



# INSPYRE

Investigations Supporting MOX Fuel Licensing  
in ESNII Prototype Reactors

# Simulation methods and multiscale modelling

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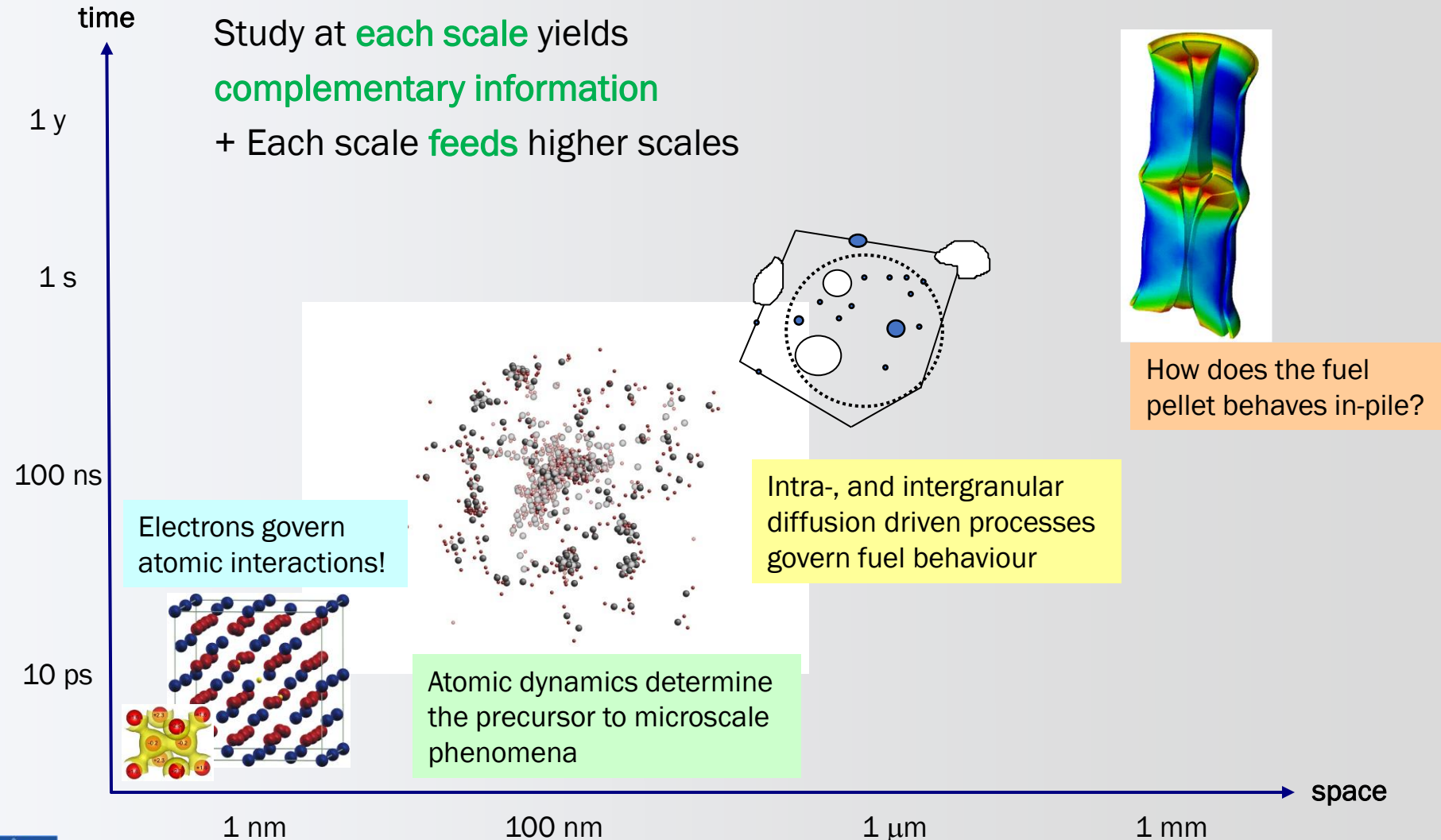
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First INSPYRE school,  
TU Delft, 2019-05-14





# Multiscale phenomena





# The structure of condensed matter

*(One equation to rule them all)*

The many-body Schrödinger equation describes condensed matter in general:

$$H\Psi = E\Psi$$

The SE Hamiltonian can be subdivided into kinetic and potential terms:

$$H = T + V$$

These terms can be divided further into ionic- and electronic terms:

$$\begin{cases} T = T_n + T_e \\ V = V_{nn} + V_{en} + V_{ee} \end{cases}$$

Thus the full Hamiltonian can be written as:

$$H = T_n + T_e + V_{nn} + V_{en} + V_{ee}$$





# The adiabatic approximation

(How we can make headway and separate stuff?)

Schrödinger equation

$$H\Psi = E\Psi$$

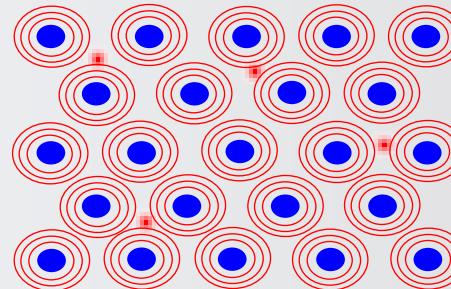
Electrons vs ions:

Electron mass  $\ll$  ion mass

$$m_n \approx 10^5 m_e$$

- **Electrons** "see" **ions** as fixed particles.
- **Ions** "see" **electrons** as a fixed potential surface.

Life according to **electrons**



Life according to **ions**

The Hamiltonian

$$H = T_n + T_e + V_{nn} + V_{en} + V_{ee}$$

Electronic part (red arrows pointing to  $T_e$ ,  $V_{en}$ , and  $V_{ee}$ )

Ionic part (black arrows pointing to  $T_n$  and  $V_{nn}$ )

Mixed term (green arrow pointing to  $V_{en}$ )

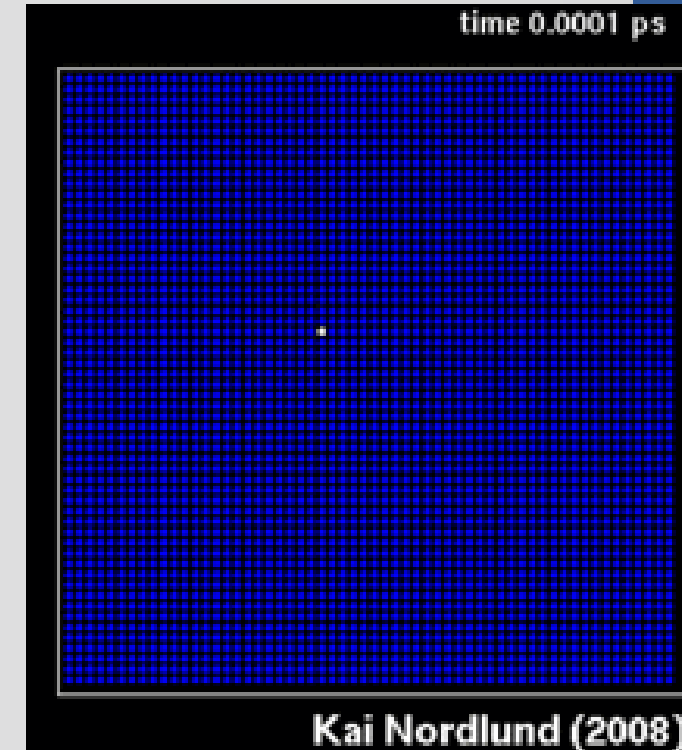
$$T_x = - \sum_x \frac{\hbar^2}{2m_x} \nabla_x^2$$



# The adiabatic approximation

(The Born-Oppenheimer approximation)

- We can separate the problem into an **electronic** one and an **ionic** one
- Materials under irradiation needs a good description of *ion dynamics*  
→ we need good potential energy surfaces!
  - OR: we need good interatomic interactions
  - OR: we need good interatomic potentials
  - OR: ...
- We can either go hard core quantum mechanics (often called *ab initio*, or *electronic structure*)
  - Best, or most efficient and reliable, method: Density Functional Theory (DFT)
- Or we can make classical approximation models (often called *empirical potentials*, or *interatomic potentials*)
- Quick walk-through of these two branches!





# Atomic scale simulations

(What level of approximation is appropriate?)

## ■ Electronic structure methods

$$H\Psi = E\Psi$$

- Approximate resolution of Schrödinger equation → **Predictive** and **precise**
- **Transferrable**, all elements and combinations possible
- **High cost** → **Size of system and time limited**
- **Density Functional Theory: ~1000 atoms**
- **Exploration of configurational space mainly through energy minimization (quasi-static) → Calculations at 0 K.**  
*Ab initio* molecular dynamics is a strongly developing field.

