Classical molecular dynamics simulations of condensed matter

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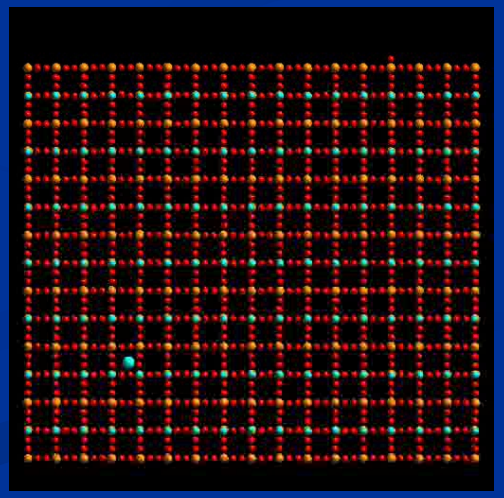
Classical molecular dynamics simulations

1. Overview of the method
2. Interatomic forces
3. Details and tricks of MD

4. Data analysis
5. Examples from recent science

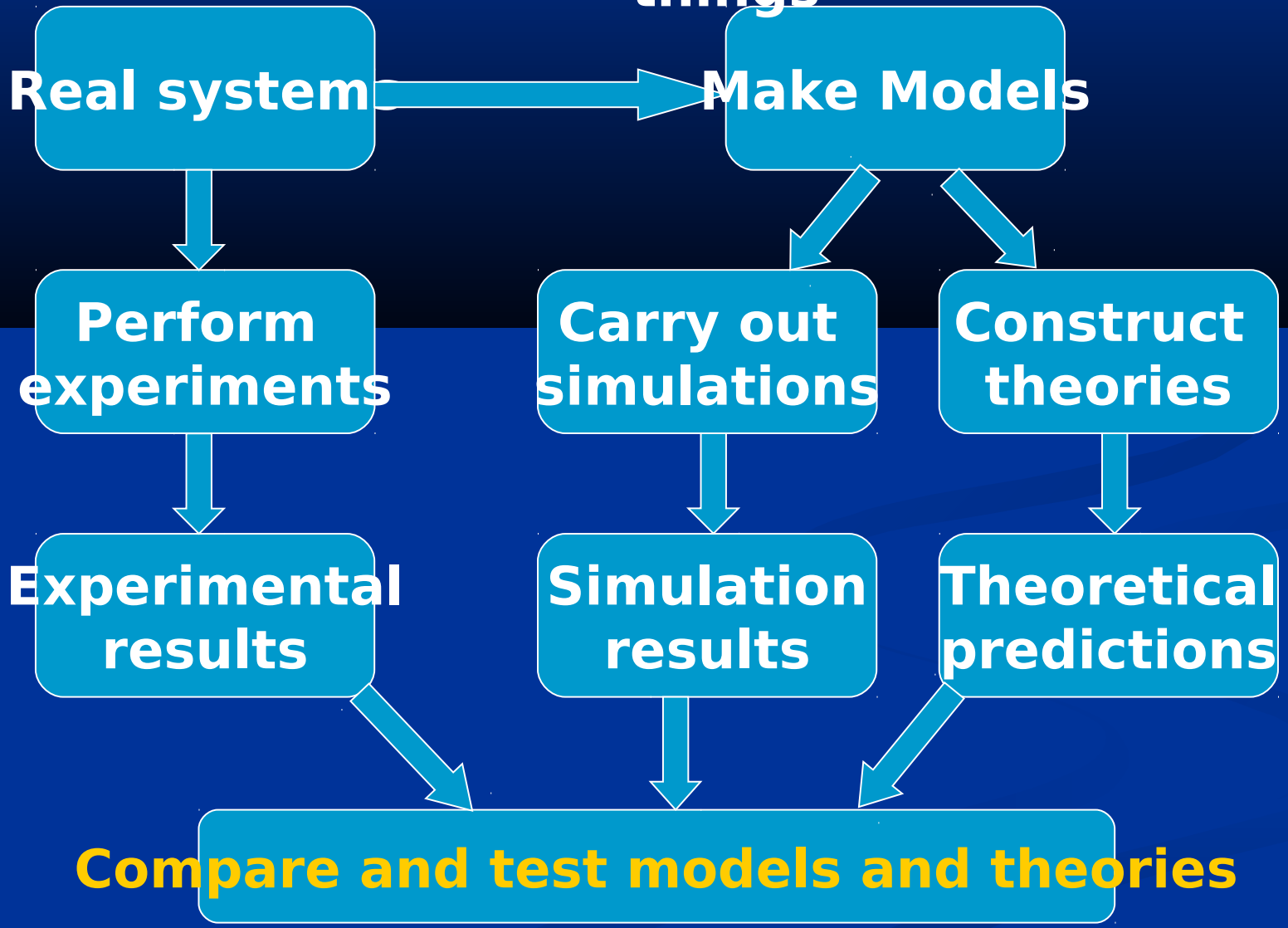
Short history

- The need to simulate liquids (Allen and Tildesley "Computer simulation of *liquids*")
- First simulation done in 1953 in Los Alamos
- A direct route from the microscopic details of a system to macroscopic properties
- Understand and interpret the experiments
- Academic and technological importance



- Complement the experiments, when it is impossible to carry out experiments at extreme conditions or access very short length scales and time scales

How it works in a grand scheme of things



Main idea of Molecular Dynamics simulations

$$\vec{F} = m\frac{\mathrm{d}v}{\mathrm{d}t}$$

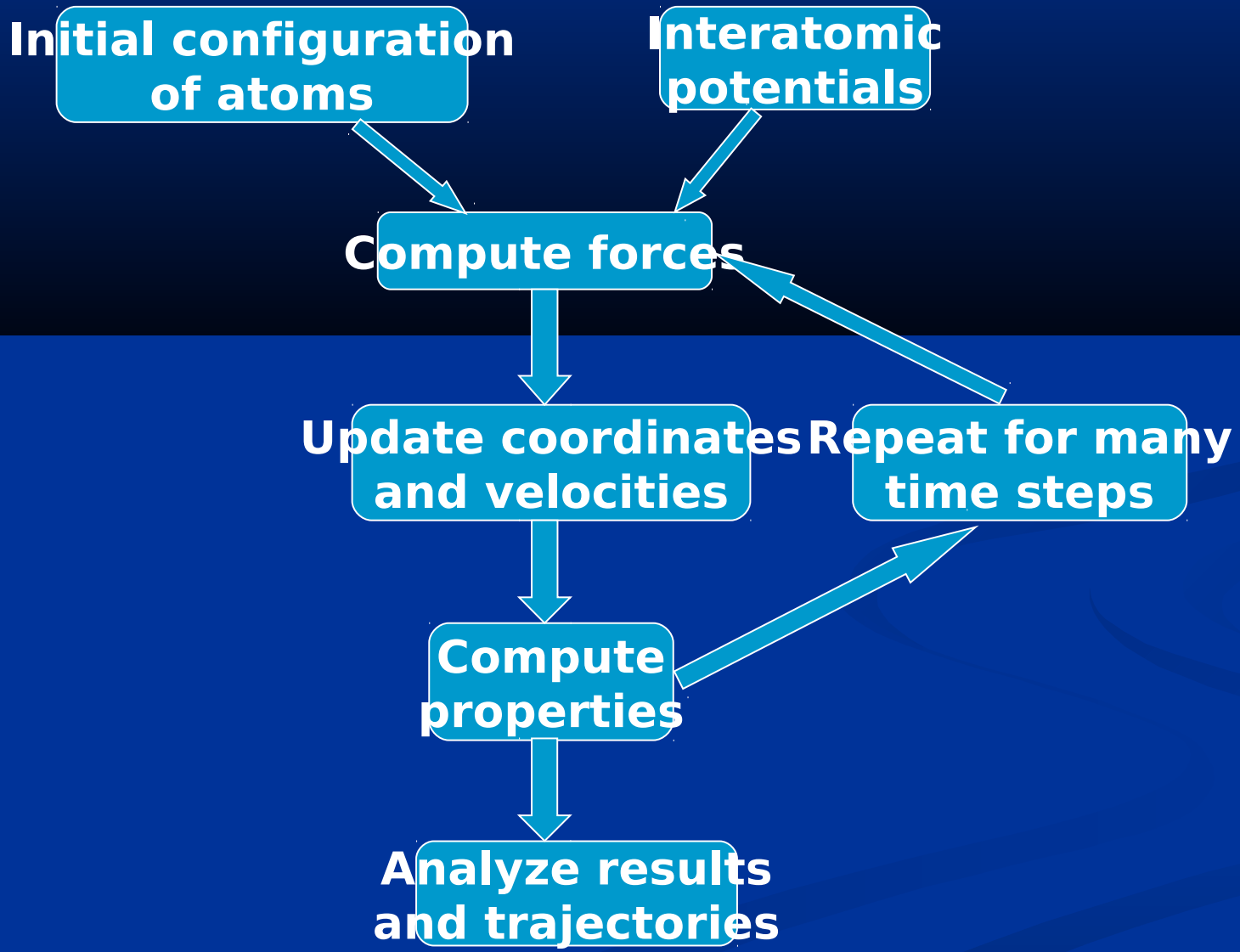
$$\vec{F} = -\frac{\partial U(\vec{r})}{\partial r}$$

- Solve these equations approximately, by substituting differential equations by finite difference equations:

$$\vec{F} = m\frac{\mathrm{d}v}{\mathrm{d}t} \approx m\frac{\Delta v}{\Delta t} \Rightarrow \Delta\vec{v} \approx \frac{F\Delta t}{m} \Rightarrow \vec{v}_{new} = \vec{v}_{old} + \frac{F\Delta t}{m}$$

- For $\Delta t \to 0$, the above is exact. Acceptable Δt is a tradeoff between efficiency and precision, dictated mostly by conservation laws (mainly energy)
- Δt should be much smaller than a typical period of atomic vibrations of 0.1 ps. A typical empirical value of timestep is

A typical MD algorithm:



