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for Non-Metallic Condensed Matter**

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**Principles of atomistic classical molecular dynamics computer simulations for  
non-metallic condensed matter**

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# Principles of atomistic classical molecular dynamics computer simulations for non-metallic condensed matter

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# Set of 3 talks

- Introduction to Molecular Dynamics for radiation effects in non-metallic systems
- Introduction to long time scale techniques with particular reference to non-metallic systems
- Applications..mainly oxides (MgO, ZnO, TiO<sub>2</sub>) and spinels MgAl<sub>2</sub>O<sub>4</sub>, and inverse and partially inverse spinels

## Landmarks in MD computer simulation

- 1782 A. L. Lavoisier postulated that classical theory could be used to model chemical phenomena
- 1957 First MD simulations using hard spheres by Alder and Wainwright
- 1960 MD simulations of radiation damage by Vineyard's group at Brookhaven
- 1960 MD simulations of sputtering by Don Harrison
- 2012 Standard packages such as DLPOLY and LAMMPS are available for use.

## The Classical Molecular Dynamics Method

Given a system of  $N$  interacting particles, the  $i$ th of which has mass  $m_i$  and position vector  $\mathbf{r}_i$ , the system evolves by **Newton's** equations of motion

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i$$

where for non-dissipative systems

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N).$$

and  $V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is a classical potential energy function. When there is no dissipation then the system is said to be a Hamiltonian system and can be formulated in another way.

The same method can also be used in Quantum MD. In this case the forces are determined from solving Schrödinger's equation.

## The Verlet algorithm

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + \frac{1}{2}\mathbf{a}(t)\delta t^2 + \dots$$

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \mathbf{a}(t)\delta t + \frac{1}{2}\mathbf{a}'(t)\delta t^2 + \dots$$

$$\mathbf{a}'(t) = \frac{\mathbf{a}(t + \delta t) - \mathbf{a}(t)}{\delta t} + O(\delta t)$$

giving

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \frac{1}{2}(\mathbf{a}(t + \delta t) + \mathbf{a}(t))\delta t + O(\delta t^3)$$

The algorithm updates the position vectors, calculates the new accelerations from

$$\mathbf{a}(t + \delta t) = -\nabla V(\mathbf{r}[t + \delta t])/m,$$

then updates the velocities.

Thus ....only 1 force evaluation per timestep and a local truncation error of  $O(\delta t^3)$ .

## Hamiltonian Systems

Hamilton's principle : 'The motion of a system from time  $t_1$  to  $t_2$  is such that the line integral of the Lagrangian  $\mathcal{L}$  is an extremum i.e.

$$\delta \int_{t_1}^{t_2} \mathcal{L} dt = 0.$$

The Lagrangian  $\mathcal{L}$  is the difference between the KE and PE of the system. The Hamiltonian  $\mathcal{H}$  is given by

$$\mathcal{H} = \sum_{i=1}^{3N} \dot{q}^i p^i - \mathcal{L},$$

$$(r_1, \dots, r_N) = (q^1, \dots, q^{3N}), \quad (m_1 v_1 \dots m_n v_N) = (p^1, \dots, p^{3N}).$$

With generalised co-ordinated  $(p, q, t)$ ,

$$\dot{q}^i = \frac{\partial \mathcal{H}}{\partial p^i}, \quad -\dot{p}^i = \frac{\partial \mathcal{H}}{\partial q^i}.$$

For modelling particle dynamics our Hamiltonians are of the form  $\mathcal{H} \approx \frac{1}{2} p^2 + V(q)$ .

## Some properties of Hamiltonian Systems

(1) In principle, if we integrate forward in time, we should be able to recover the initial state by integrating backwards in time.

(2) Defining  $x = (q, p)^T$ ,  $x(t) = T_M(t)x(0)$  where  $T_M$  is called the transfer matrix. A map of this kind is called symplectic iff the Jacobian  $M$  of the transformation  $T_M$  satisfies

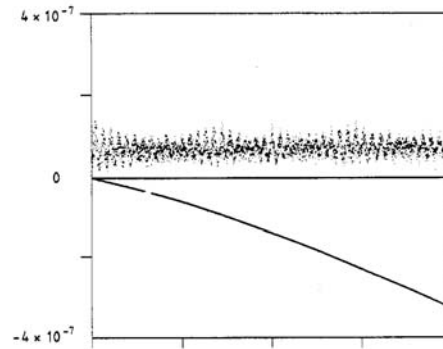
$$M^T J M = J \quad \text{where} \quad J = \begin{pmatrix} 0 & -I \\ -I & 0 \end{pmatrix}.$$

Such maps preserve the area of phase space (Liouville's theorem). This is important because it means that trajectories that start off close remain close after the Hamiltonian system has evolved.