## ■ Empirical potentials

- $E = f(r_i)$

- Atoms interact through parameterized analytical potential → **Very quick!**
- Possible to study large systems:  $10^6 - 10^9$  atoms, and time evolution up to ns (molecular dynamics)
- **Results only as good as the data on which model is fitted**
- **No description of electronic or magnetic effects**
- **Low transferrability**





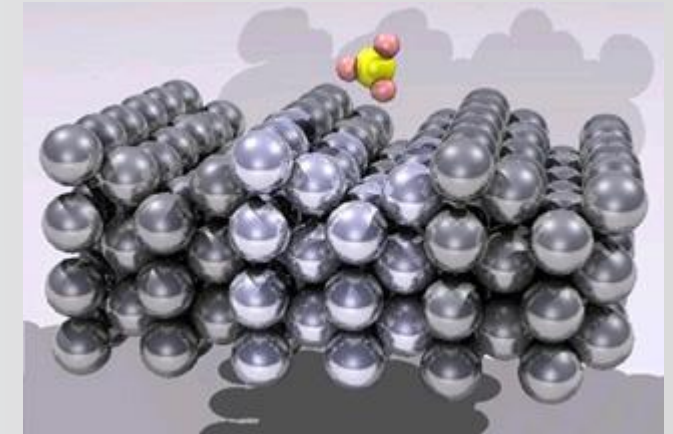
# Data yielded by atomic scale methods

(What can we actually calculate?)

## Fundamental results: total energy of a system

From this energy, its derivatives and the simulation of the system evolution in time one can get

- Cohesion energies, formation enthalpies
- Relative stability of various phases or configurations
- Equilibrium structures
- Mechanical properties (bulk modulus, elastic constants)
- Formation energies of point- and extended defects in materials
- Activation energies for migration of defects or solutes
- Incorporation energies and site of solutes in materials
- Precipitation or solution of solutes in materials
- Bonding and dissociation energies of complex/extended defects
- Vibration modes - phonons
- Thermodynamic data: free energies, calorific capacities...
- Simulation of irradiation damage: displacement cascades
- ...



So how do we do this?



# Electronic structure





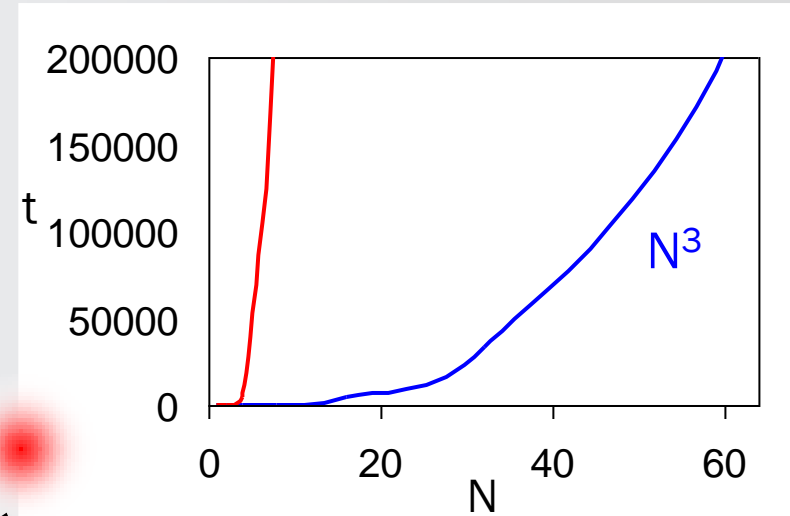
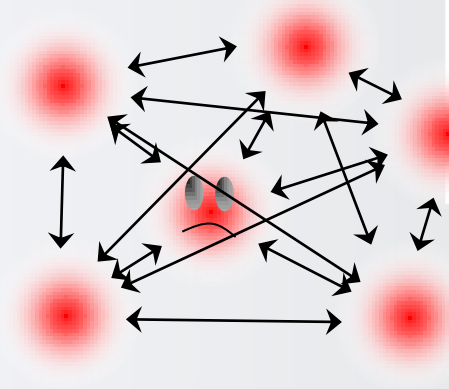
# Electronic Structure Theory

(How do electrons feel about one another?)

Problem reduced to treat electrons only

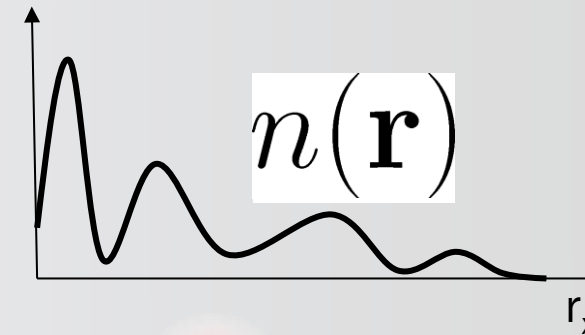
$$H\Psi_e = \epsilon\Psi_e$$

Many-body problem scaling:  
**Horribly steep!**



Kohn, Hohenberg and Sham (1964-65):  
The total energy for the ground state is an **exact** functional of the electron density  $n(\mathbf{r})$ .

Nobel Prize 1998!





# Kohn-Sham equations

(Electron group therapy)

Only one electron at a time!

$$H\Psi_{1e} = \epsilon\Psi_{1e}$$

More explicitly:  
(In atomic units:  
 $\hbar^2=e^2/2=2m_e=1$ )

$$[-\nabla^2 + V_{\text{eff}}(\mathbf{r})] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

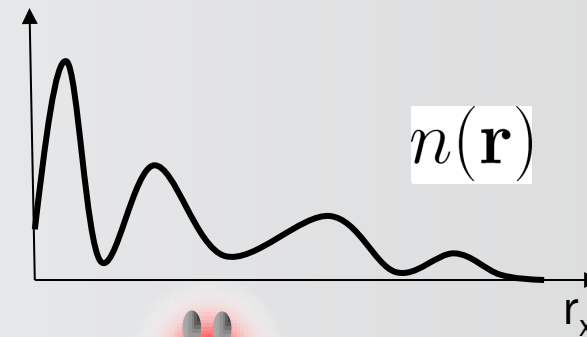
The effective potential:

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{eff}}[n(\mathbf{r})] = V_{\text{ext}} + 2 \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}[n(\mathbf{r})]$$

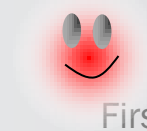
Unknown!

...and the electron density:

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$



Self-consistency!





# Remaining issues

*(The really hard stuff)*

How do we approximate the exchange-correlation?

$$V_{\text{xc}}[n(\mathbf{r})]$$

How do we represent the orbitals?