A typical MD algorithm

- There are different algorithms for calculating the trajectories
- They vary in accuracy, drift and noise
- Verlet is a popular, good quality integration algorithm:

$$r(t+\Delta t) = r(t) + \Delta t v(t) + \frac{1}{2}\Delta t^2 a(t) + \ldots$$

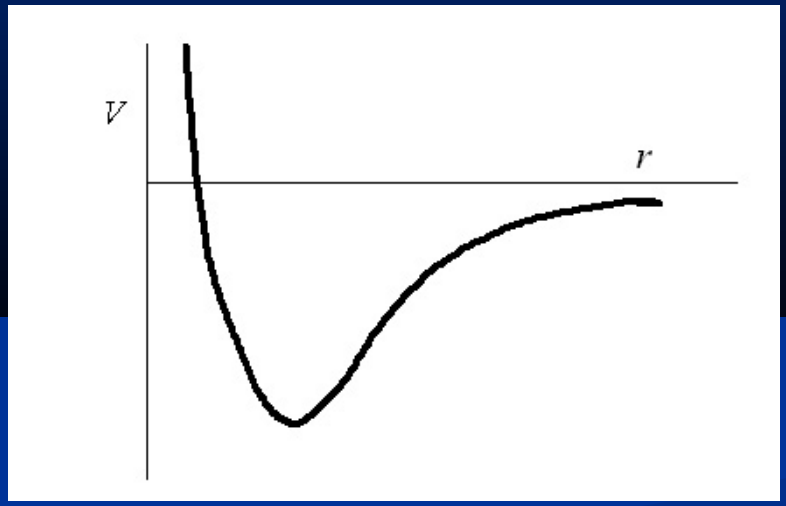
$$r(t-\Delta t) = r(t) - \Delta t v(t) + \frac{1}{2}\Delta t^2 a(t) - \ldots$$

$$r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \Delta t^2 a(t) + O(\Delta t^4)$$

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + O(\Delta t^2)$$

Empirical potentials: a brief introduction

$$\vec{F} = -\frac{\partial U(r)}{\partial r}$$

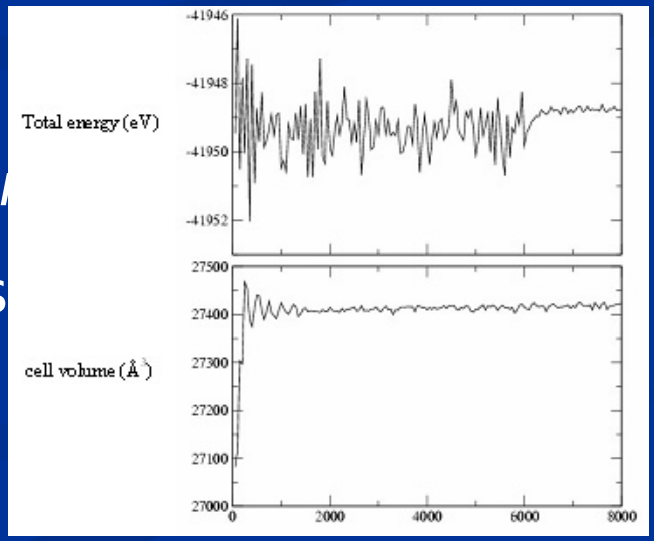


(r) is given as an input in MD simulations to describe interatomic f

ill talk about potentials in more details later on in the course

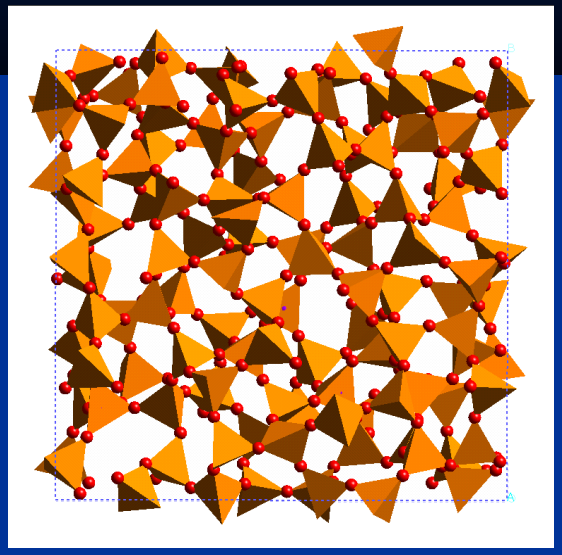
Stages of MD simulation: initialisation, equilibration, production

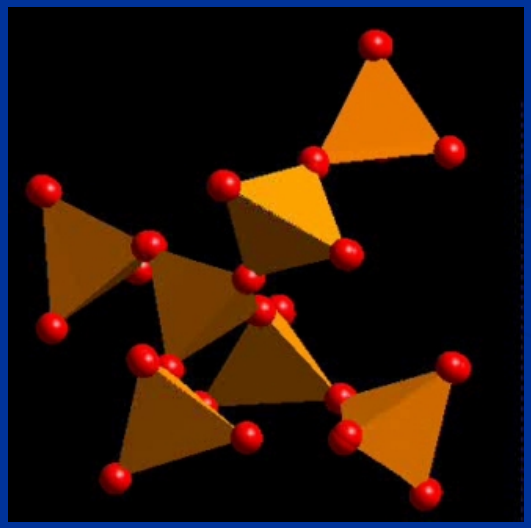
- Initial structure (collection of atomic coordinates) is a standard input
- Initial velocities are given, often with a Maxwellian distribution corresponding to a specified temperature.
- Initial velocities conform to $\vec{P} = \sum_{i=1}^{N} m_i \vec{v}_i = 0$
- The structure evolves to the *equilibr*
- After this we reach the *production* s and collect the data we need

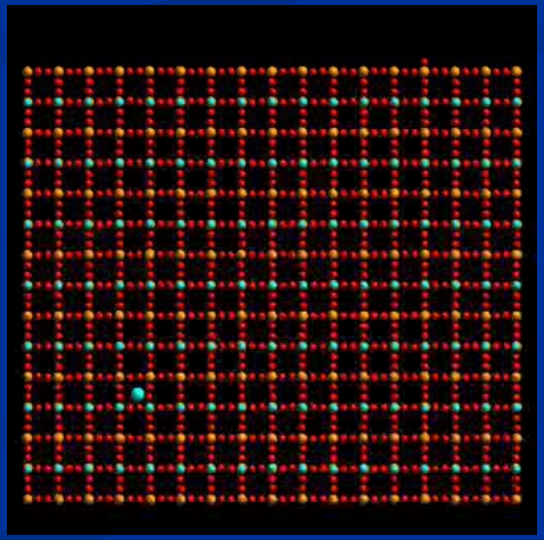


What can we calculate?

- Structure
- Dynamics
- Emergent/collective behaviour







The actual code

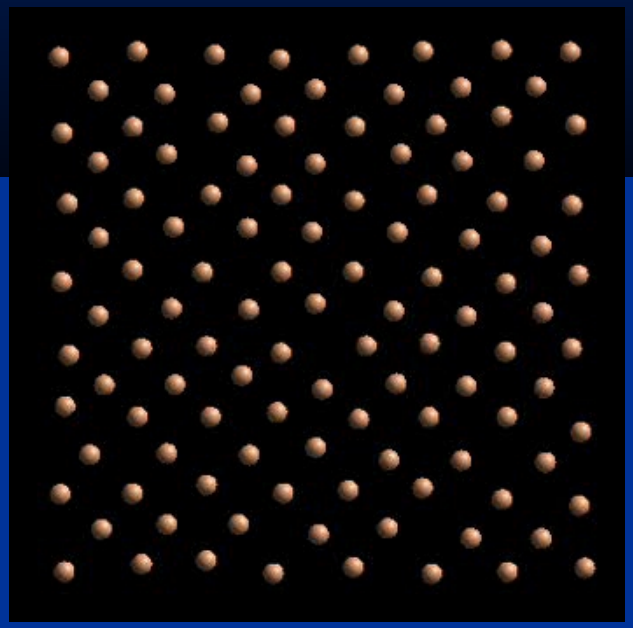
- There was a time when everyone would write their own MD code…

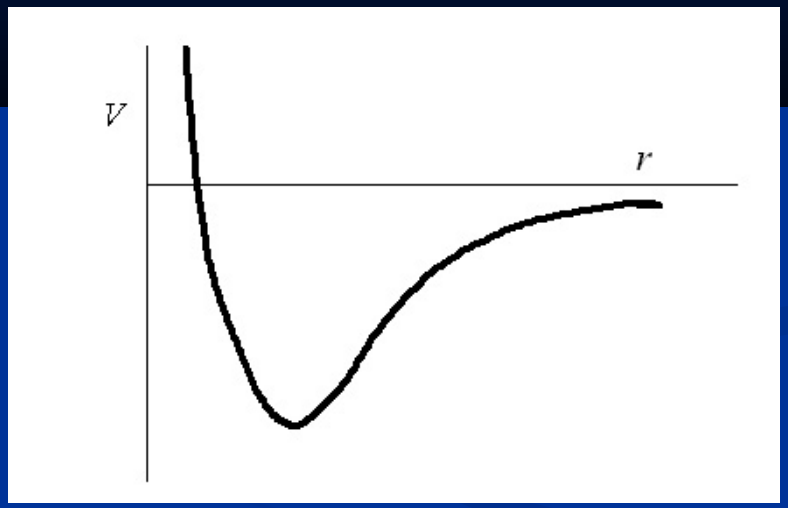
- Nowadays there are a number of good quality, off-the-shelf, codes. DL_POLY is arguably the top classical MD package around (and it's free!). An online version of the manual is at:

http://www.cse.scitech.ac.uk/ccg/software/DL_POLY

- We are using DL_POLY, arguably one of the best around

Interatomic interactions





$$\vec{F} = -\frac{\partial V(\vec{r})}{\partial \vec{r}}$$

Interatomic forces

- The interatomic interaction is due to the electromagnetic (electrostatic) forces

- Quantum-mechanical nature of interatomic interactions (i.e. why is H atom stable?)

$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(r) \right)\psi = E\psi$$

- *V(r)* is the Coloumb interaction.

