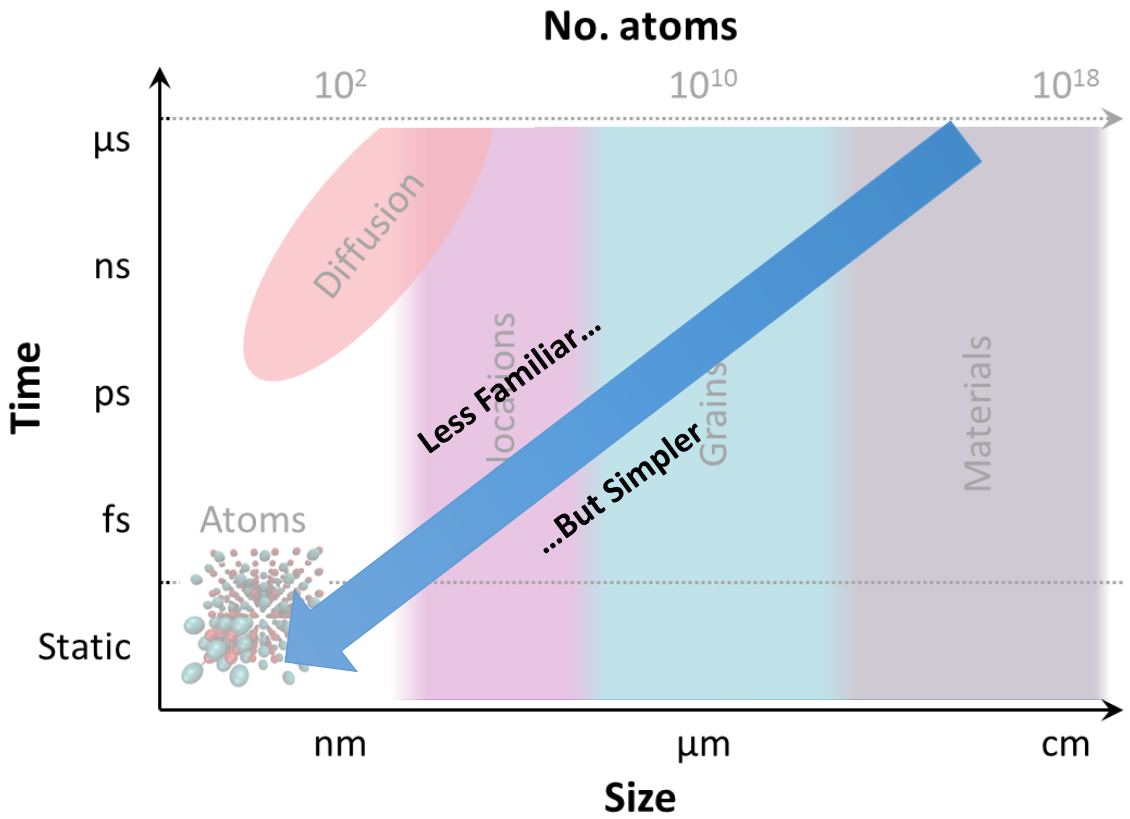
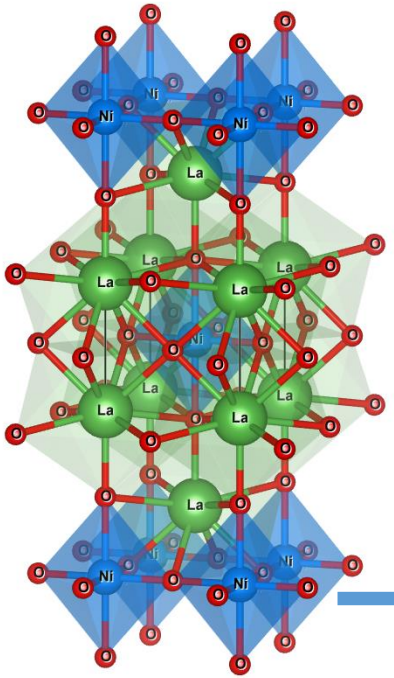


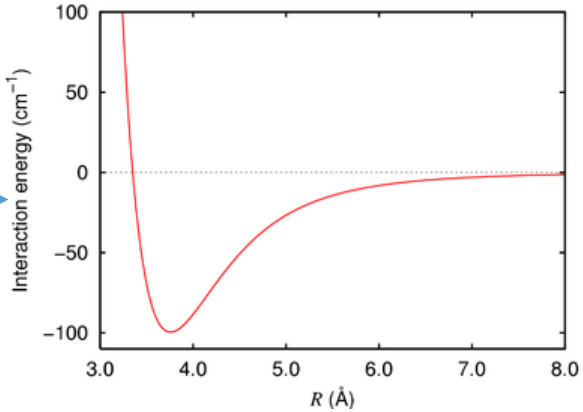

**Coventry Expertise**

- Combination of **DFT** and **empirical potentials**
- Targeted atomic scale models to refine existing semi-empirical parameters
- Modelling to help us interpret experimental data
- Part of Engineering Department, therefore **focus on applications**

# The Atomic Scale: Molecular Dynamics




- Atoms form bonds which can either be predicted or fitted:
- **Density Functional Theory** (DFT) used to directly predict this energy using quantum mechanics
- **Empirical Potentials** made by fitting to physical properties (e.g. thermal expansivity)



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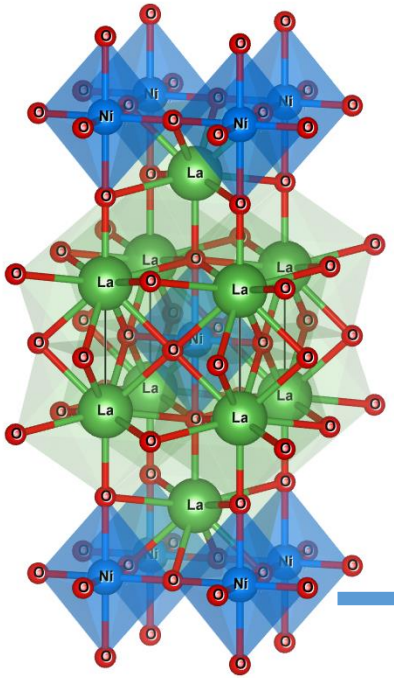
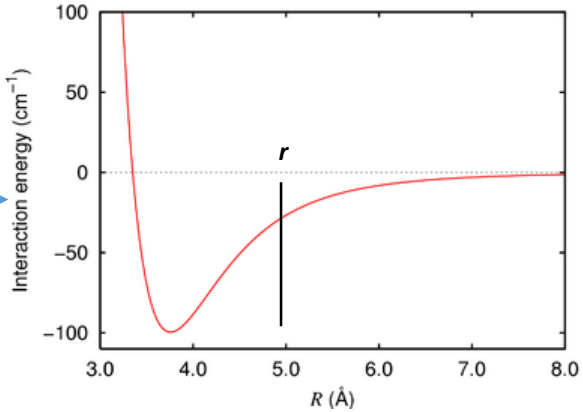
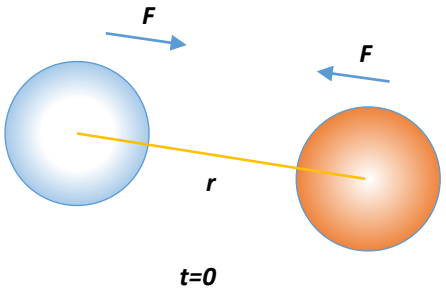



- If we know the **energy** of the atoms as a function of position, we know the **forces**.
- If we know the **force** we know the **acceleration**,
- If we know the **acceleration**, we can work out the **position** a short time later