$$\psi_i(\mathbf{r})$$

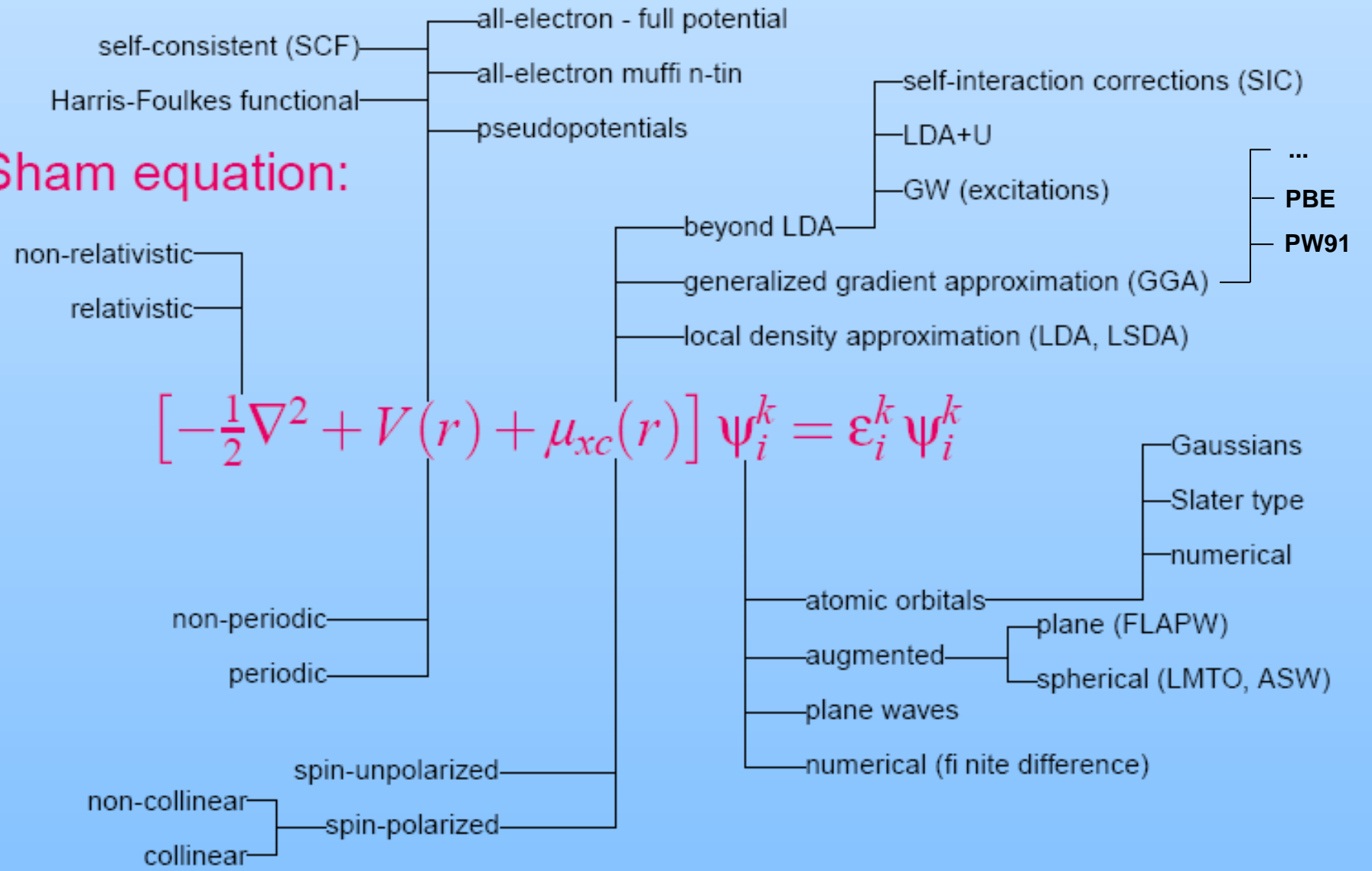
How do we represent the potential?

$$V_{\text{eff}}(\mathbf{r})$$

Very technical  
problems!



# Kohn-Sham equation:



DFT

From  
E. Wimmer





# How to calculate stuff

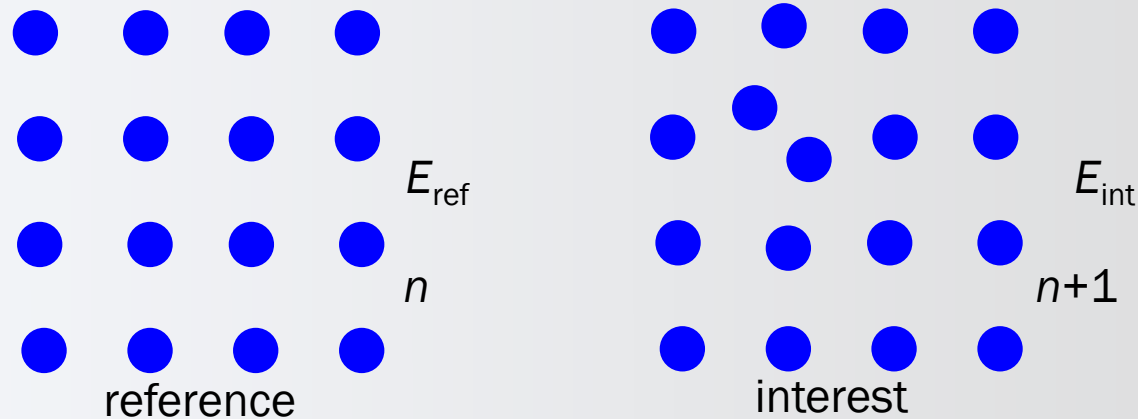
Absolute DFT energy usually not so good.

In certain cases it can be!

but...

## Relative energies!

Comparison of "as similar as possible" simulation boxes.



$$E_f = E_{\text{int}} - E_{\text{ref}} \frac{n+1}{n}$$

In order to get the best possible energetics:

- Keep the boundary conditions identical.
- Keep all (possible) internal parameters identical.  
k-point grid, cut-off energy, etc.
- Compare the same number of atoms.
- **Converge** as far as possible/necessary the internal parameters.

The  $\Delta E(\text{ref-int})$  can reach about 0.01 eV precision!



# Particularities for nuclear fuels

(Why heavy elements cause heavy calculations)

## Actinide compounds

- Complex materials
- Cations exhibit several oxidation states
- 5f electrons are localized in many compounds  
⇒ Strong electronic correlation

## UO<sub>2</sub>: Mott insulator

- Insulating character due to electronic correlation
- Gap between two like character bands (5f)
- Different from charge transfer insulators:  
gap between anion and cation states
- Band theory finds it metallic

## Standard approximations of Density Functional Theory (LDA, GGA)

- Do not take into account strong electronic correlations
- Mott insulators, in particular UO<sub>2</sub>, predicted as metals
- DFT+U, or more sophisticated, method needed

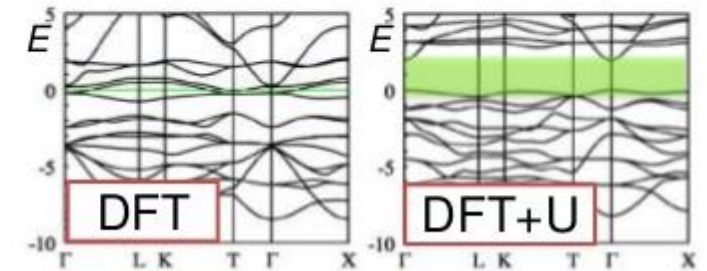
## DFT + U

$$H_{\text{Hub}} = t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}$$

Conductor to  
insulator transition

$$E_{\text{DFT}+U} = E_{\text{DFT}} + E_U = E_{\text{DFT}} + E_{\text{Hub}} - E_{\text{dc}}$$

DFT conductors to  
DFT+U insulators



conductors ↔ insulators



# Classical interatomic potentials



# Empirical interaction potentials

(Classic!)

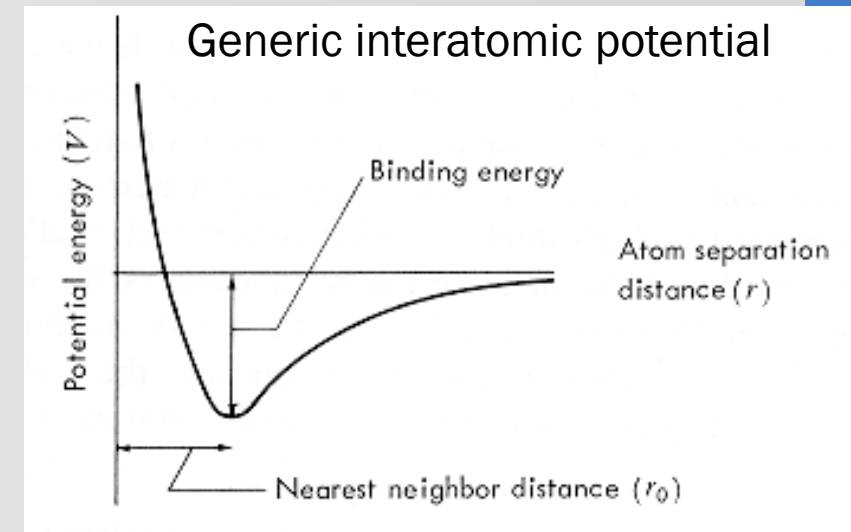
- Analytical functions representing interatomic interactions depending only on atom coordinates

- General form:

$$V = \sum_i^N V_1(r_i) + \sum_{i,j}^N V_2(r_i, r_j) + \sum_{i,j,k}^N V_3(r_i, r_j, r_k) + \dots$$

External field    Pair term    Three-body term    n-body terms

- Parametrized on structural, physical and thermodynamical properties from experiments or electronic structure calculations.
- Mathematical function different for each type of system (bonding)
  - Ionic: Buckingham
  - Covalent solid: Tersoff, Stillinger-Weber, EDIP
  - Metallic: (Modified) Embedded atom method ((M)EAM)
  - Van der Waals: Lennard-Jones, Morse
  - Organic molecules: Force fields
- Parametrization different for each system/material







# Empirical potentials for $\text{UO}_2$

(The compulsory example for INSPYRE)

- $\text{UO}_2$ : mostly ionic material with polarisable ions
- Potentials: sum of several terms

Very short range (Ziegler-Biersack-Littmark) for cascades

Short range (SR) term: Buckingham, Born-Mayer-Huggins or Morse

$$V_{SR}(r_{ij}) = A_{ij} \exp(-r_{ij} / \rho_{ij}) - \frac{C_{ij}}{r_{ij}^6}$$

Long range Coulomb interaction

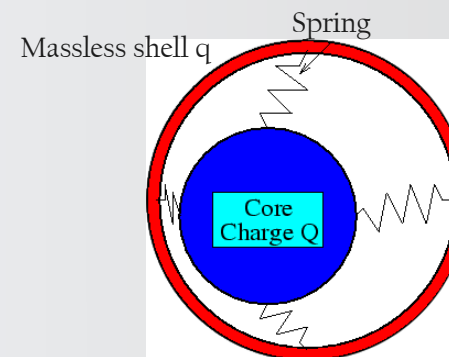
$$V_{Coulomb}(r_{ij}) = \frac{Q_i Q_j}{4\epsilon_0 r_{ij}}$$

- Polarizability can be taken into account through core-shell formalism

Atom: core + shell linked by a spring

Pair interaction between atoms  $i$  and  $j$ :

$$\begin{aligned} & \text{Core}(i) \text{Core}(j) + \text{Core}(i) \text{Shell}(j) + \\ & + \text{Shell}(i) \text{Core}(j) + \text{Shell}(i) \text{Shell}(j) \end{aligned}$$





# Existing potentials for $\text{UO}_2$

(Potentially the state of the art?)