- For many atoms, it also includes quantum-mechanical terms related to quantum statistics (e.g. exchange energy term)

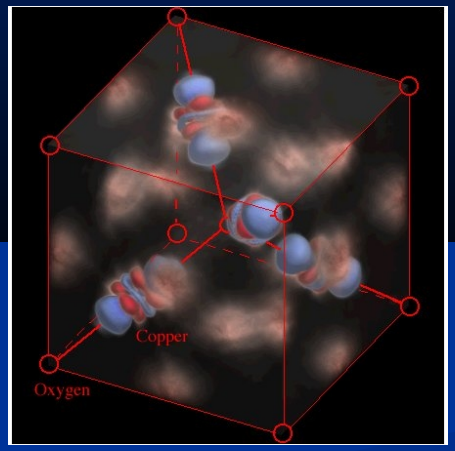
- The change in *V as a result of change of r gives rise to a force that can be calculated*

Interatomic forces

- Why not do full quantum-mechanical calculations?
- Empirical potentials give worse accuracy but access to larger system sizes and longer simulation times
- ~100 atoms in ab-initio (density functional theory methods) in terms of size and several tens of ps in terms of time
- ~100 millions of atoms in classical MD simulations in terms of size and up to ms in terms of time
- Many collective and emergent phenomena can only be studied using classical MD, because they involve many atoms

MD empirical potentials

Forget about quantum mechanics,
electrons,
and their complex distribution

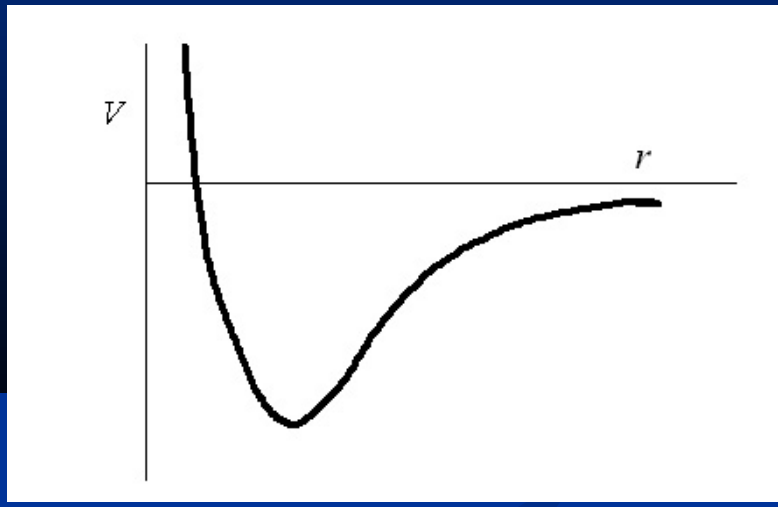


Think balls (points) interacting via a given empirical potential

MD empirical potentials

A typical empirical potential often includes:

Lennard-Jones $V(r)=A/r^{12}-B/r^6$ or Buckingham-type potentials $V(r)=A*\exp(-r/\rho)-B/r^6$



and Coloumb interactions $V(r)=q_1 q_2/r$

- Strong short-range repulsion (Pauli principle)
- Weaker attraction. Can include Van del Waals dipole interactions:

For neutral atoms, $q=0$. Also, $\langle p_1\rangle=\langle p_2\rangle=0$ in average for non-interacting atoms.
However, a fluctuating dipole on atom 1 generates electric field $E\sim p_1/r^3$, which induces an instantaneous extra dipole on atom 2 $\Delta p_2\sim E\sim p_1/r^3$. The additional energy is $V\sim -p_1\Delta p_2/r^3\sim -1/r^6$

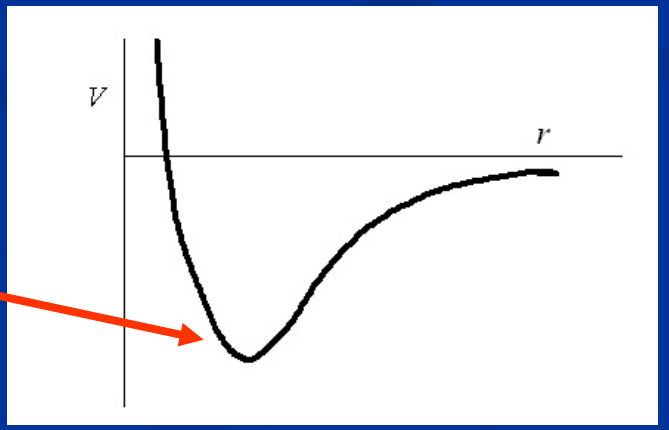
- Van del Waals interactions are weak, and come in addition to

MD empirical potentials

At very close approach (r<0.5 Å), “screened Coloumb potential” generally applies:
$V(r) \sim \exp(-r/\rho)/r$, where ρ is the screening radius

Encountered at either very high temperatures (T>100,000 K) or in radiation damage

- We are often interested in small-amplitude vibrations anyway, where harmonic approximation applies



MD empirical potentials

Lennard-Jones $V(r)=A/r^{12}-B/r^{6}$ or Buckingham-type potentials $V(r)=A*\exp(-r/\rho)-B/r^{6}$

and Coloumb interactions $V(r)=\alpha q_1 q_2/r$

with parameters and charges chosen to reproduce material's properties

Two main methods:

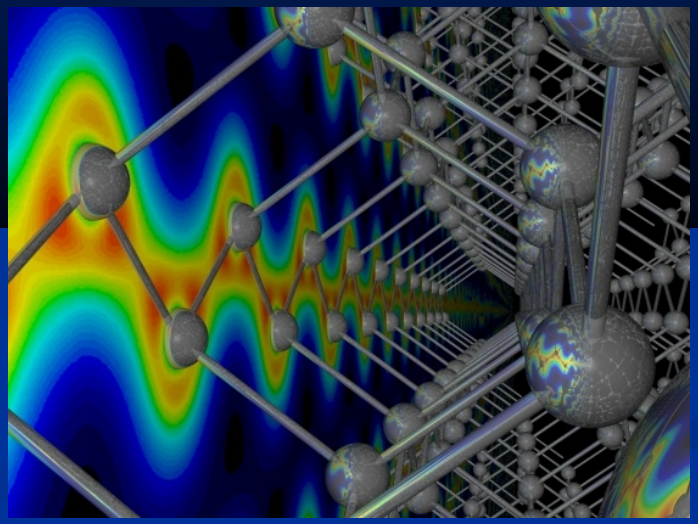
- Fitting to experimental data (structure and elasticity)
- Fitting to the results of quantum-mechanical calculations (either to structure and elasticity, or to the calculated potential energy surface)

Good empirical potentials give ~1% agreement with experimental lattice constants and ~10% agreement with bulk modulus

Selecting the parameters can depend on the nature of the chemical bond in a material

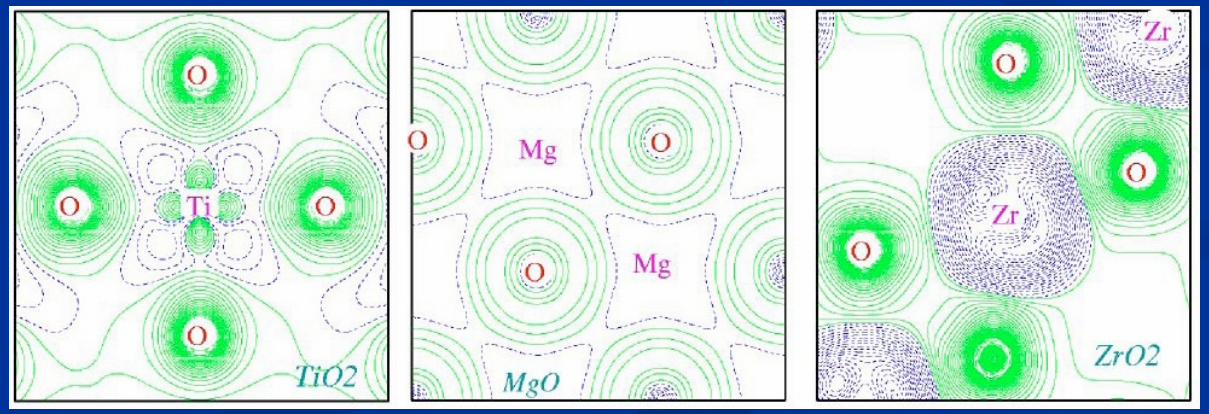
Main types of interatomic interactions and bonds

- Charge transfer and electronegativity (Pauling)
- Ionic (MgO, NaCl)
- Covalent (Si, C)
- Most materials are mixed



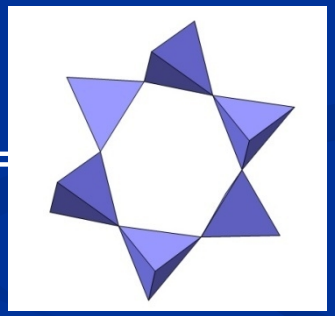
Pauling and Phillips ionicity measures
SiO_2 is ~50% ionic and ~50% covalent

- Metallic (Fe, Ni)

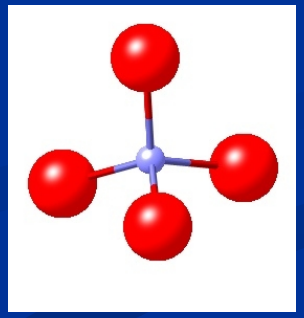


Main types of interatomic interactions and bonds

- Depending on the nature of the chemical bond, charges can be added or adjusted in the force field of empirical potentials
- No charges for Si or Ge
- Full (formal) charges for MgO or NaCl q=±1
- Partial charges for SiO2 , q_{Si}=2.4, q_O=