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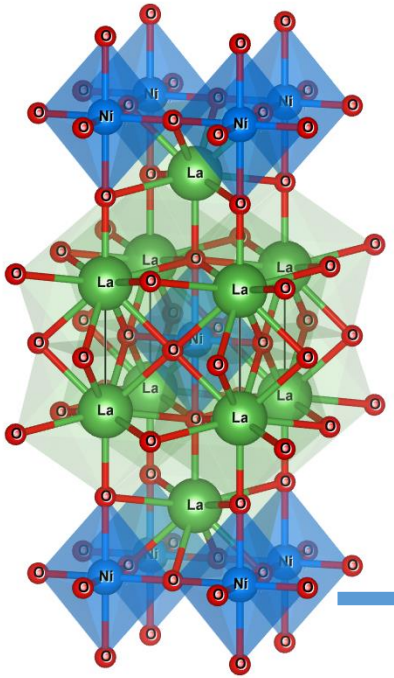


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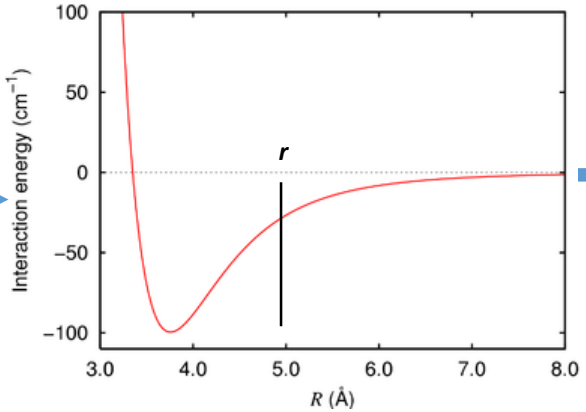
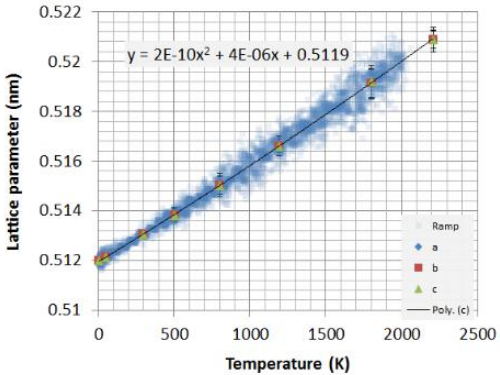


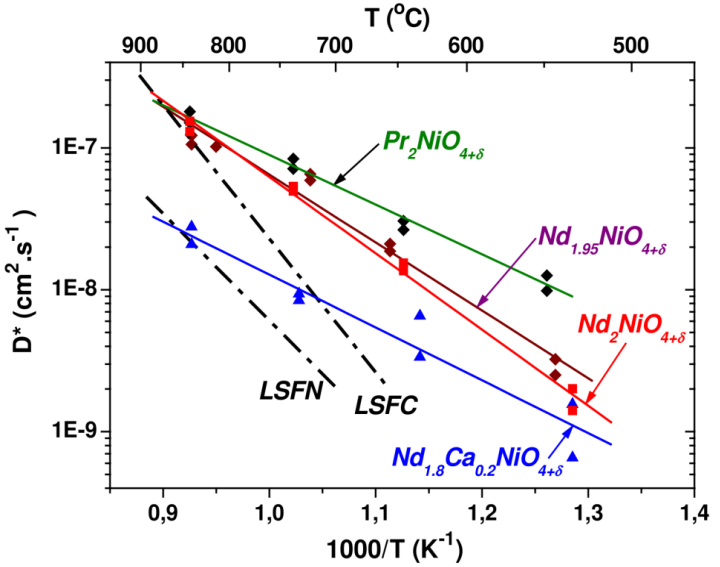




Material Properties, e.g. thermal expansion

# Optimising the Performance of Energy Materials

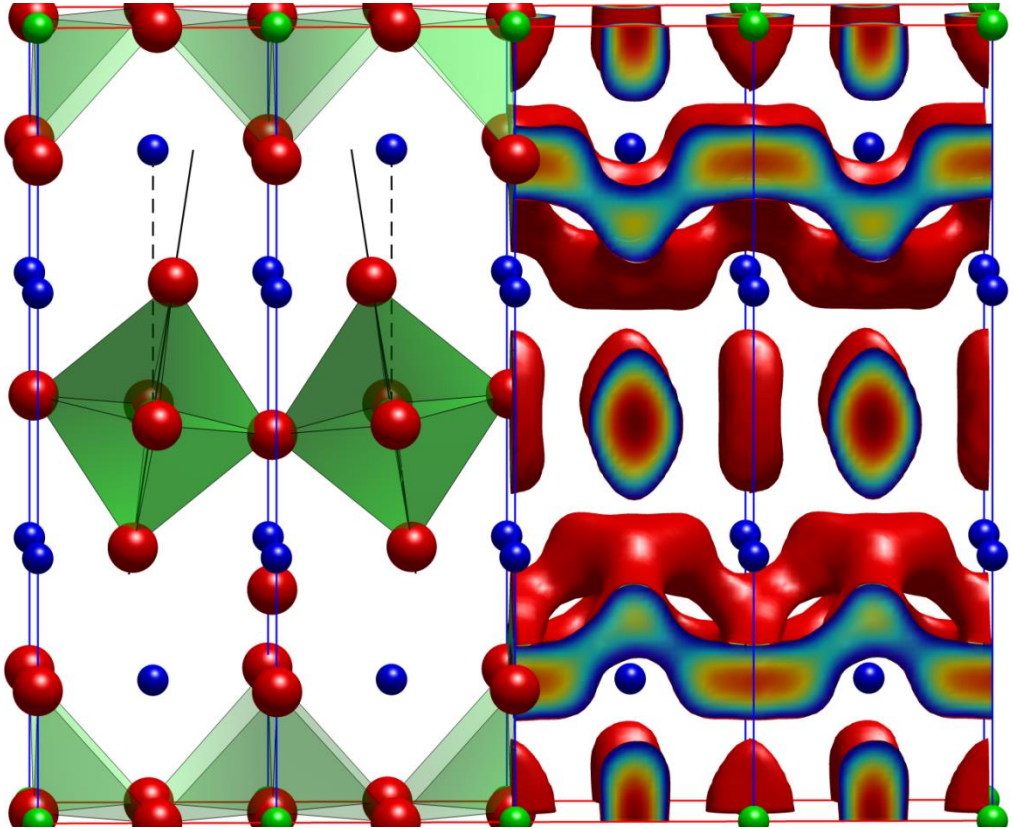
Good ionic conductors are normally found ‘by accident’:

- They can then be improved by considering basic chemistry
- e.g.: $La_2NiO_{4+\delta}$ is a good candidate so is $Pr_2NiO_{4+\delta}$ as is $Nd_2NiO_{4+\delta}$
- …But what about $La_xPr_{1-x}NiO_{4+\delta}$ or $La_xPr_{1-x}Ni_yCo_{1-y}O_{4+\delta}$?
- It is not possible to synthesis and test all of the different material combinations
- (It’s also not possible to simulate them all either)
- We need to use atomic scale simulations to understand the migration pathway and identify good candidate systems for further investigation.



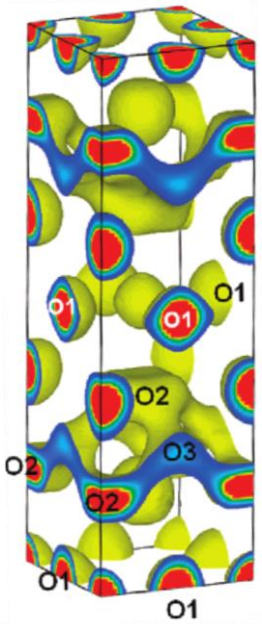

Boehm et al, Solid State Ionics, **176** 2717 (2005)