- Pair potentials
- Some core-shell models
- Different potentials: analytic form + parametrization
- Currently no decent charge transfer potential

Interaction	Polarisation	Potential
Buckingham	Rigid	Arima, Sindzingre
Buckingham/Morse	Rigid	Basak, Yamada, Morelon
Fitted	Rigid	Tiwary
Buckingham	Rigid/Shell	Walker
Buckingham	Shell	Grimes

T. Arima *et al.*, J. Alloys. Compd. 400, 43 (2005)

P. Sindzingre *et al.*, J. Phys. C: Solid State Phys. 21, 4017 (1988)

C.B. Basak *et al.*, J. Alloys Compd. 360, 210(2003)

K. Yamada *et al.*, J. Alloys Compd. 307, 10 (2000)

N.-D. Morelon *et al.*, Philos. Mag. 83, 1533 (2003)

P. Tiwary *et al.*, Phys. Rev. B 80, 174302 (2009)

J.R. Walker *et al.*, J. Phys. C: Solid State Phys. 14, L979 (1981)

R.W. Grimes *et al.*, Philos. Trans. R. Soc. Lond. A 335, 609 (1991)





# Molecular dynamics



# Molecular dynamics

(How to move atoms around)

- Once we have a way to calculate the interactions between atoms, we can use molecular dynamics (MD)
- A general way of solving the equations of motion for an N-body system
- Kinematics and Newton's equations applied

$$\frac{d}{dt}(m_i \mathbf{v}_i) = \mathbf{F}_i = -\nabla V$$

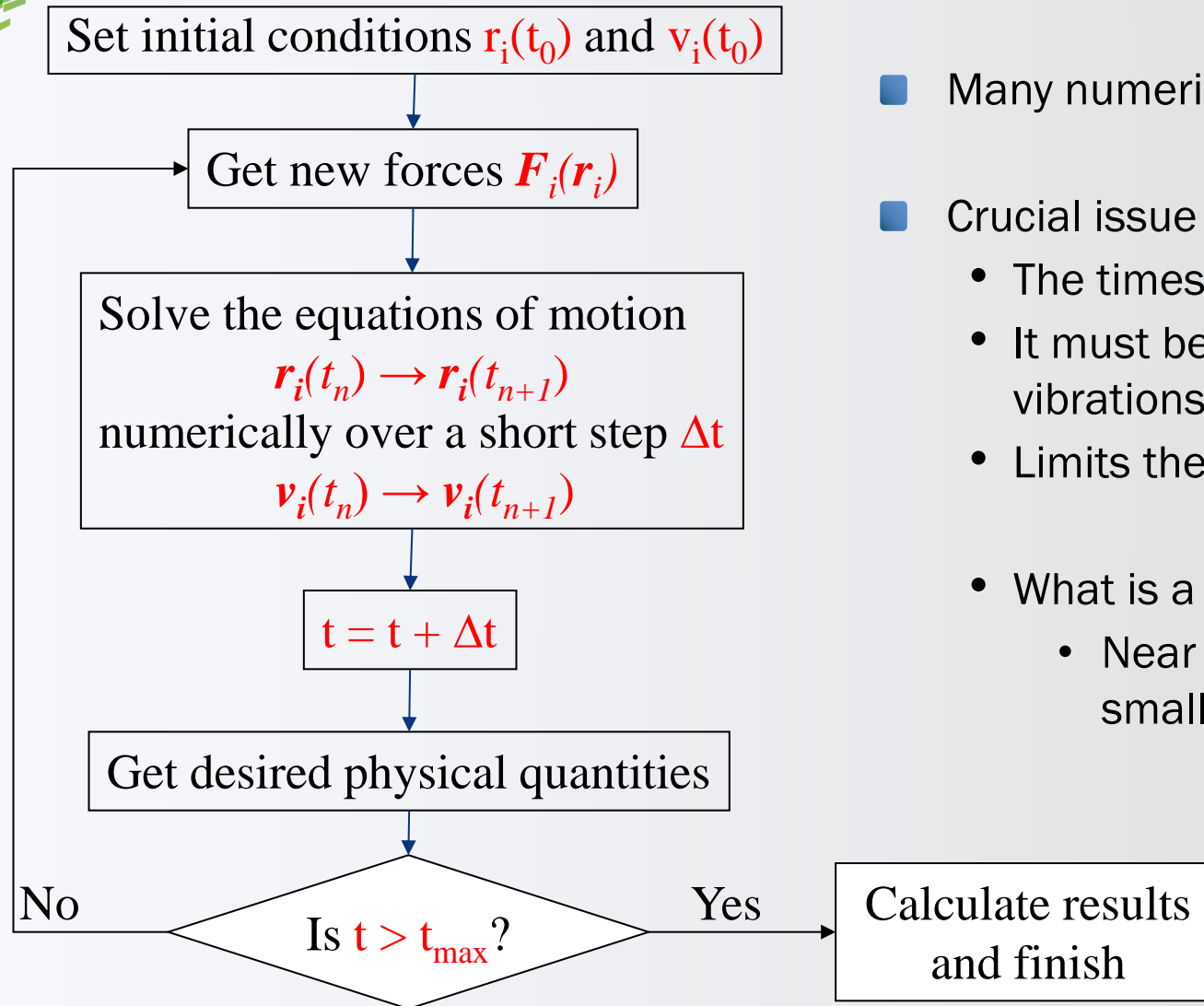
$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i$$

- **Ab initio MD** – forces are directly given by *ab initio* calculations:
  - Hellmann-Feynman theorem. Precise but **slow!**
- **Classical MD** – the true electronic interactions are approximated by an interatomic potential, using some functional form, **fitted** to *ab initio* and experimental data.
  - Low transferability but **fast!**

# Molecular dynamics considerations

(A question of stepping in time)

- Many numerical recipes for MD implementations
- Crucial issue
  - The timestep!
  - It must be small enough to capture typical atomic vibrations, or the results will be unphysical.
  - Limits the achievable simulation time (drastically)
  - What is a reasonable timestep then?
    - Near the femtosecond scale (sometimes much smaller)!