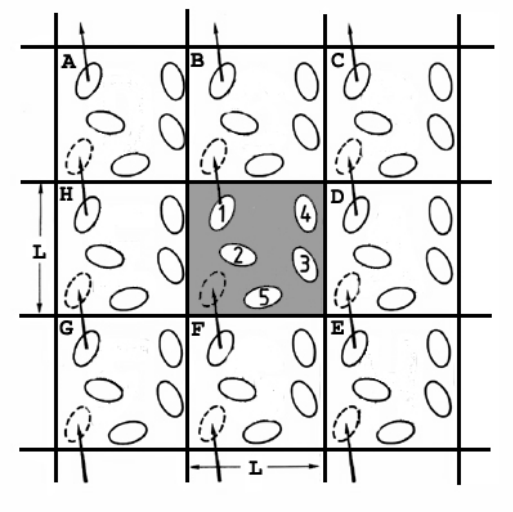


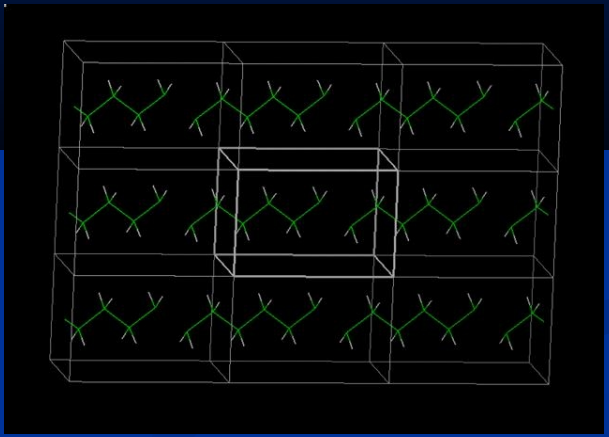
- 3-body forces can be used to reflect covalency (e. g. in Si): $V(\beta)=1/2*k*(\beta-\beta_0)^2$



Periodic boundary conditions

Why have periodic boundaries?





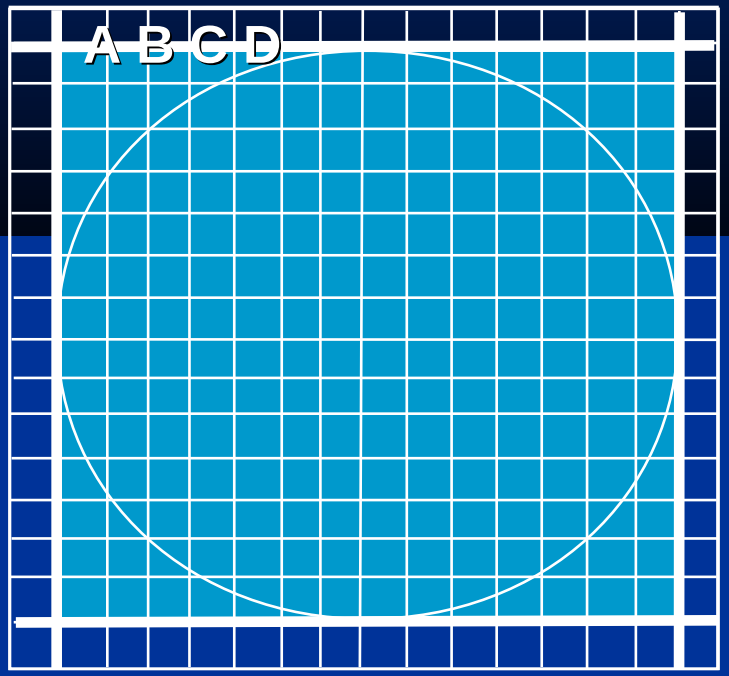
Running in parallel

Two popular strategies:

1. Replicated data strategy

2. Domain decomposition strategy

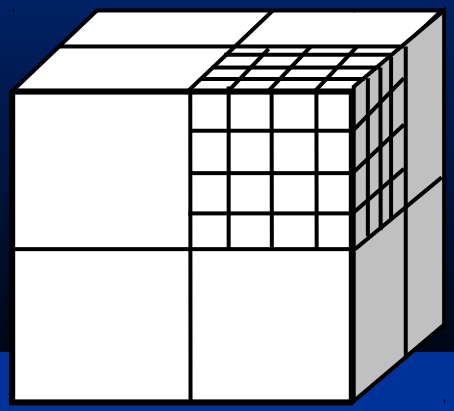
Replicated data strategy

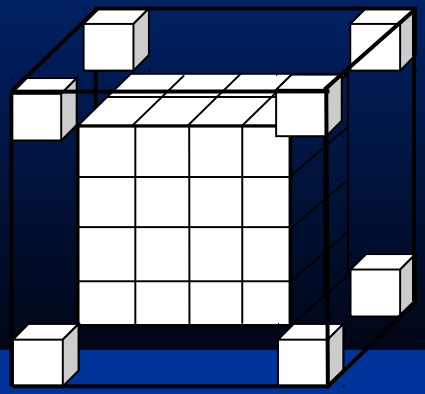


Each processor sees the whole system

Each processor calculates a particular type of force (LJ, Coloumb etc)

Domain Decomposition Strategy

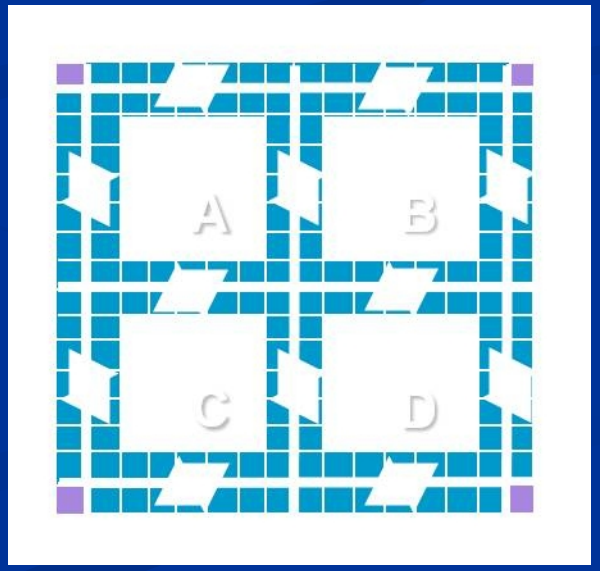




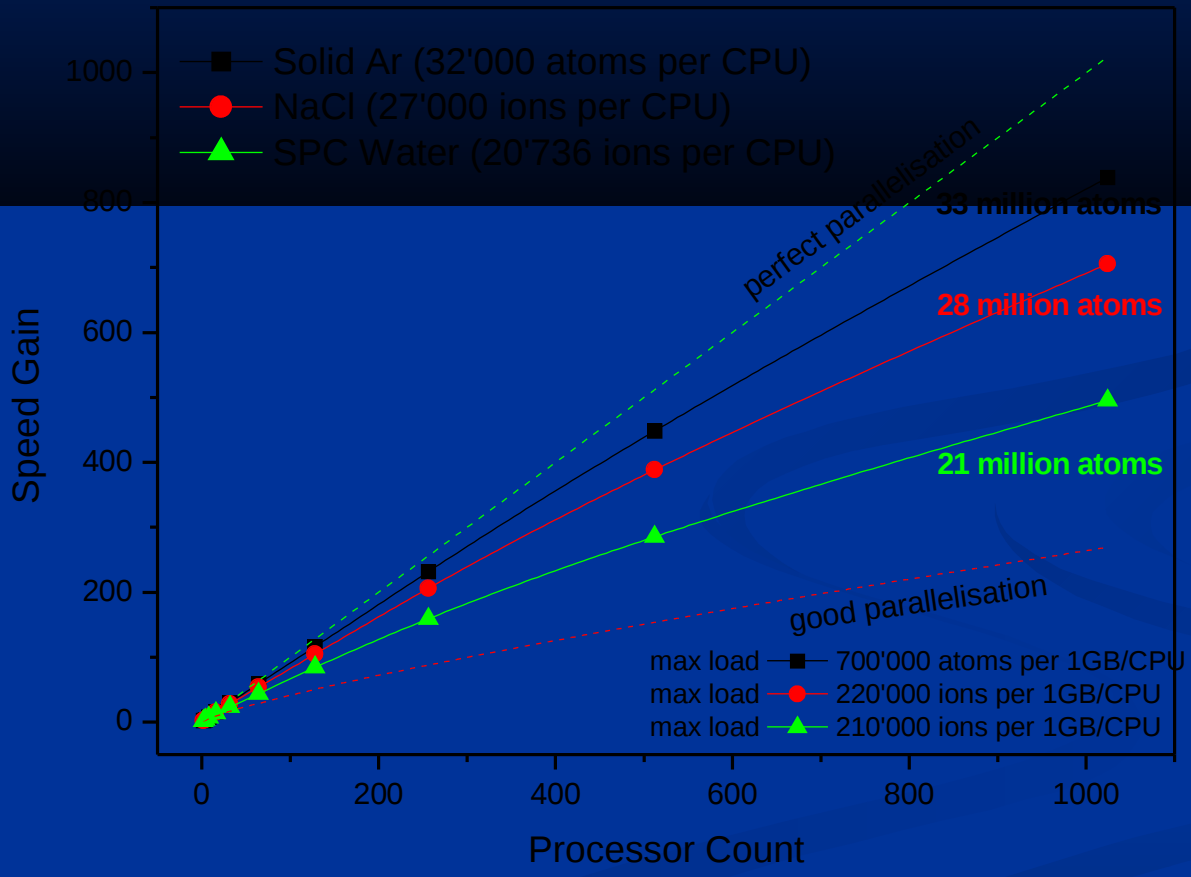
Each processor simulates a geometrically different part of the system (forces, velocities, positions) **independently**

Processors communicate through the boundaries

Very well suited for very large systems



Parallelisation efficiency



MD simulations of very large systems

(stimulated by large systems in radiation damage)

300,763,000 NaCl with full electrostatics evaluation on 1024 CPU cores

Timestep time ≈ 60 seconds (1 second on the new HPC with 16 thousands of parallel processors)

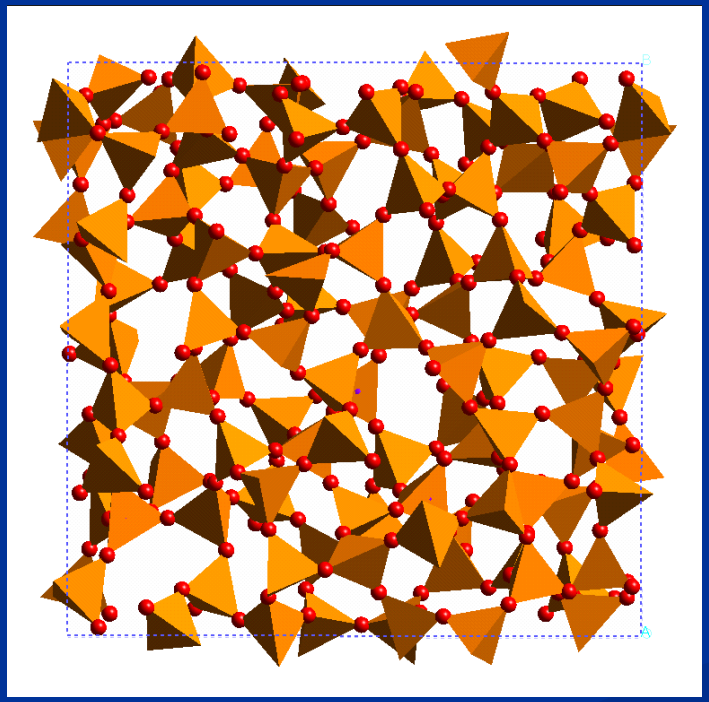
(world record by a general MD package)

~1 billion atoms on 16,000 parallel processors, system size approaches one micrometer !