# $K_2NiO_{4+\delta}$ Materials for Oxide Fuel Cells



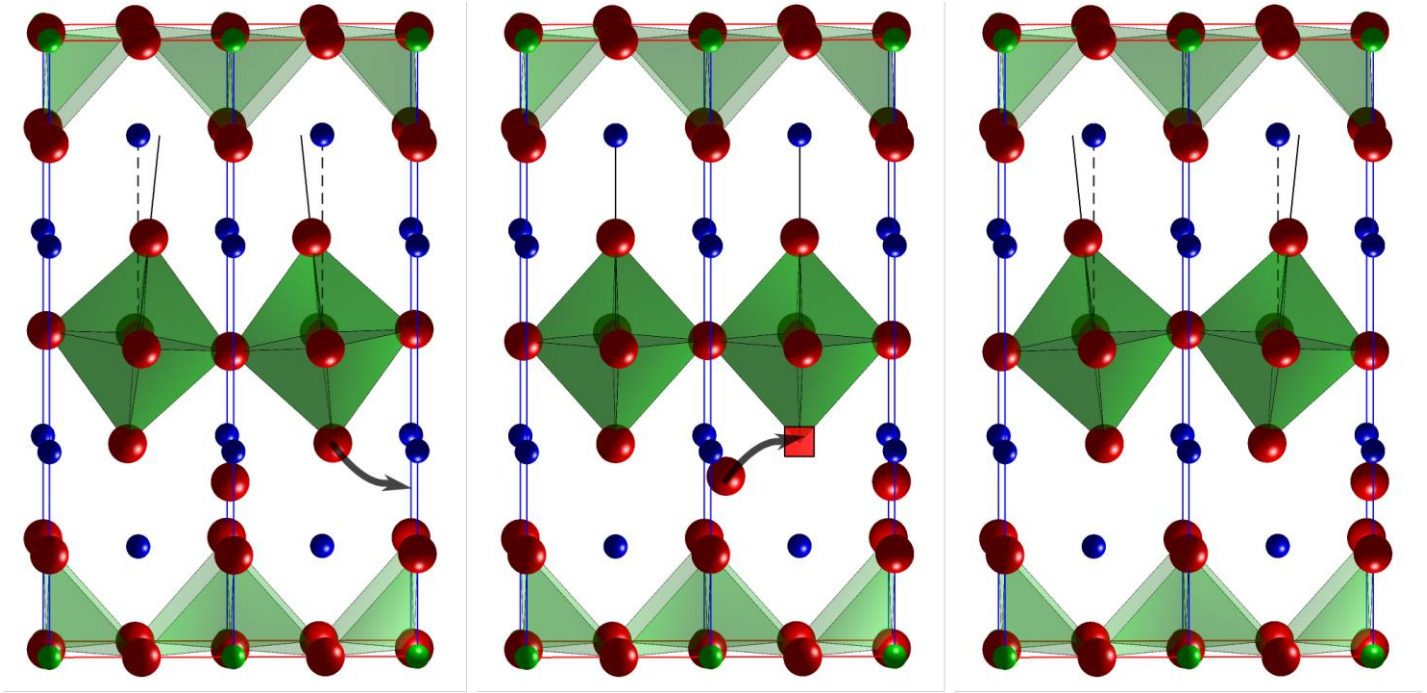
**$Pr_2NiO_{4+\delta}$, δ=0.098, *T*=1000K**

Time averaged oxygen ion density from molecular dynamics simulations




Rev. Monte Carlo neutron diffraction data (Yashima et al, J. Chem. Soc. **23** (2008))

# $K_2NiO_{4+\delta}$ Materials for Oxide Fuel Cells



Diffusion driven by an interstitialcy migration mechanism in the *a*-*b* plane.
Potential to tune the material composition to optimise diffusivity.

# Modelling Oxygen Diffusion in Nuclear Fuels

Uranium dioxide ($UO_2$) is a well characterised nuclear fuel with established material properties.

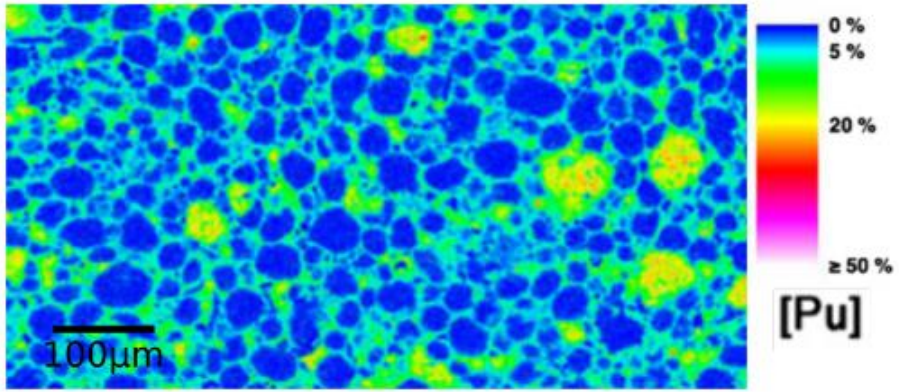
Mixed oxide (MOx) fuels are:

- $Pu_xU_{1-x}O_2$
- $Th_xU_{1-x}O_2$

Significantly less data on these materials. Material is highly heterogeneous so bulk composition does not represent actual local composition.

*What properties should we use for these mixed compositions?*

*We don't expect nuclear operators to be running LAMMPS calculations for their specific fuels.*




Oudinet, G. *et al.* J. Nucl. Mater. **375**, 86-94 (2008)

# Fitting MOx Properties

- Several hundred MD simulations using CRG potentials at a range of temperatures, pressures and compositions.
- Bulk modulus from Rose-Vinet EoS:

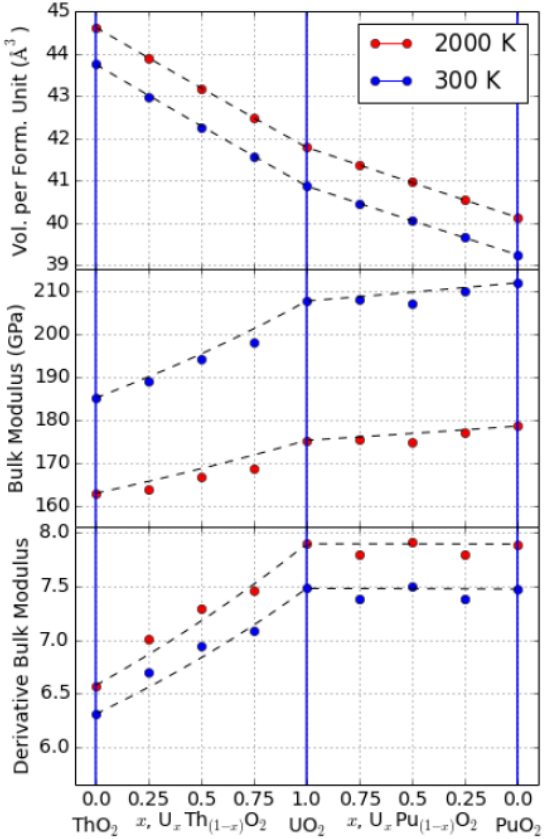
$$P(T,X) = \frac{3B_0(T)}{X^2}(1 - X(V))\exp[\eta_0(T)(1 - X(V))]$$

- And for a theoretical mixed oxide composition ($M_xN_{1-x}O_2$):

$$B(x) = B_N \frac{f(x)}{g(x)} \quad \text{With:}$$

$$f(x) = 1 + x\left[\left(\frac{V_M}{V_N}\right) - 1\right] \quad \text{and} \quad g(x) = 1 + x\left[\left(\frac{B_N V_M}{B_M V_N}\right) - 1\right]$$

See: P.A. Varotsos, K.D. Alexopoulos, Thermodynamics of point defects and their relation with bulk properties, North-Holland, 1986 for a discussion of this