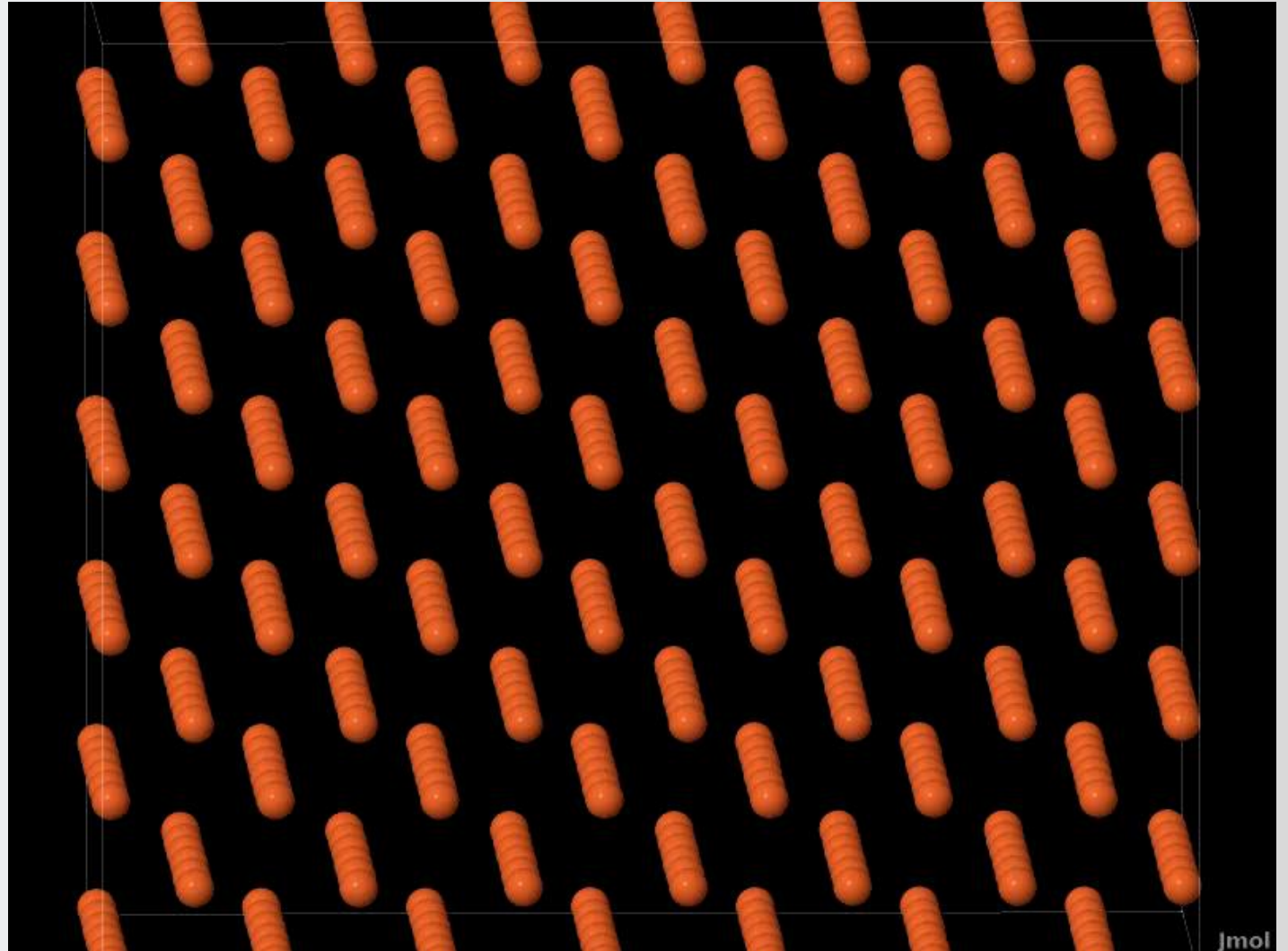


# Example: Threshold displacement damage simulation

*(How hard do we need to hit?)*

## Example:

- MD simulation of threshold damage conditions
- bcc Fe lattice (504 atoms)
- 20 eV impulse near  $\langle 211 \rangle$  direction
- Time step: Varying from 0.1 to 3 fs
- 1.5 ps simulated time
- AIMD: 20.000 core-hours
- CMD: 6 core-seconds





## Partial conclusions

- Atomic scale simulations can give a lot of important information for
  - Direct comparison with experiment
  - Input data for larger scale methods
- Electronic structure:
  - predictive
  - transferrable
  - very expensive
- Empirical potentials:
  - very fast
  - entirely dependent on fitting data
  - low transferrability
- Molecular dynamics is a method of moving atoms
- Can use either electronic structure or empirical potentials as force field





# Beyond the atomic scale

(in baby steps)

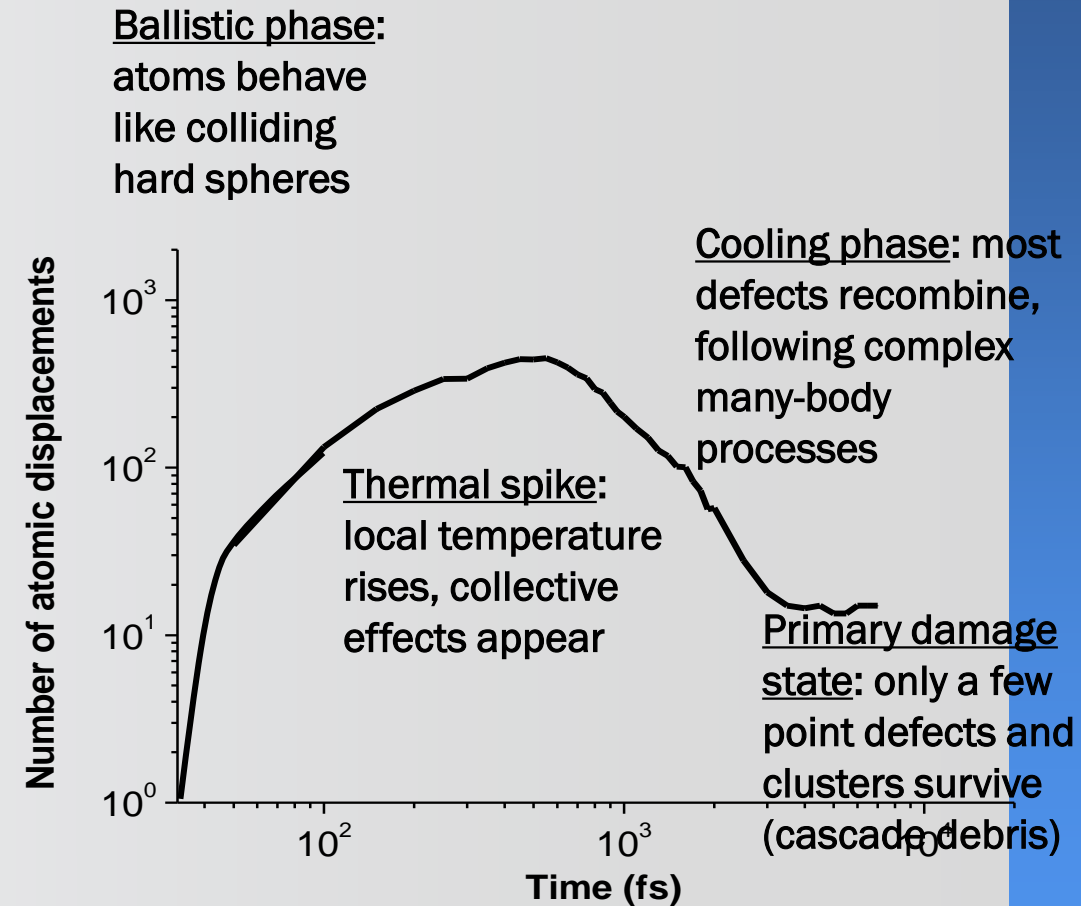




# Diffusion

(What really matters in the long term)

- Molecular dynamics can be used to evolve a system of atoms the "real" way
- MD is limited to ns time (or  $\mu\text{s}$  at some rare conditions)
- Microstructure evolution (post cascade dynamics) is generally driven by *diffusion*
- Diffusion is the large scale effect of atomic scale jumps
- Defect diffusion, atomic diffusion (through defect mechanisms): essentially all diffusion is driven by defect jumps
- How can we **track** defect jumps without explicitly treating all the vibrations that **lead** to the jump transitions?



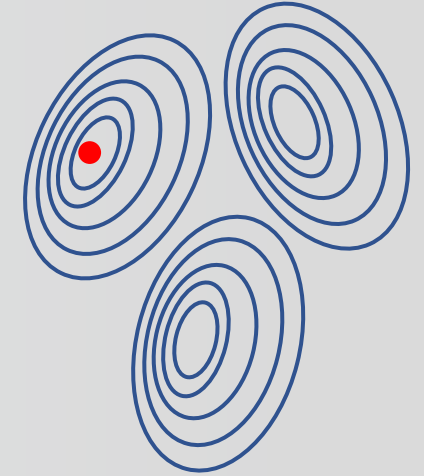


# Kinetic Monte Carlo

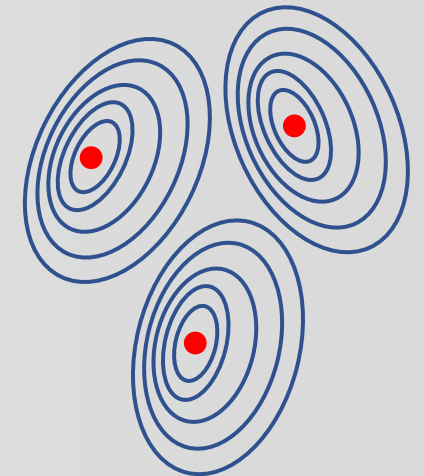
*(Playing dice with atoms)*

- Kinetic Monte Carlo to the rescue!
- Diffusive transitions are generally rare events: a jump only occurs after many, many vibration periods, or "attempts"
- The system suffers memory loss, it doesn't remember where it came from -> a Markov chain, with Poisson statistics!
- The probability of the system staying in a certain basin is:  
$$P_{\text{stay}}(t) = \exp(-r_{\text{tot}}t),$$
where  $r_{\text{tot}}$  is the total rate for escape from the particular state.