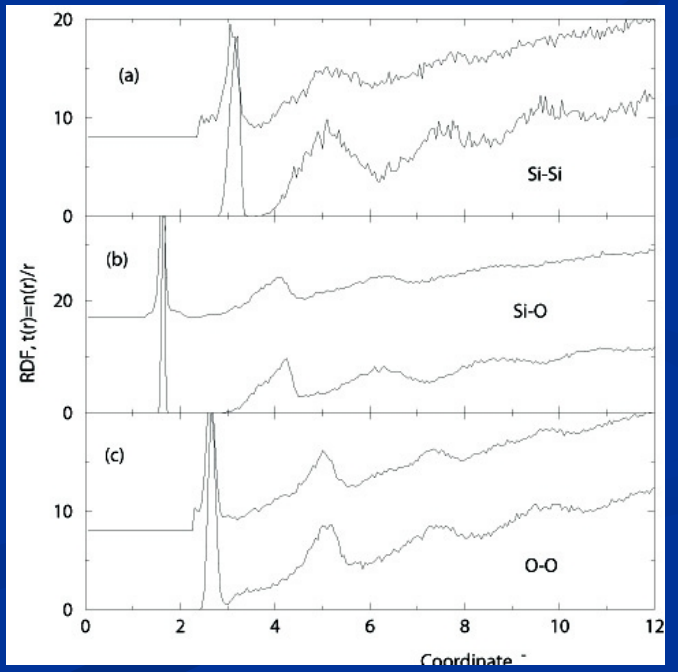
MD simulations meet many important effects and experiments at this length scale (eg microcracks, composite materials, interfaces, proteins, biomolecules)

What can we calculate?

- Structure
- Dynamics
- Emergent behaviour

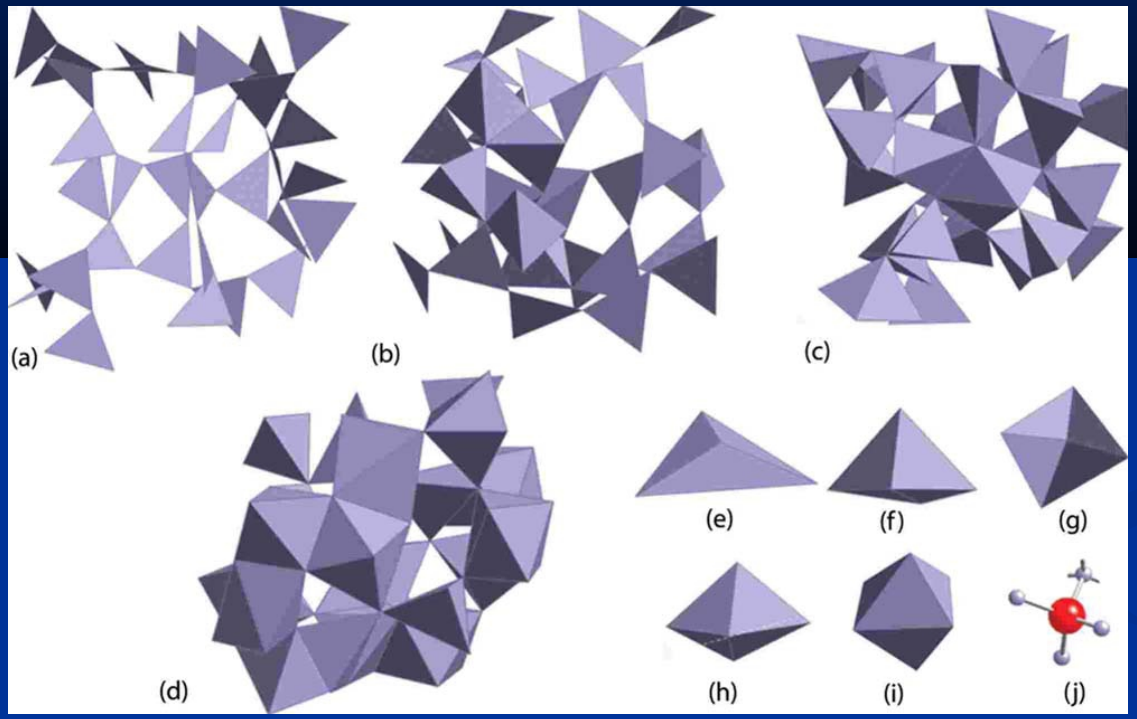


Radial distribution functions

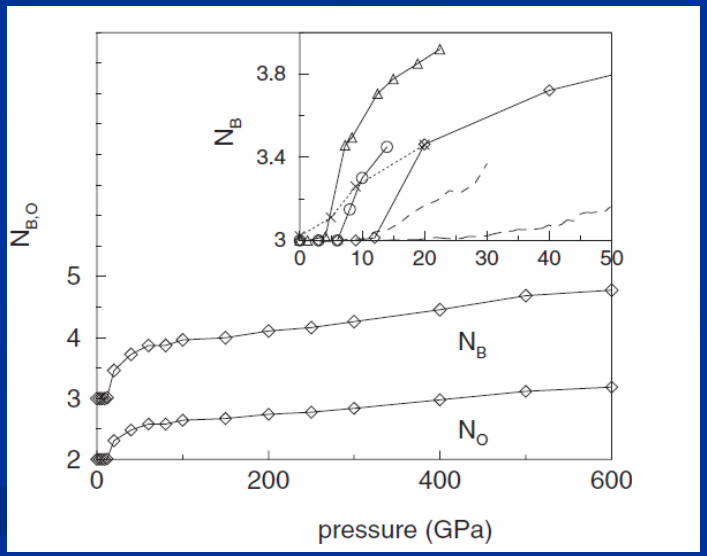


Analysis of local structure (B2O3 glass under press

way from averages (RDFs). Look at the particular local structural modifi

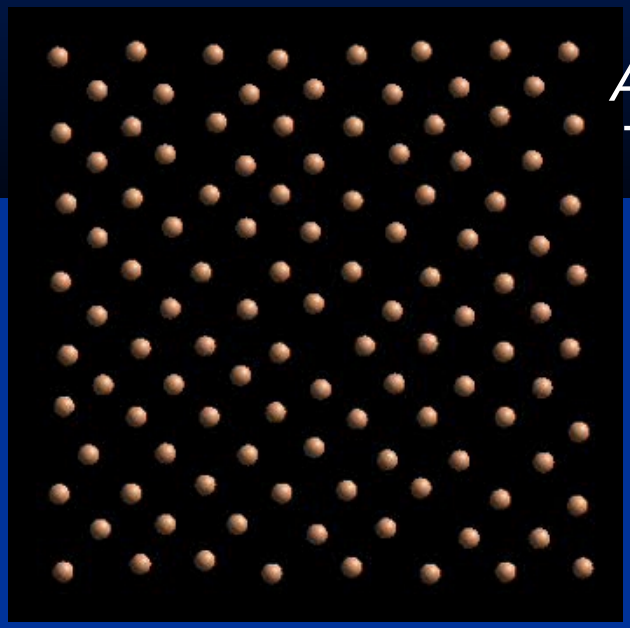


ee with experiments at low pressure and
redict behaviour at very high pressure
up to 600 GPa



What can we calculate - examples of dynamics

Phonons



$A(t)$ that depends on positions and velocities
The “autocorrelation function” is defined as

$$C_{AA}(t) =< A(t)A(0) >= \frac{1}{t_{\max}} \sum_{t_0=1}^{t_{\max}} A(t_0)A(t_0+t)$$

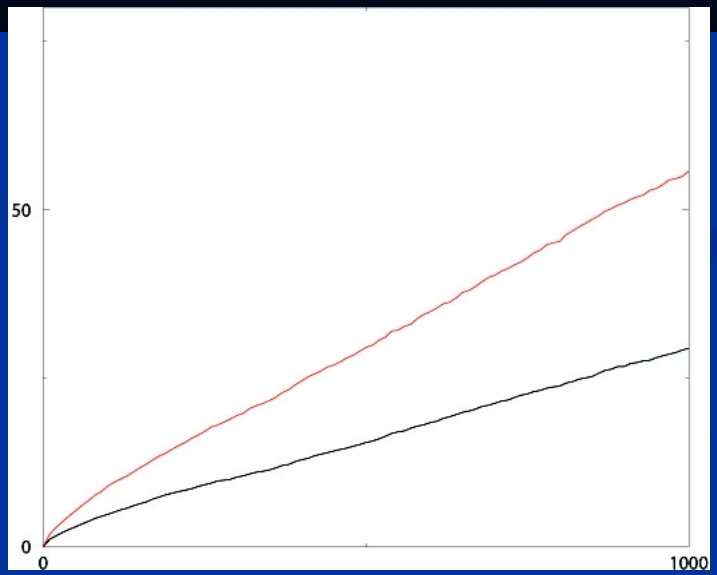
Can calculate velocity-velocity correlation function and phonon density of states