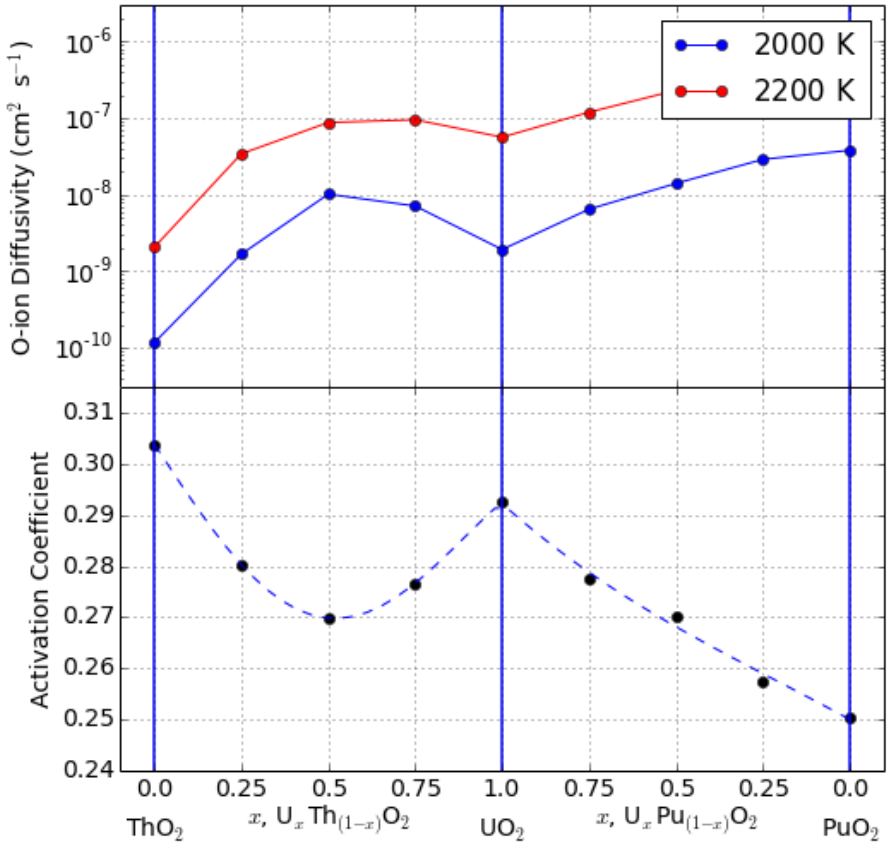


# Fitting MOx Properties

- Fitted oxygen diffusion from *cBΩ* model:

$$D_{cB\Omega}(M_xN_{1-x}O_2) = D_0 e^{\frac{-C_{act}(x)B\Omega}{k_BT}}$$

- *B* & *Ω*, bulk modulus and atomic volume from EoS.
- $c_{act}$ is a temperature independent constant linking *B* and *Ω* to the activation energy.



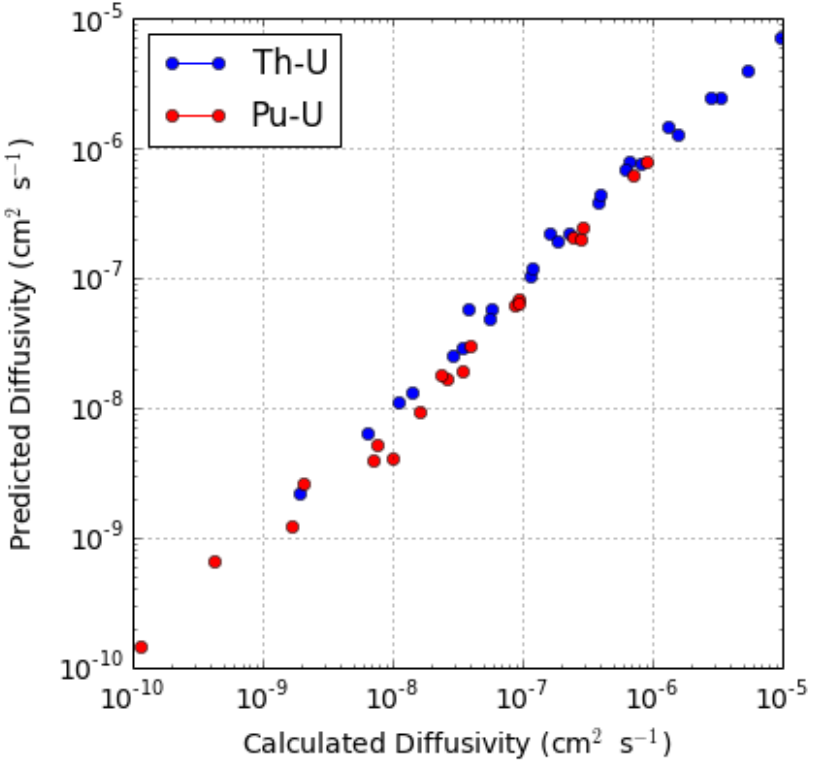
# Fitting MOx Properties

Model consists of,

Rose-Vinet EoS for thermoelastic properties

*cB*Ω model for diffusion properties

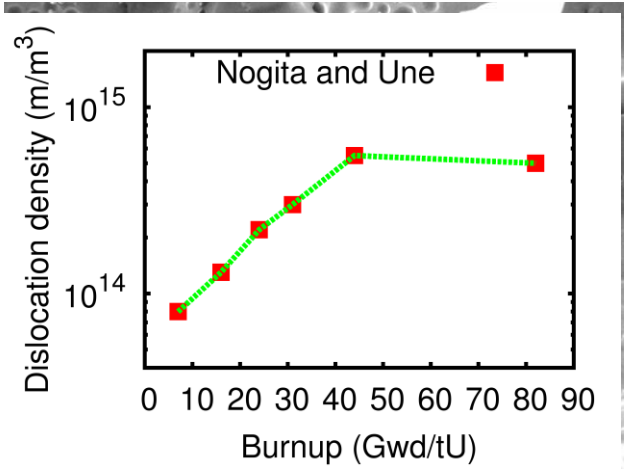
Allows us to parameterise a general MOx composition, *without* needing to run the individual simulations.




See: Parfitt et al. Thermodynamic calculations of oxygen self-diffusion in mixed-oxide nuclear fuels. RSC Advances, 6, 74018-74027.

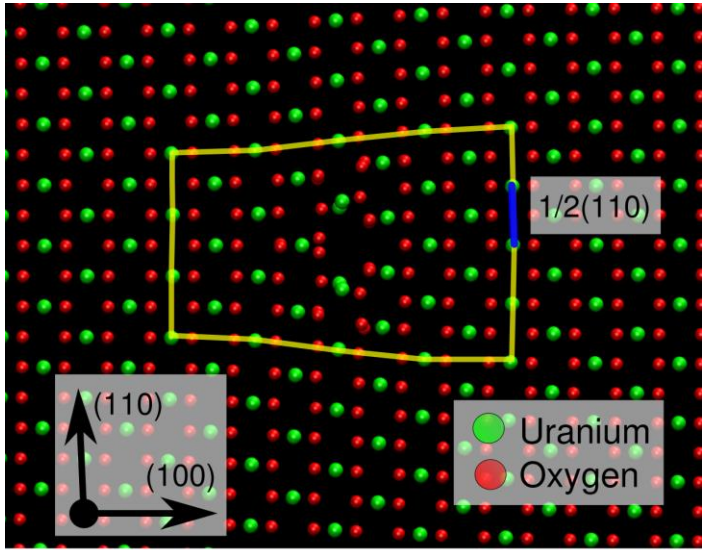
# Microstructural Evolution in Nuclear Fuels

- Gas formed through the fission process is one of the key factors limiting the performance of current and future nuclear fuels
- Increase in rod temperature due to thermal feedback
  - Clad loading due to swelling
  - Increase in end of life rod pressure
- Empirical models of this process are complicated by the presence of microstructural features such as gas bubbles, dislocations and grain boundaries.