Molecular dynamics  
(what really happens)



Kinetic Monte Carlo  
(how we could model it)





# The KMC method

Each pathway has its own rate constant  $r_{ij}$ , thus the total escape rate is:

$$r_{\text{tot}} = \sum_j r_{ij}$$

The staying probability  $P_{\text{stay}}(t)$  is usually not the most interesting quantity in a simulation.

$$P_{\text{stay}}(t) = e^{-r_{\text{tot}}t}$$

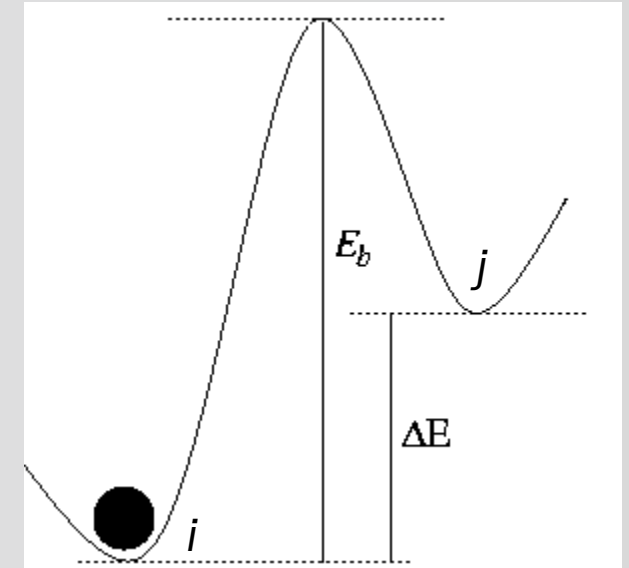
From the definition of  $P_{\text{stay}}(t)$  we can deduce the probability distribution  $P(t)$  for the time of first escape:

$$\int_0^{t'} P(t) dt = 1 - P_{\text{stay}}(t')$$

$$P(t) = r_{\text{tot}} e^{-r_{\text{tot}}t}$$

and the average time  $\Delta t$  for escape will be:

$$\Delta t = \int_0^{\infty} t P(t) dt = \frac{1}{r_{\text{tot}}}$$



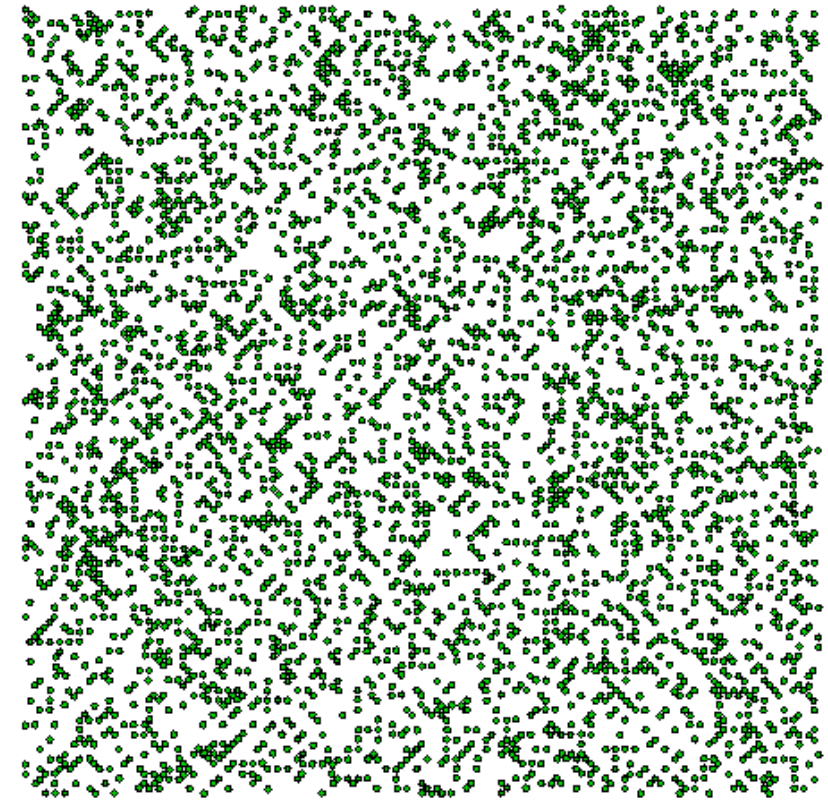
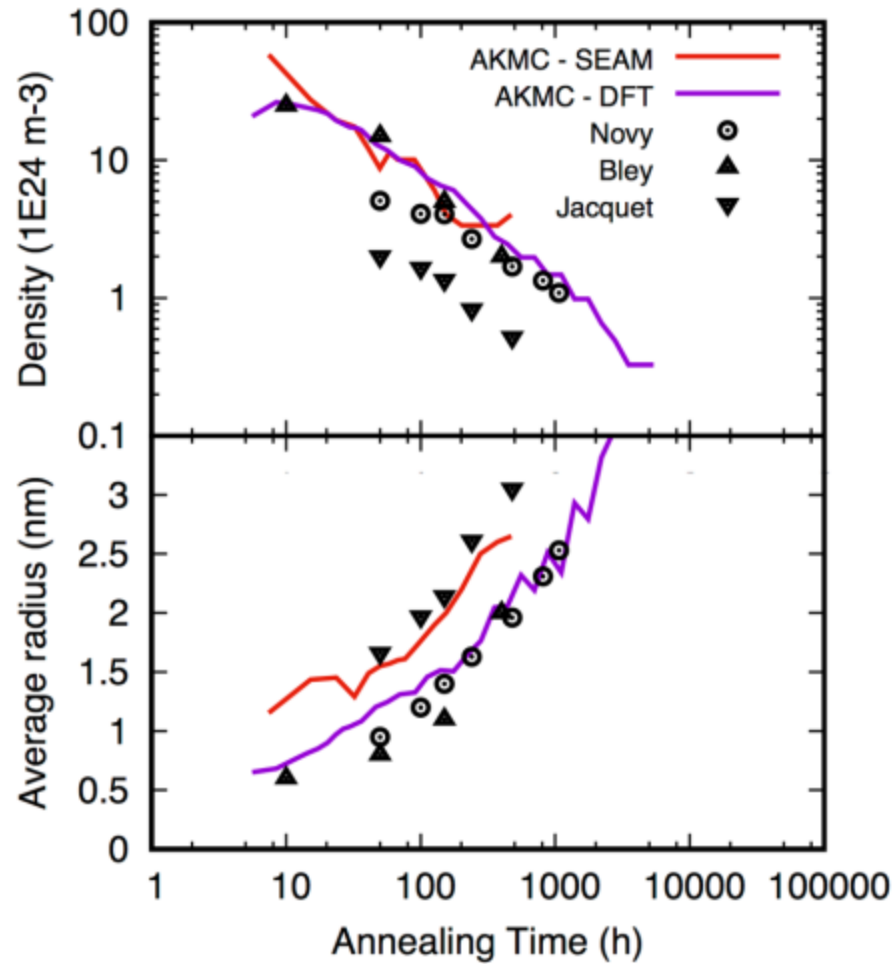
$$r_{ij} = \nu e^{-E_b/k_B T}$$

Barrier energy and attempt frequency can be had from electronic structure or empirical atomistic methods!