Analyze dynamics: transport properties

Einstein relation $\langle (r-\langle r \rangle)^2 \rangle = 6Dt$

From atomic coordinates, calculate diffusion coefficient D

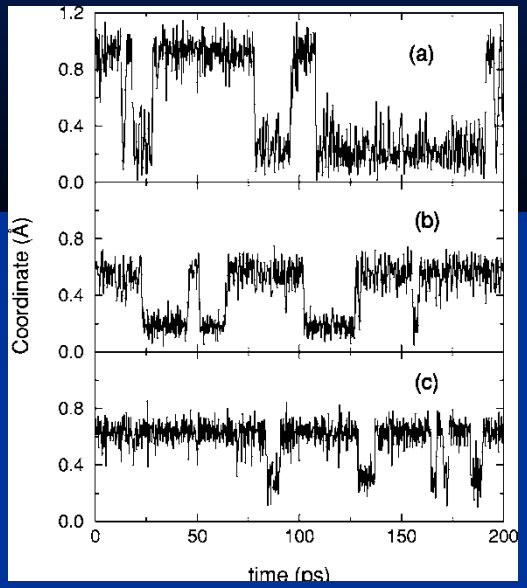
MSD

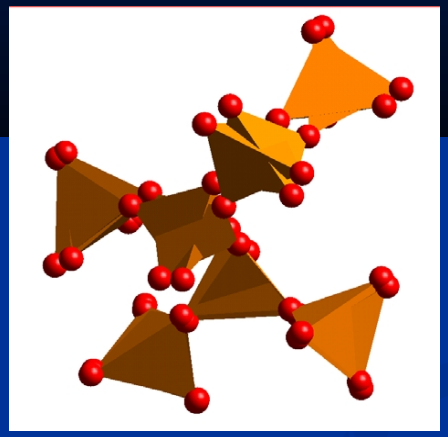


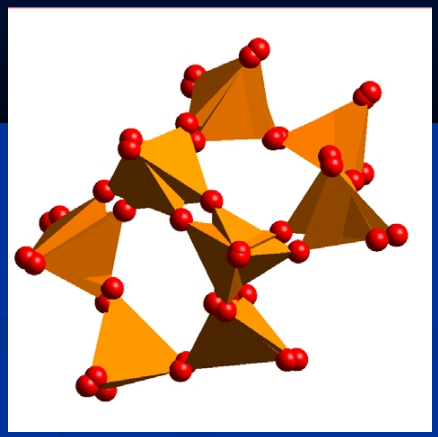
Time

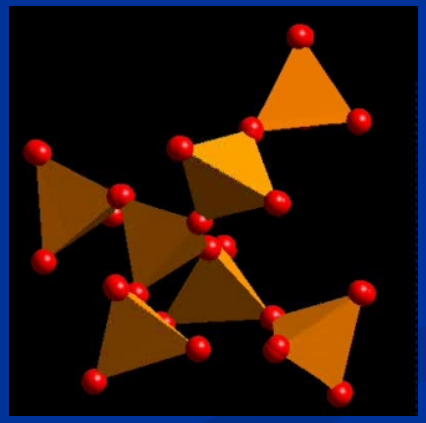
What can we calculate - examples of dynamics

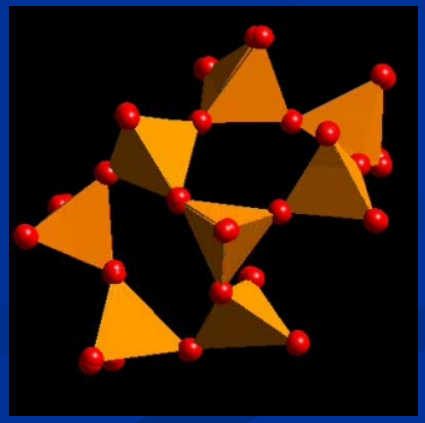
Two-level systems in glasses









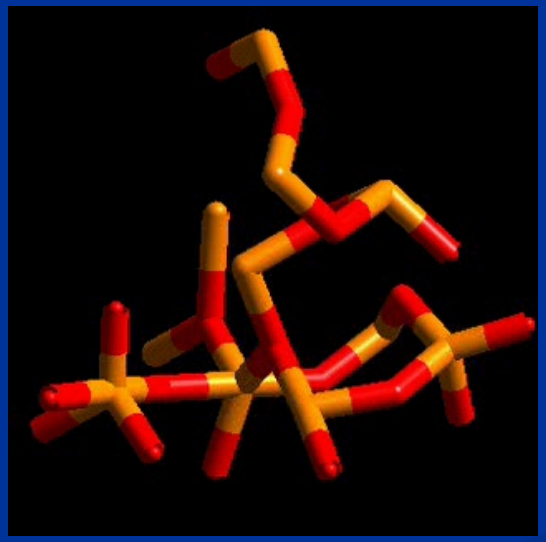


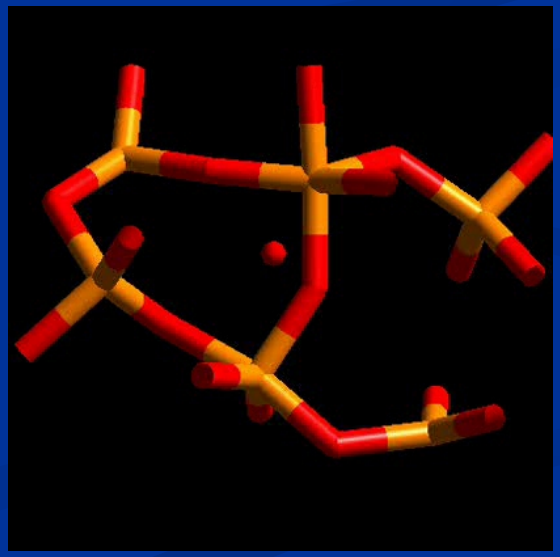
Analysis of local structure

Silica glass under high pressure

Glasses relax very slow, $q \sim \ln(t)$

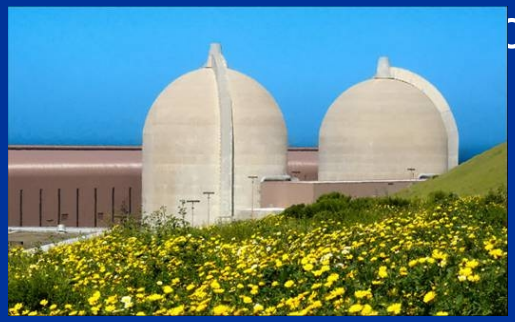
Can relax longer than the age of the Universe!





Radiation damage effects in ceramics

- Motivation: pressing need to safely encapsulate radioactive nuclear waste that comes from power plants and surplus plutonium
- HLW accounts for 95% of the total radioactivity produced during nuclear electricity generation. The amount of HLW worldwide is increasing by 12,000 metric tons a year, equivalent to 100 double-decker buses
- Pu stockpile in the UK: ~100 metric tons (reprocessed from waste and from decommissioned weapons), of which 20 tons has been declared as waste (Am)



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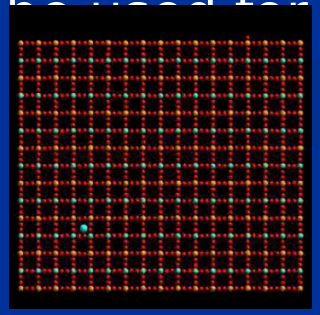
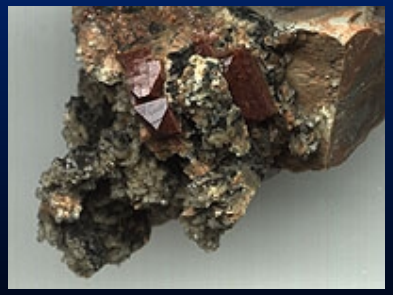


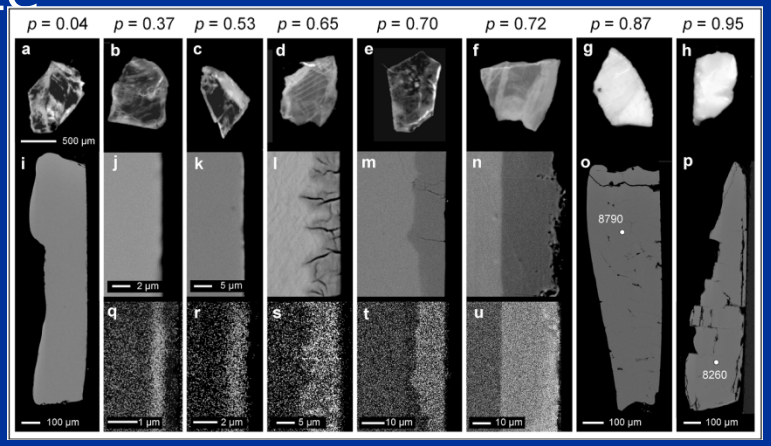
Actinides are long-lived. A waste form should be stable during millions of years. Traditional glasses are not an option. UK NDA wants to use ceramics.