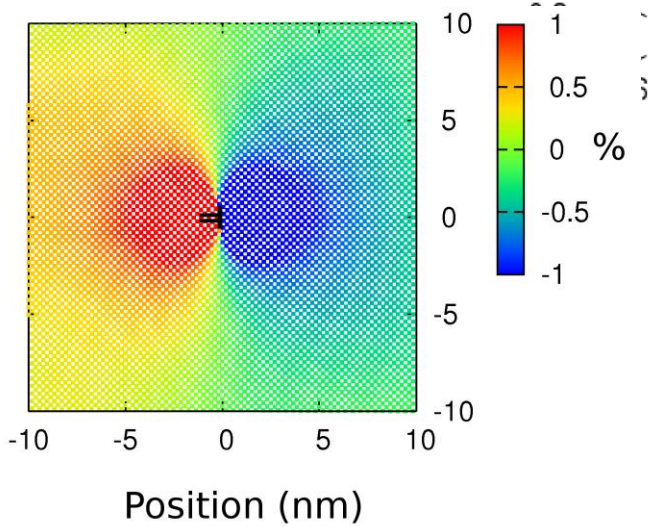



Nogita K., Une K., Nucl. Inst. Meth.Phys. Res. **B91** 301 (1994)

# Microstructural Evolution in Nuclear Fuels




{100} ½ <110> edge dislocation

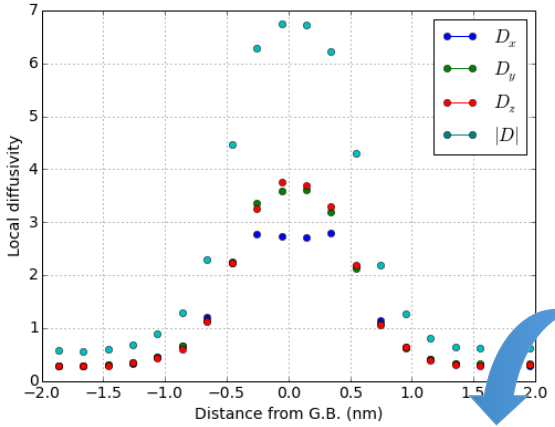


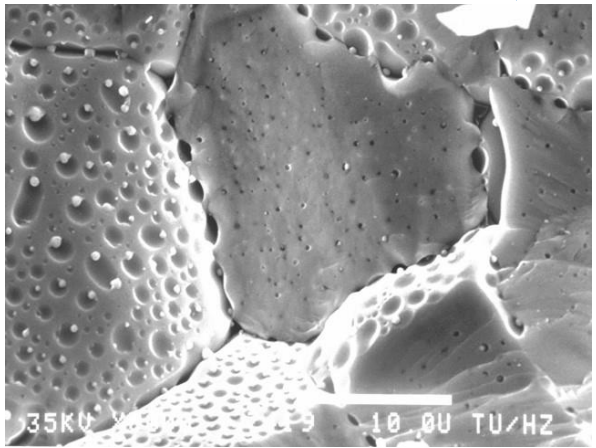

Strain field surrounding an edge dislocation

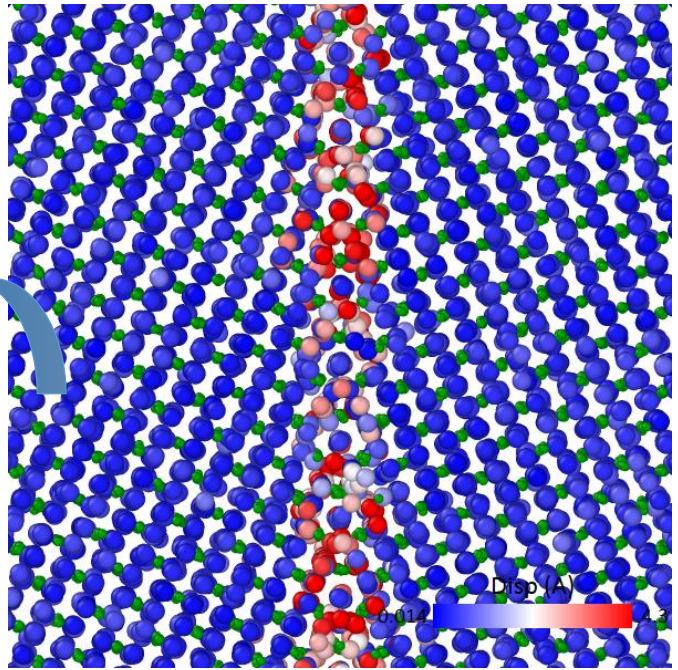
Suggested elastic energy calculations of dislocation mobility

Nudged elastic band calculations of atomic dislocation jumps

# Microstructural Evolution in Nuclear Fuels




Current project to understand bubble formation at grain boundaries.

Link to HARVESTORE EU H2020 project

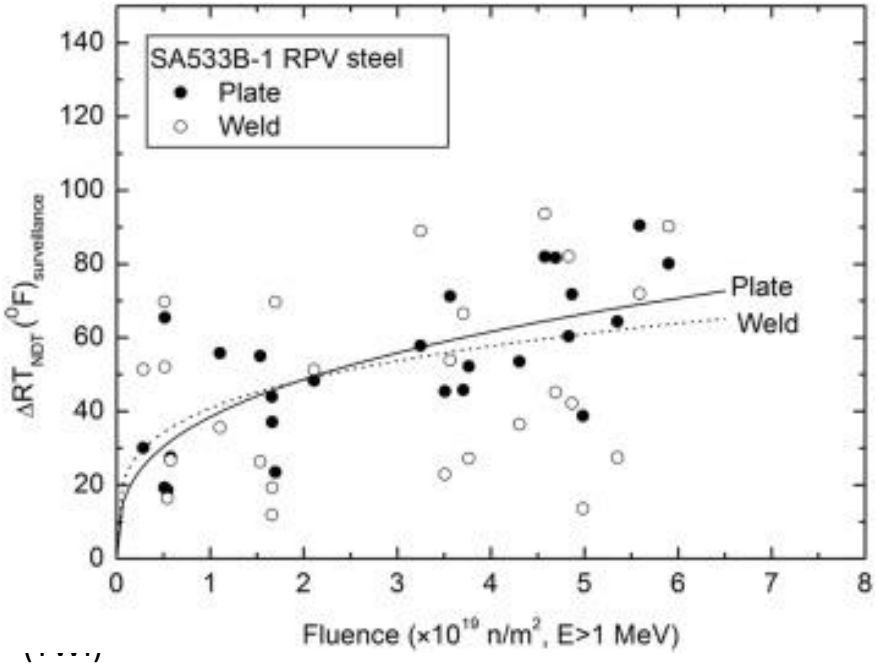
# Modelling Embrittlement in Nuclear Steels

Nuclear pressure vessels have a very high safety requirement, in particular they must be shown to be sufficiently ductile.

During exposure to neutron irradiation, the steel becomes more brittle due to the formation of precipitates and interstitial loops.

Many modern shift predictions are based (fundamentally) on rate theory models of defect migration and lifetime, e.g. JEAC-2007, EONY Reg. Guide 1.99.

We can use atomic scale simulations to help refine these models without reducing their predictive accuracy.

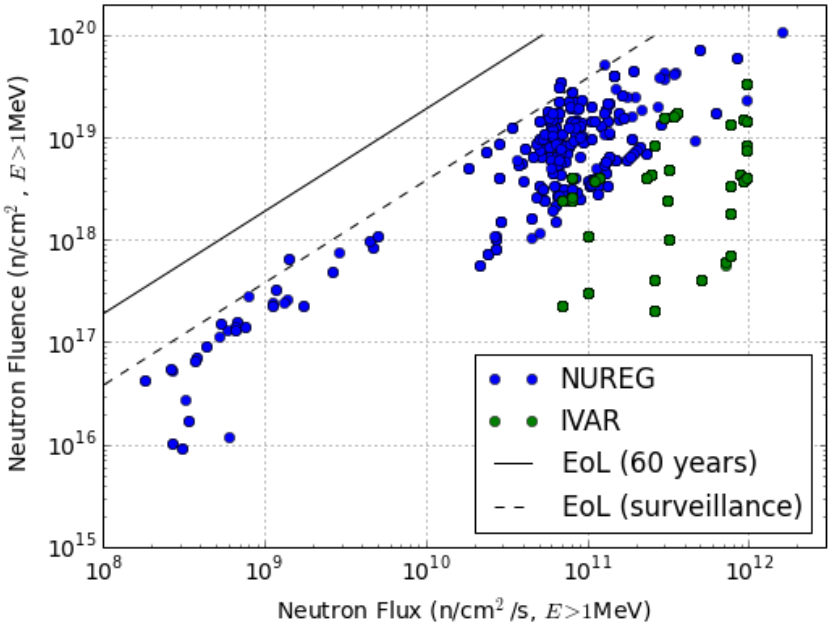



Yoon et al. Comparison of applicability of current transition temperature shift models to SA533B-1 reactor pressure vessel steel of Korean nuclear reactors, Nuclear Engineering and Technology, Volume 49, Issue 5, 2017