# KMC example: homogeneous nucleation in A-B alloy

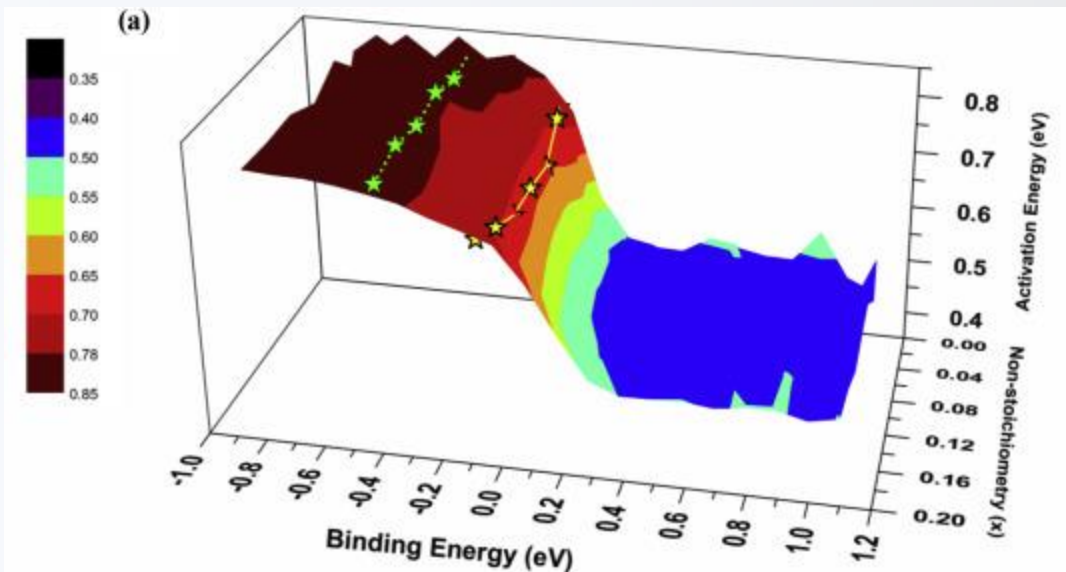
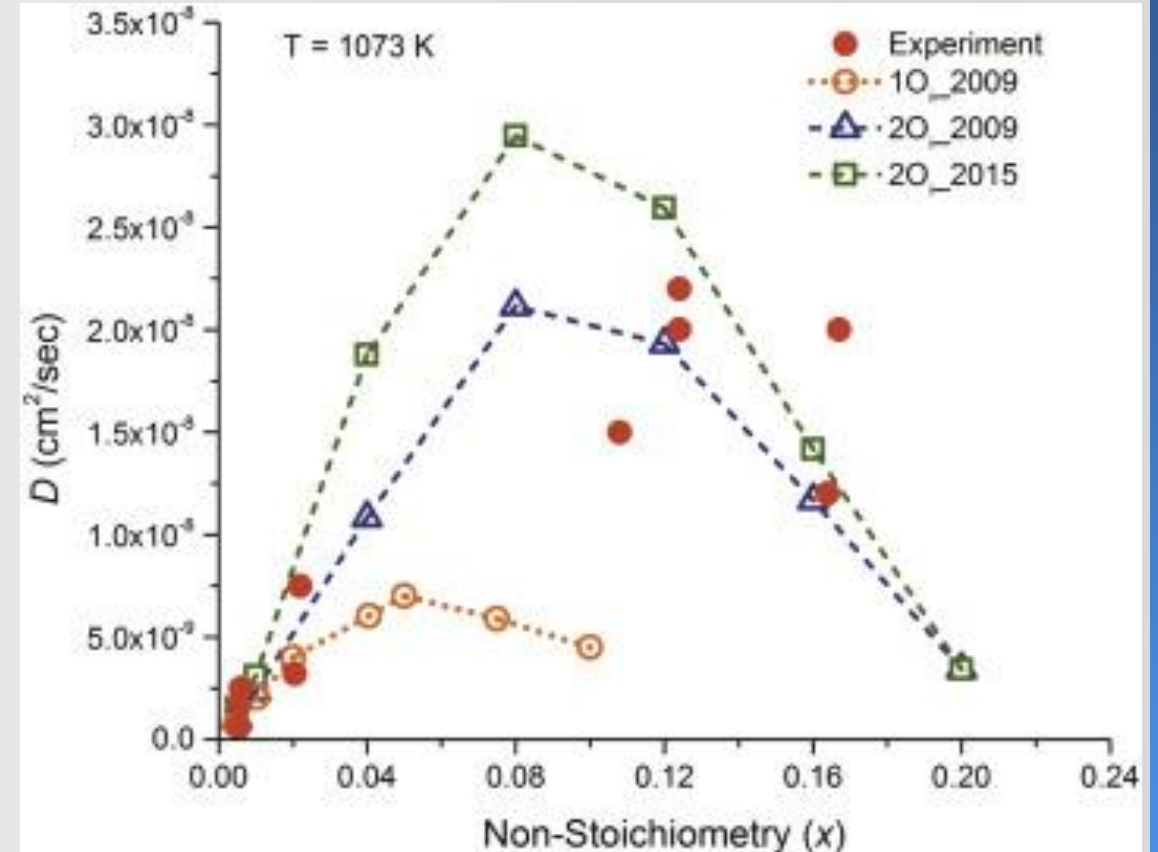
Frame 001 | 15 May 2006





# Oxygen diffusion in $\text{UO}_{2+x}$

- Behera et al studied oxygen diffusion in  $\text{UO}_{2+x}$  using KMC
- Three models, simplest one seems not to capture diffusion properly
- Results depend sensitively on binding energy of di-interstitial O



Behera et al, JNM 472 (2016) 89



# Beyond the atomic scale

(for real)

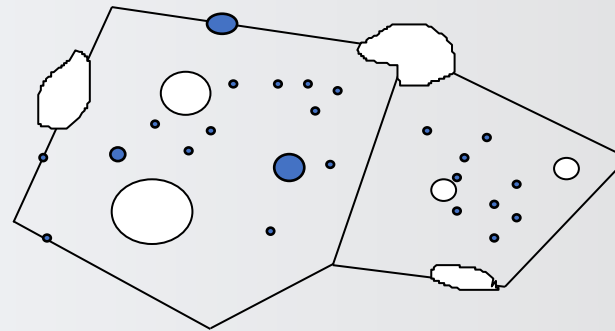




# Mesoscale modeling

(Atoms? We don't need no stinkin' atoms!)

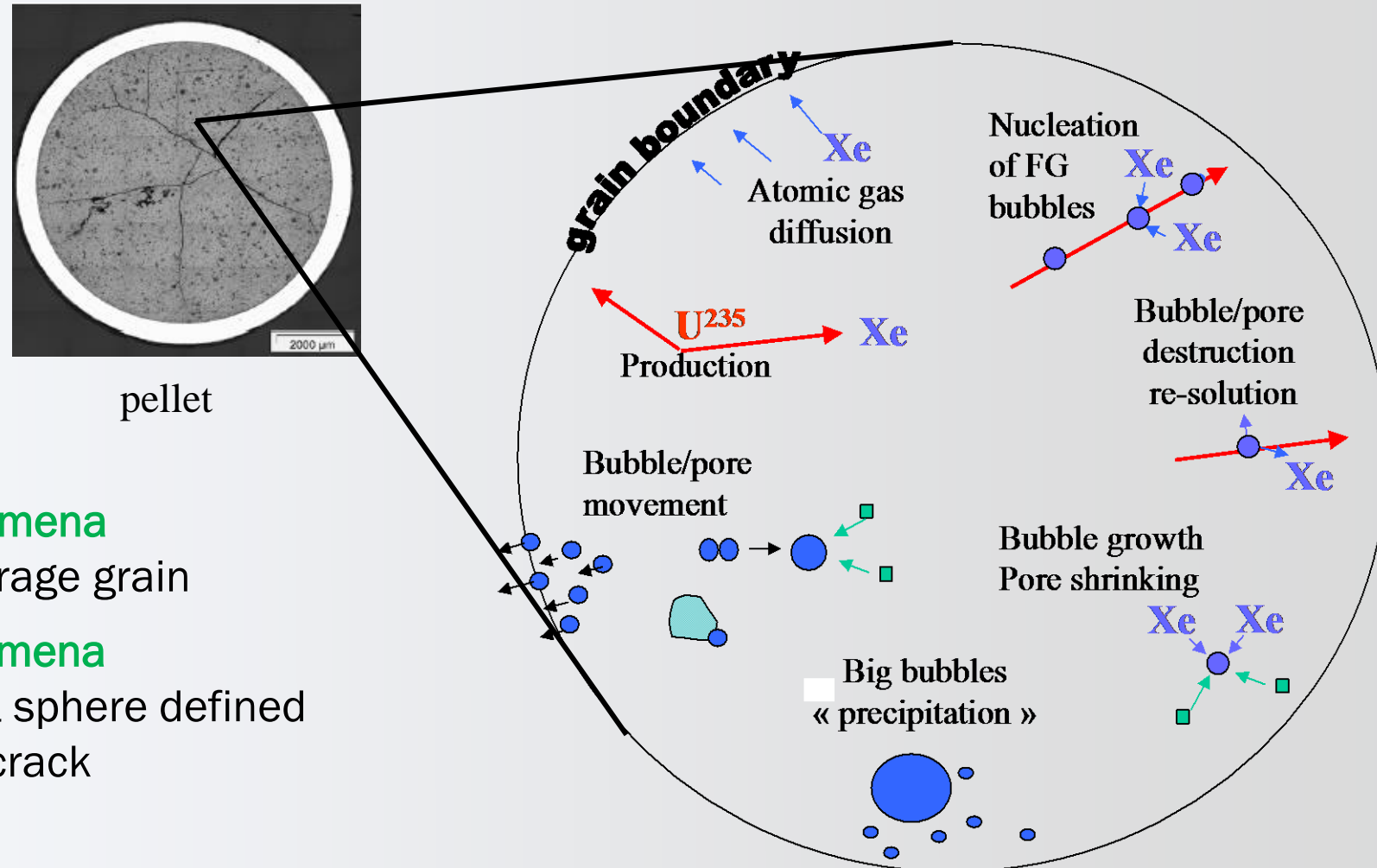
- Mesoscale modelling aims at describing the evolution of microstructure under in-pile or ion irradiation
- In particular, evolution of the populations of point defects, defect clusters and fission gas atoms and bubbles
- Defect populations control a large number of properties of material and macroscopic evolution, e.g. nucleation and growth of bubbles and dislocation loops, porosity, re-densification, radiation enhanced diffusion
- Scales considered: one or several grains, macroscopic times