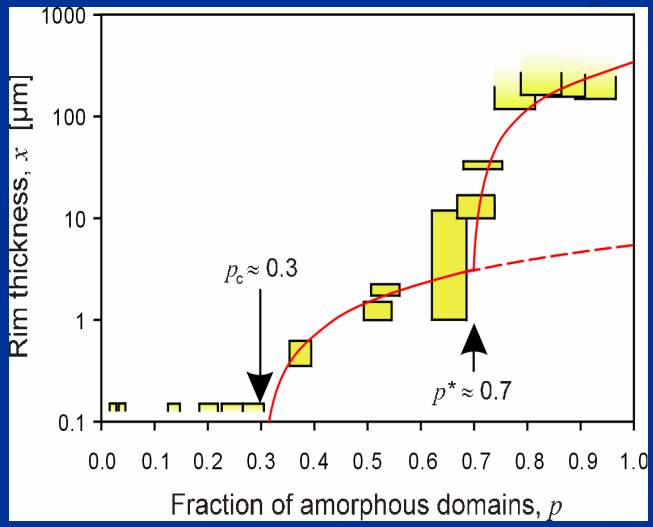
Effect of radiation-induced amorphization on diffusion

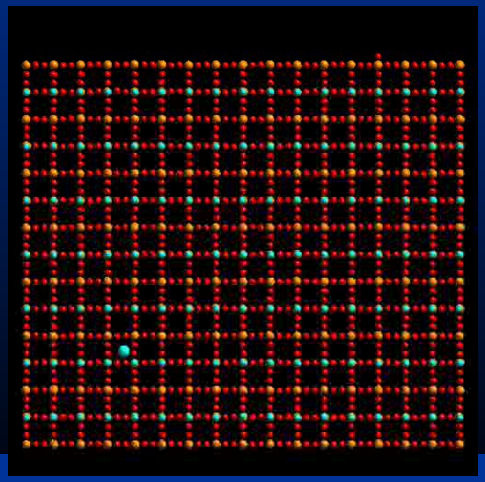


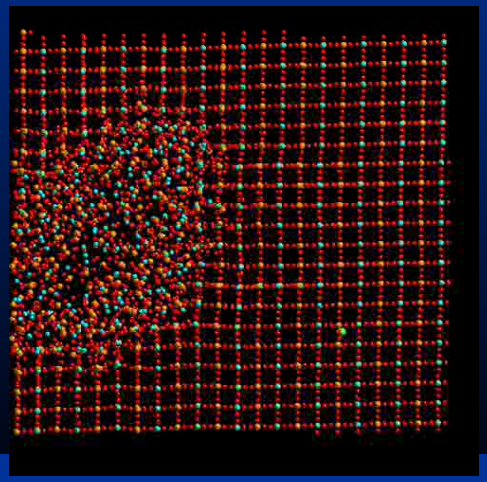
Case study: zircon $ZrSiO_4$ found minerals are ~1 billion years old, completely amorphous yet intact

Absorbs large ions like Pu on Zr site



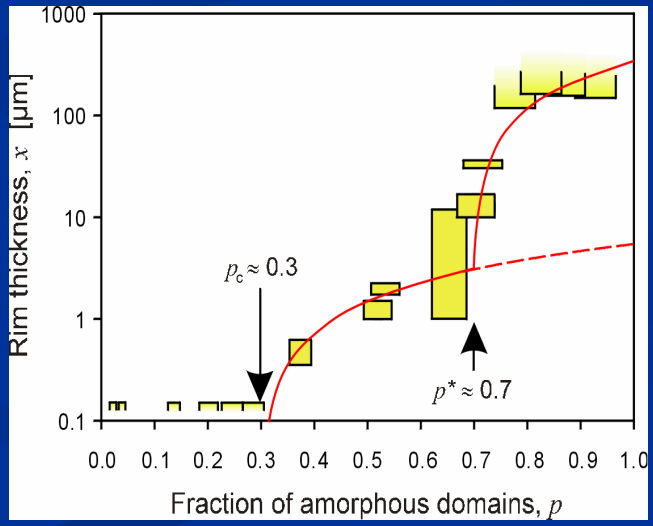






Channels of low density appearing along the track

This gives channels of increased diffusion and explains percolation-type increases of transport



Resistant vs amorphizable materials

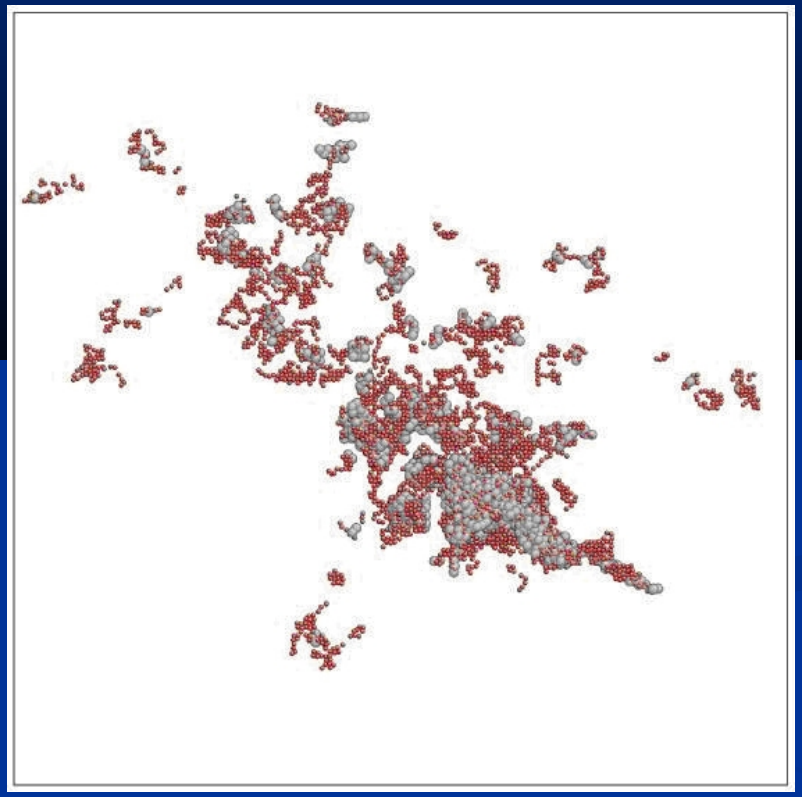
$Gd_2Ti_2O_7$ – "official" US Department of Energy waste form. Amorphizes easily under irradiation

$Gd_2Zr_2O_7$ – does not amorphize even at very large radiation doses!

What is the nature of the process of resistance to amorphization by radiation damage?

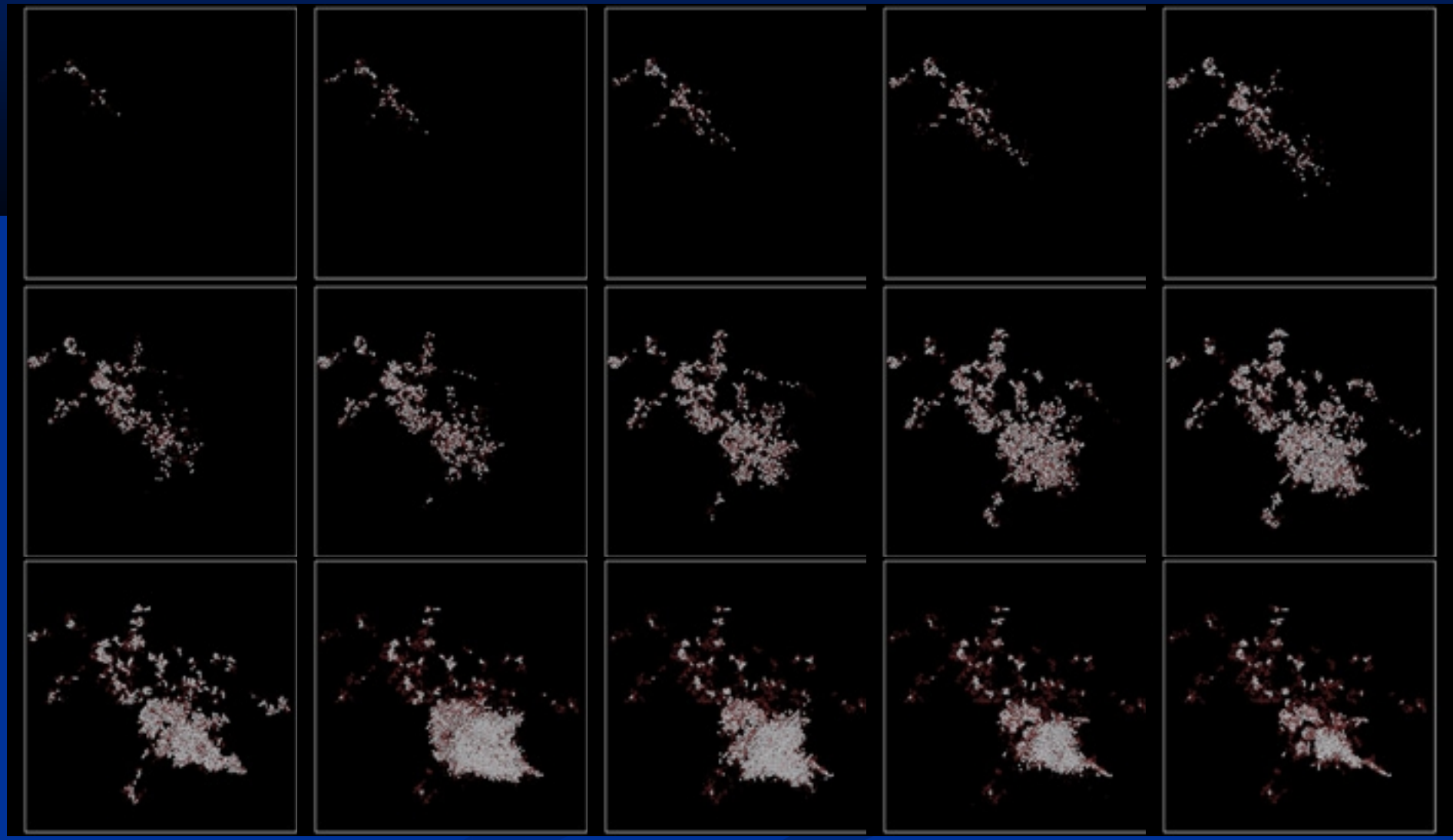
Also important in fusion reactors: 14 MeV neutrons, ~1 MeV recoils, 200 dpa over reactor lifetime. **No experiments are possible!**

delling resistance to amorphization by radiation dama



- 100 keV in rutile TiO_2, ~5-10 mln atoms, MD box size is ~500 Å
- 512-1024 parallel processors