# A Key Research Question

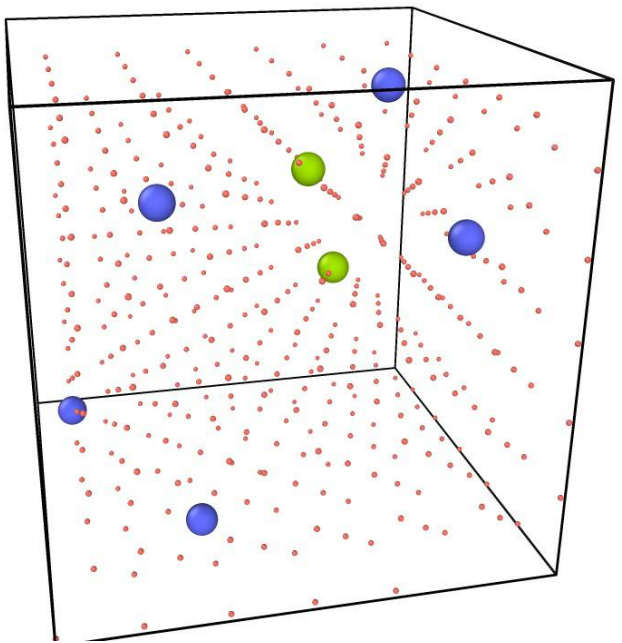
Why does it matter for nuclear pressure vessels?

- All embrittlement predictions require *some* extrapolation.
- Advanced manufacturing may significantly reduce nuclear costs, but we need to demonstrate equivalence / improvements over existing materials
- Increased internationalisation means we can no longer rely on ‘our’ data. UK Nuclear reactors may be built to a different nation’s design, using materials from a third country.



# Cu Precipitation in Low Allow Steels

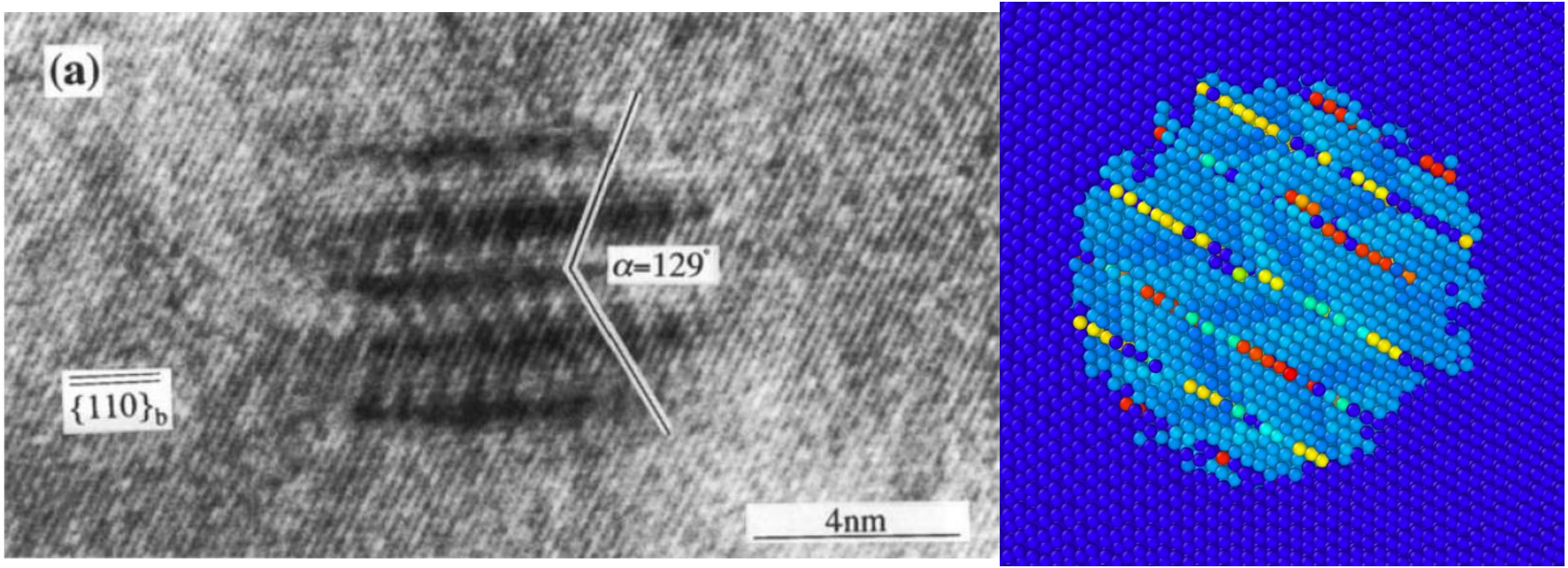
- Model precipitation using molecular dynamics + KMC/TAD
- Predict precipitate size and distribution as a function of time & temperature.
- Extract (simulated) electron diffraction patterns, precipitate size and magnetic structure
  - Compare with TEM data. Compare with SANS and APT data.
- Use time / temperature to investigate effects of dose rate and chemical composition.
  - Compare with literature embrittlement trend curves
  - Why does Ni-content promote Cu precipitation?
  - What is the long term fate of small amounts of Cu in the steel matrix?




Diffusion of Cu and Ni at 550K via temperature accelerated dynamics

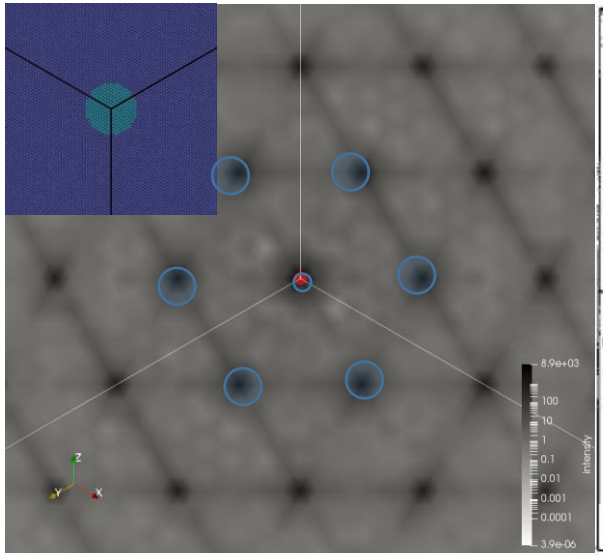
TAD: Sorensen and Voter, J. Chem Phys, 112,. 9599 (2000))

# Simulation of Electron Diffraction Patterns

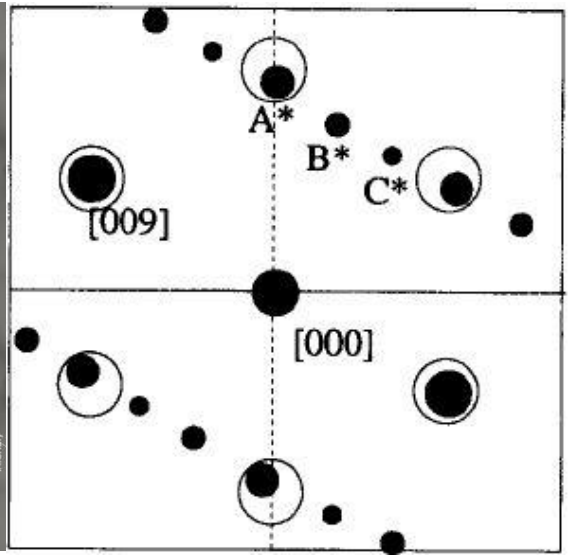



Comparison of TEM and MD simulation of Cu precipitate (~6nm)