- At this scale both intra- and intergranular diffusion is active



# Mesoscale modeling of fission gas behaviour



## ■ Intragranular phenomena

Modelling of an average grain

## ■ Intergranular phenomena

- Use of an equivalent sphere defined by a free surface / crack

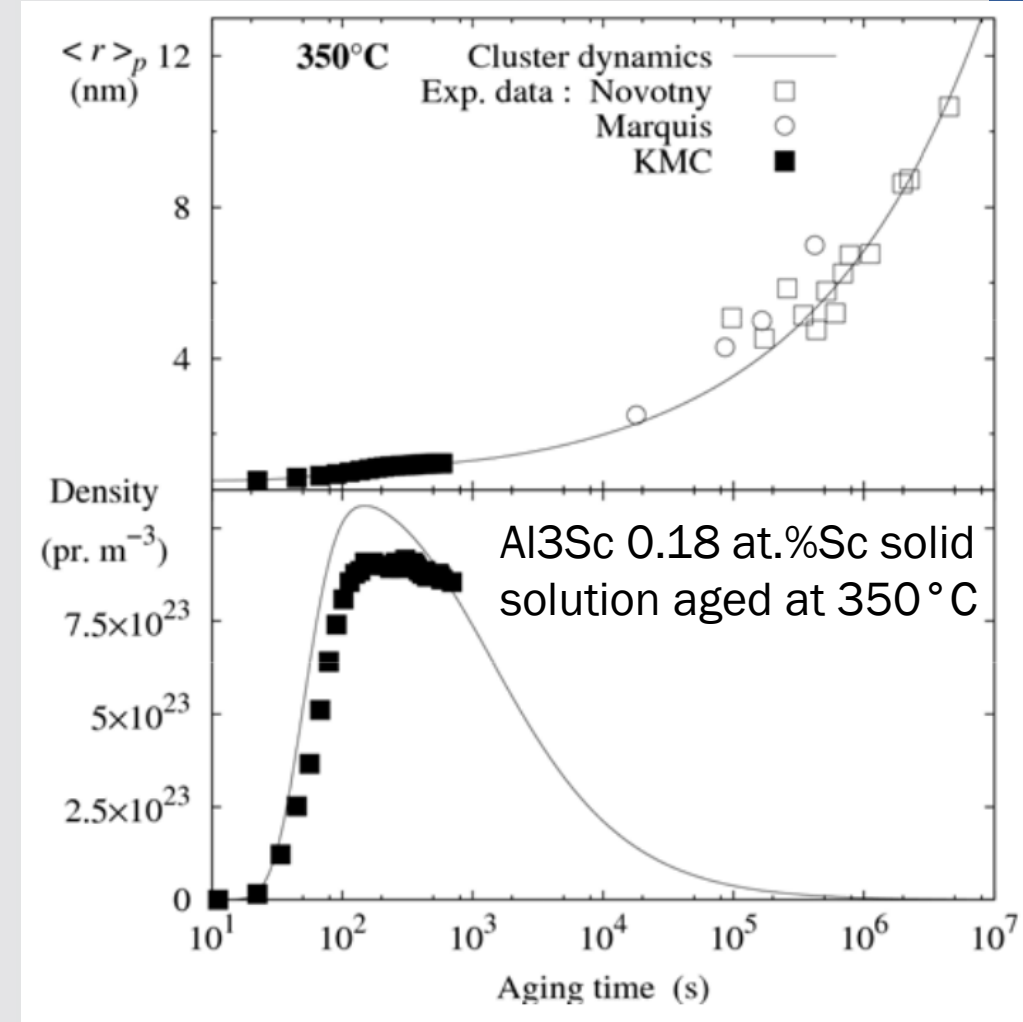




# Mesoscale methods

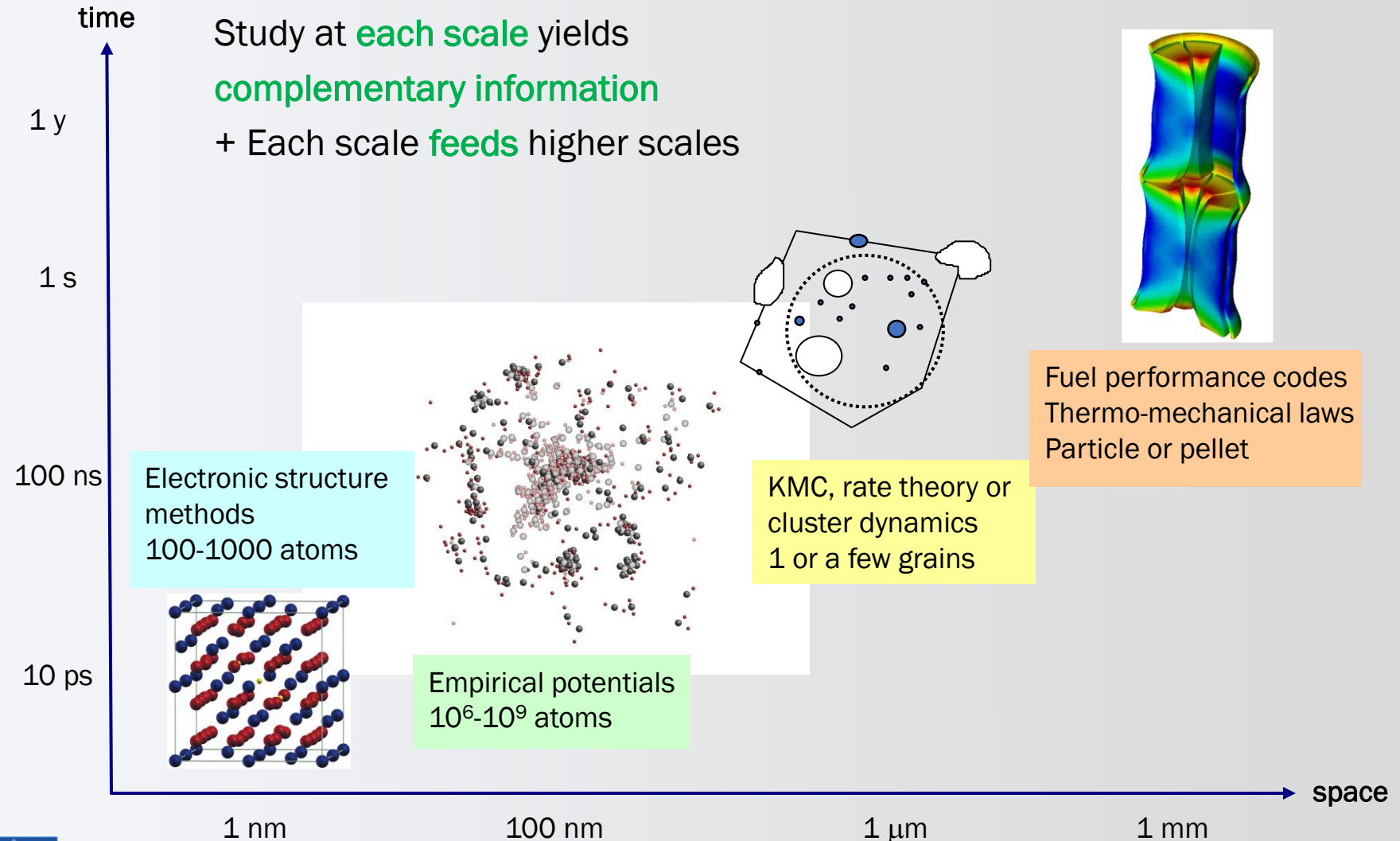
(I wish we had more time...)

- Kinetic Monte Carlo
  - Lattice KMC (what we talked about – actually atomistic)
  - Object KMC (no atoms, only defects and other objects)
- Rate theory methods, including cluster dynamics
  - Forget spatial correlations (everything governed by concentration equations)
- Phase fields, FEM, etc
  - There are many levels of methods on the way up to component scale, if you want/need to





# Modelling of multiscale phenomena



# Thank you for your attention



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