Look at the process in detail
Rutile TiO_2

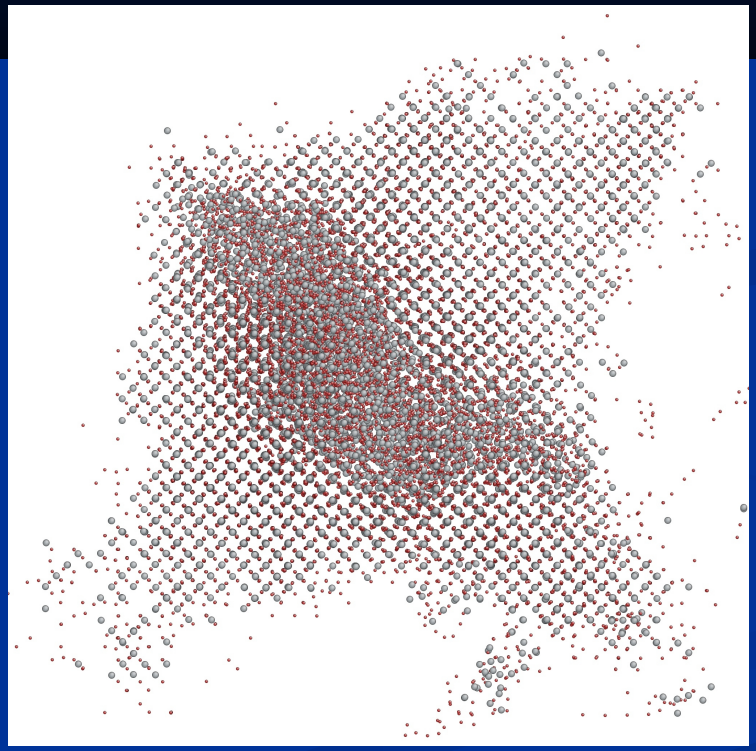


Two types of relaxation:

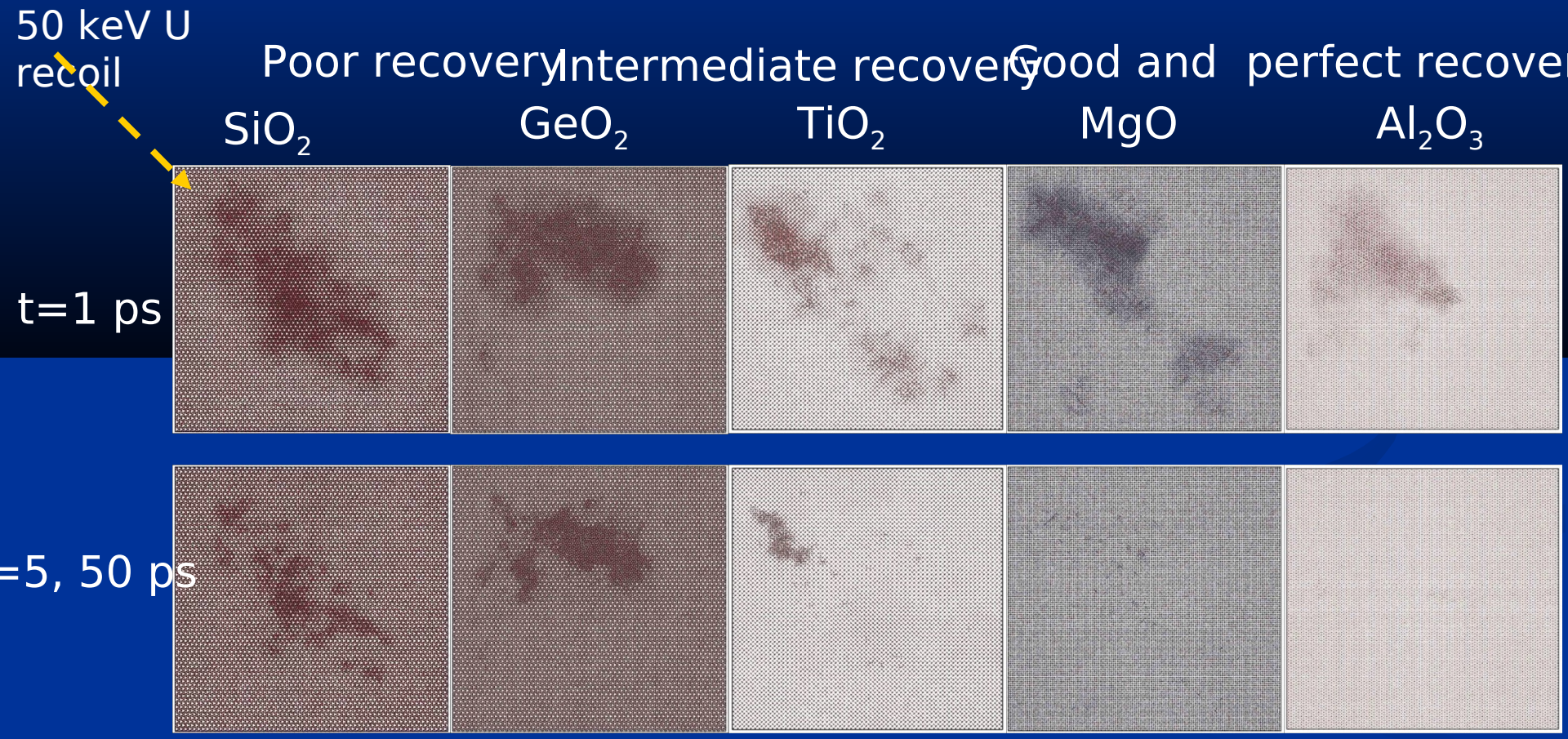
1. Elastic relaxation. Reversible.

2. Relaxation and recovery of the true structural damage

Both happen on the few picosecond timescale.



Resistance to amorphization

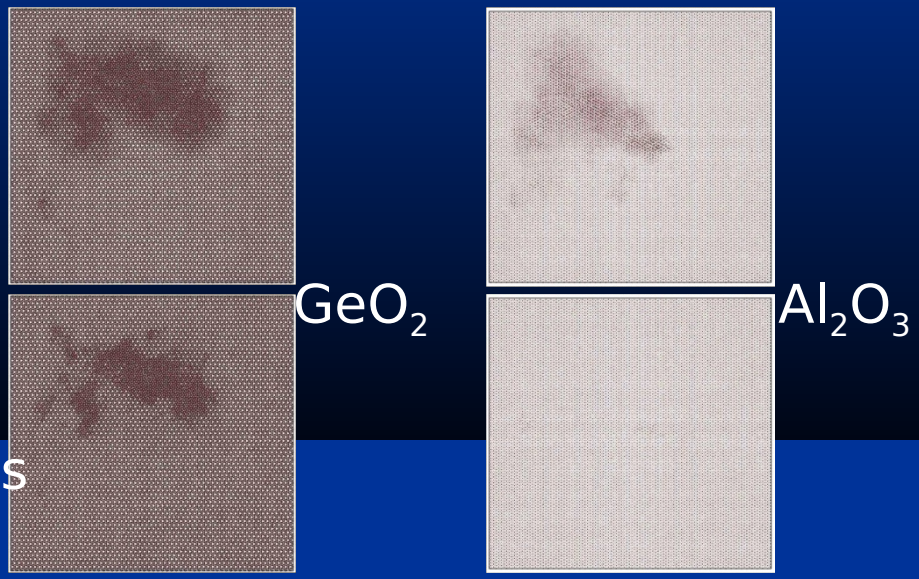


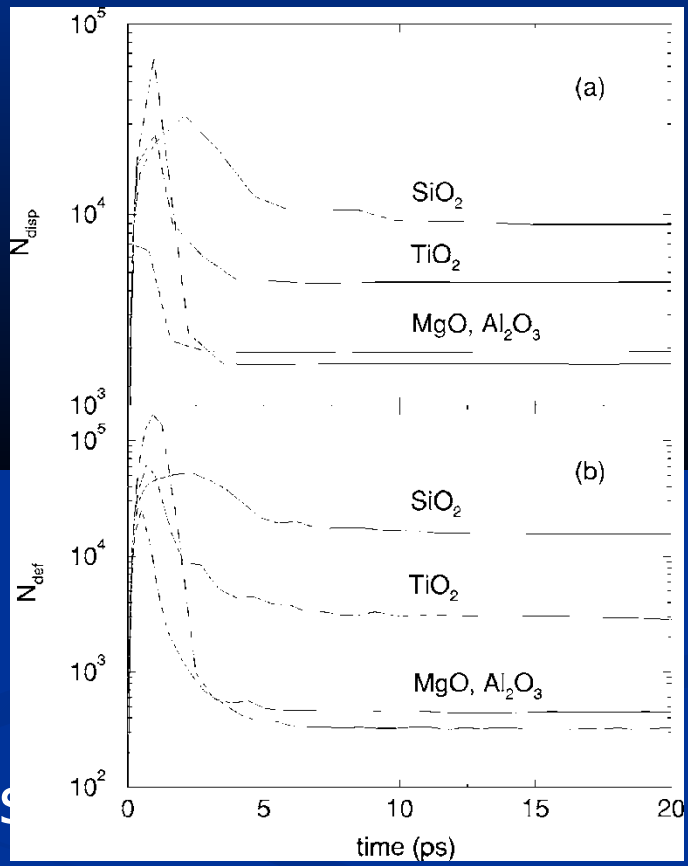
lations **reproduce** experimental behaviour of resistance to amorp
vation barriers correlate with the curvature of the potential at equ

Resistance to amorphization

t=1 ps

=5, 50 ps





- Time scales of damage recovery: s

- Correlate the details of interatomic potentials with damage recovery: damage increases with the **stiffness** of O-O interaction

Limitations of MD simulations

1. Simulations are limited by the accuracy of empirical interatomic potentials

2. The use of finite-size sampled and periodic boundary conditions
   (a) interactions with reappearing waves is not understood
   (b) the use of finite sizes restricts the range of allowed wave vectors
   (although this becomes of less an issue with massive parallel computers)

3. Short simulation times
   (a) may not be enough time to explore its phase space and have an ergodic system
   (b) may not be enough time to observe a phenomenon that lasts longer than simulation time

But because these limitations are different from those in theory and experiment, a combination of MD with

Thank you!

PhD opportunities in condensed matter physics in Queen Mary University of London:

Theory
Simulations
Experiment

Email <k.trachenko@qmul.ac.uk>