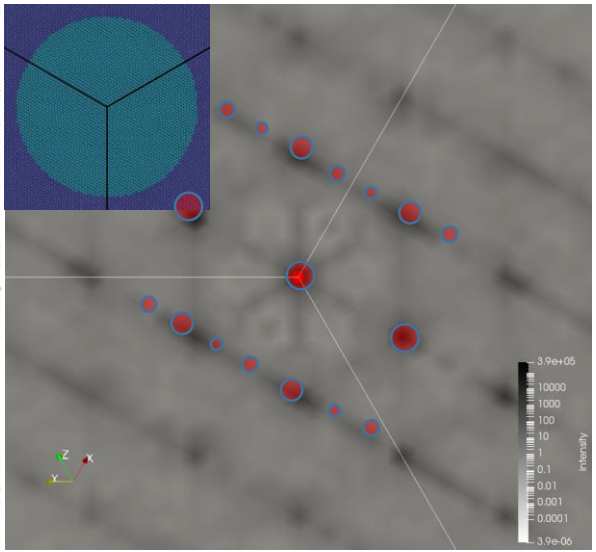
# Simulation of Electron Diffraction Patterns



3.7nm (just before transition)




Theoretical BCC and 9R peak positions



13.4nm (post-transition)

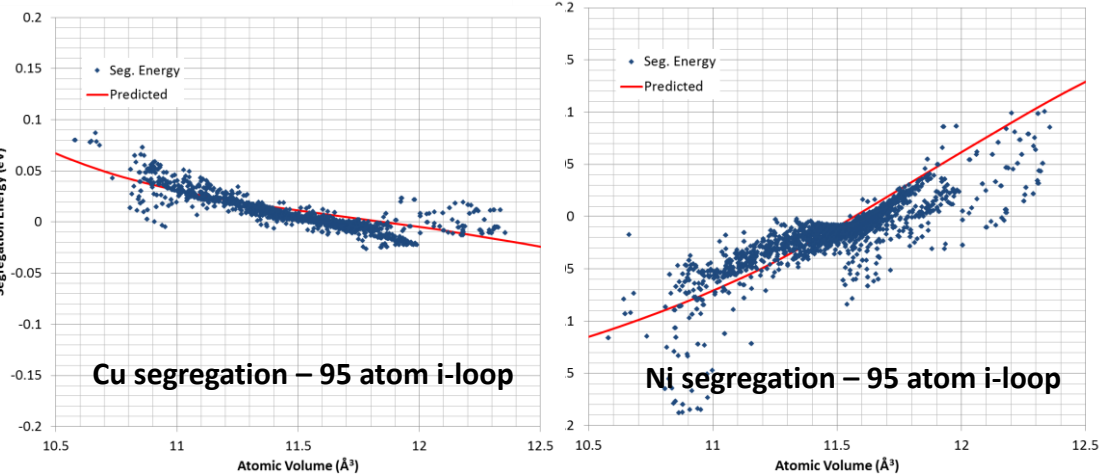
**MD plus selected area electron diffraction patterns of Cu precipitates**

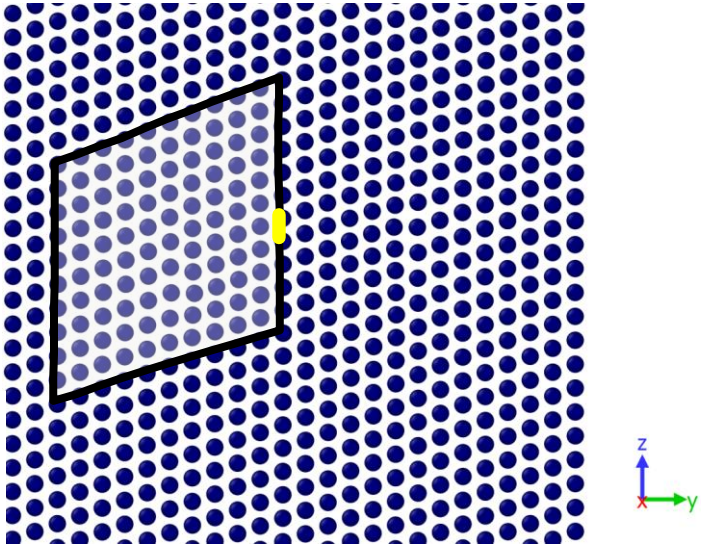
# Modelling Precipitation around Interstitial Loops

- When we actually compare the results of the empirical potentials with DFT, e.g. the comparison of interstitial loops:

  C. Domain and C.S. Becquart, JNM 499 (2018) 582-594

The results are often not favourable for the empirical potentials.

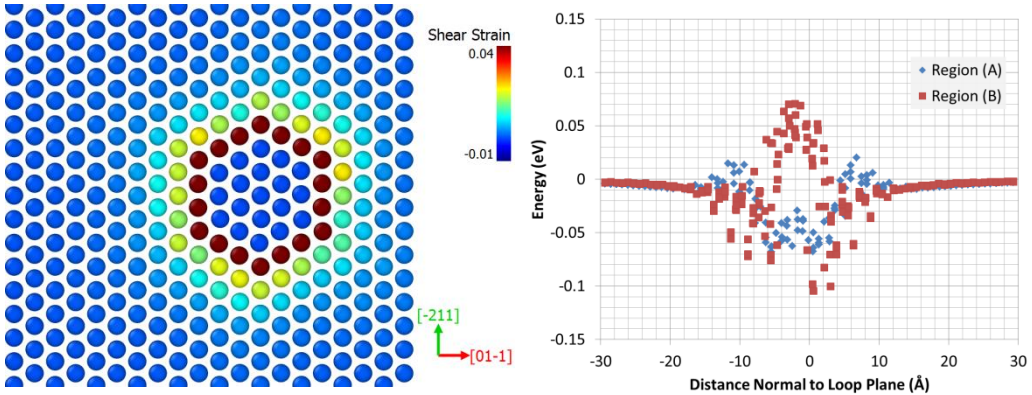


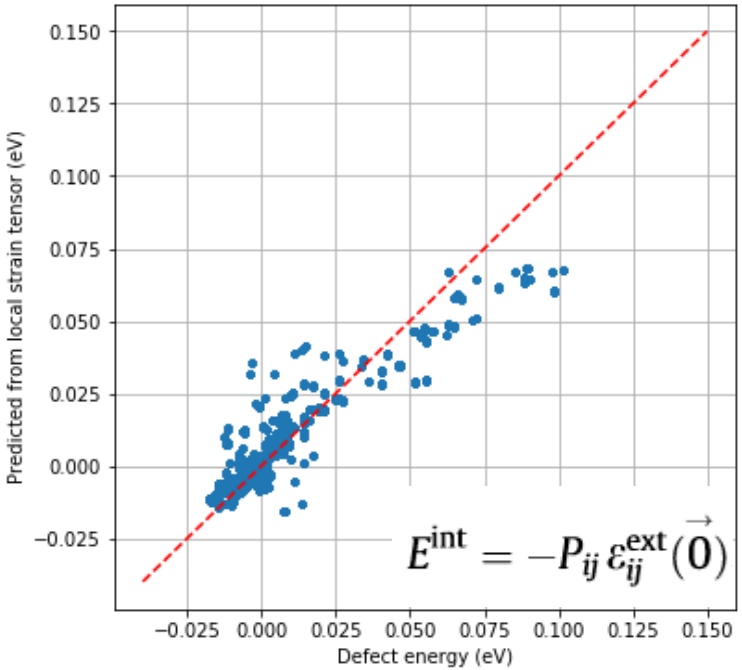

½<111> interstitial loop in BCC Fe

# Modelling Precipitation around Interstitial Loops

- However, we can use a combination of the DFT point defect energy (which we can calculate easily) plus the strain fields from the empirical potentials (which we trust)

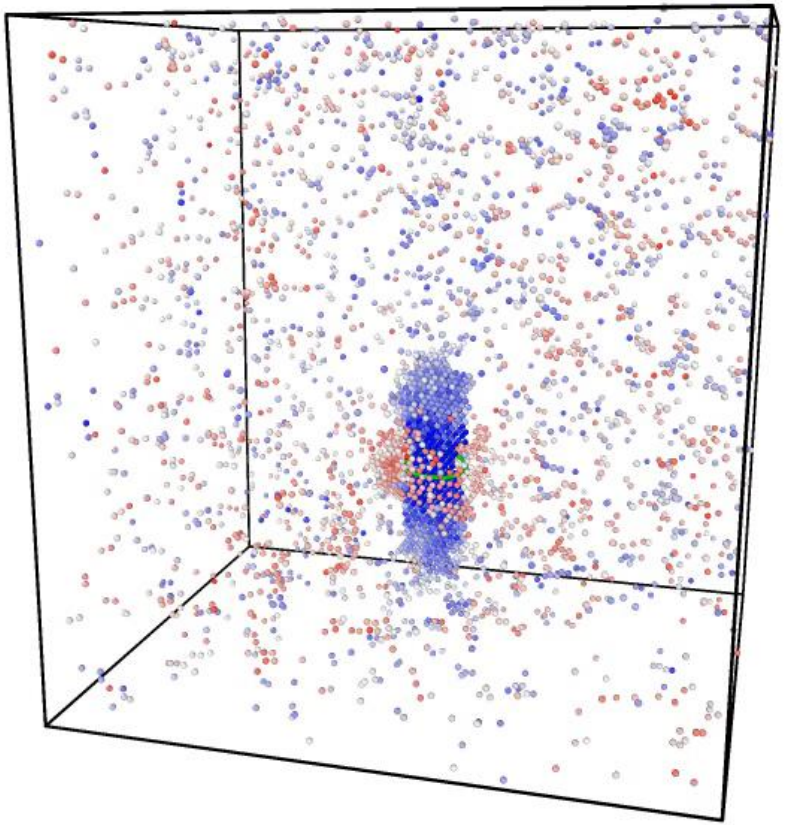


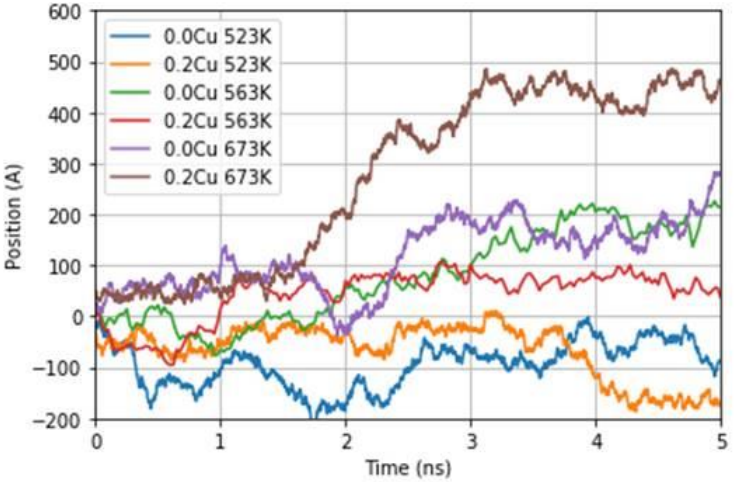

see Clouet *et al* Computational Materials Science, Volume 147, (2018) for a review of methods




Calculated segregation energy versus energy predicted from first order elastic theory for a 19-atom interstitial loop

# Defect Creation and Loss in Steels

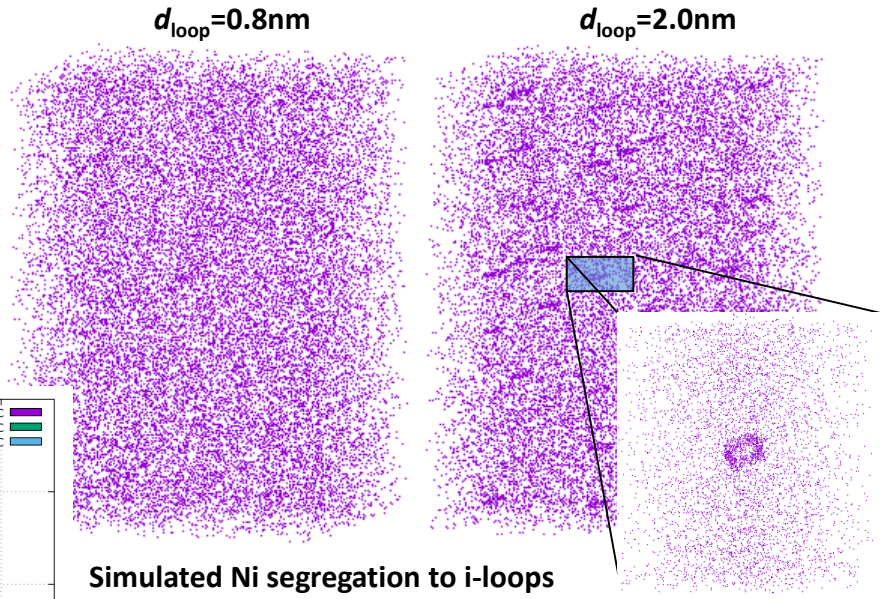




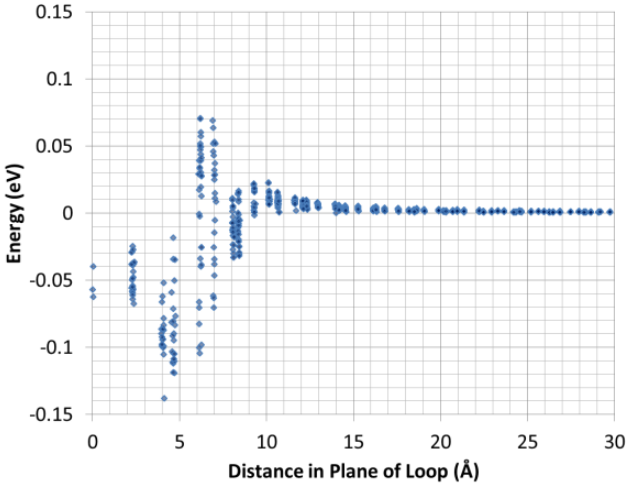

Diffusion of a single <111> interstitial loop in bcc-Fe, colour is elastic strain in the loop-normal direction

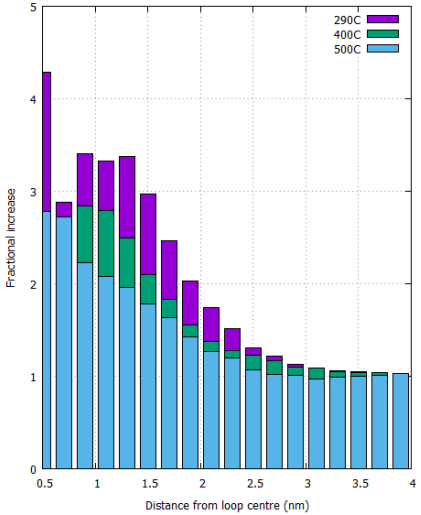
# Modelling Experimental Data

From atomic scale simulations we obtain huge amounts of detail about the material. It is far easier to take these data and simulate an experiment than the other way around.




**Simulated Ni segregation to i-loops**




Simulated atom probe tomography datasets for Ni decorated interstitial loops.

# Conclusions

- Very exciting time for atomic scale simulations:
  - Can simulate real microstructures, long(er) timescales
  - Increasing sophistication in passing data and parameters between DFT and empirical potentials
  - Dramatic improvements in visualisation will help interpret experimental data
- Batteries and fuel cell materials will be lead application for a lot of these new techniques
  - Combination of commercial importance and high value of diffusivity mean these are most accessible to new techniques.
- Great number of challenges for Gen-III / Gen-IV nuclear reactor systems
  - Cost is main driver – justifying new materials and manufacturing techniques is crucial
  - Understanding risk and uncertainty in high integrity steels through:
    - Risk reduction (mechanistic understanding)
    - Better understanding our data (artificial neural networks)
    - Reducing conservatism – *in situ* monitoring of degradation