Radiation event MD simulations are inherently chaotic. Different computers can give different results for the trajectories after the initial stages of a simulation

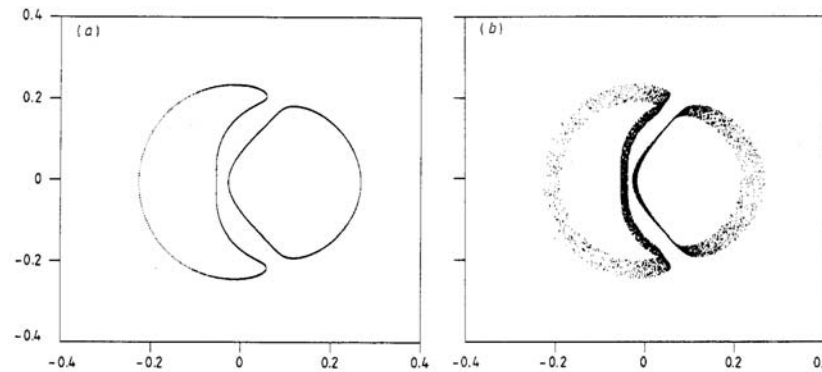


# Why symplectic integrators ?



Comparison of relative energy error of a second-order SIA and a fourth-order RKI for the Fermi-Pasta-Ulam system of oscillators. The timestep for the SIA was 0.001 and 0.02 for the RKI and the final time was 7500.

Figure 1: Energy v Time plot for the Fermi-Past-Ulam problem



Comparison of third-order SIA (a) and a fourth-order RKI (b) for the Hénon-Heiles system. The initial condition was (0.12, 0.12, 0.12, 0.12) and energy 0.029 952. The timestep was 1/6 and 1200 000 timesteps were computed.

Figure 2: Phase space plot  $(p_2, q_2)$  when  $q_1 = 0$  for the system  $H(q, p) = \frac{1}{2}(q_1^2 + q_2^2 + p_1^2 + p_2^2) + q_1^2 q_2 - \frac{1}{3} q_2^3$

**Energy drift is a common problem in MD simulations that do not use the Verlet algorithm**

## Units for use in the MD simulation

The time step  $\delta t$  typically ranges from 0.1 to 1.5 fs.  
(1 fs =  $10^{-15}$  s)

A typical length scale is 1Å

The mass of an atom  $m \approx Z \times 1.627 \times 10^{-27}$  kg

The potential function  $V$  has units of eV. Suitable units of force are eV/Å.

1 eV/Å = 1.602 nN ( $1.602 \times 10^{-19}$  eV = 1 Joule)

Thus we can use units of Å, fs and eV/Å in

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i$$

if we scale the mass by replacing  $m_i$  with  $\frac{Z \times 1.627 \times 10^2}{1.602}$

**Note a 1 fs time step means  $10^{15}$  steps to simulate 1s of real time so MD simulations usually are restricted to ~ nanoseconds**

## Initial and boundary conditions

- *Bulk Radiation Event initiated by a neutron* : Impart a given energy usually a few keV to an atom in a crystal and follow the evolution of the trajectory. Average over many such trajectories
- *External Impact event (keV energies)* : Impart energy to an atom above the surface of a crystal, directed towards the surface and follow the evolution (sputtering, crystal growth)
- *Swift Heavy ion impact (GeV energies)* : Set in motion atoms along an ion track and follow the evolution of the resulting cascade.
- *Boundary Conditions* : Periodic, Fixed or Free. Usually the simulation region is taken as a rectangular box.

## Time step Control

$$\delta t = \frac{\alpha}{\sqrt{(\alpha + \beta * \gamma)}} \text{ fs.}$$

The time step depends on the parameter  $\gamma$  which is given by:

$$\gamma = E_{KE}^{max} + |E_{PE}^{max}|, \quad (0.1)$$

where  $E_{KE}^{max}$  and  $E_{PE}^{max}$  is the maximum kinetic energy and potential energy of an atoms at time t. Typical values for  $\alpha$  and  $\beta$  are 1.5 and 0.1 respectively.

# Temperature control

(non-Hamiltonian)

## 1. Berendsen thermostat

The method of temperature control relies on the scaling of the velocity vectors at every time step with a factor  $\lambda$

$$\lambda = \left[ 1 + \frac{\delta t}{\tau_T} \left( \frac{T_0}{T} - 1 \right) \right]^{\frac{1}{2}}, \quad (0.2)$$

in which  $T$  and  $T_0$  are the actual and desired temperatures,  $\delta t$  is the time step of the integration algorithm and  $\tau_T$  is a coupling parameter between the heat bath and the system. The system is brought towards the desired temperature at a rate determined by  $\tau_T$ .

Temperature  $T$  is defined by  $\sum m_i v_i^2 = 3 N k_B T$

## Temperature control

### 2. Nosé-Hoover thermostat

The Nosé-Hoover method uses a modified equation of motion:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F} - \zeta \frac{d\mathbf{r}_i}{dt}. \quad (0.3)$$

The rate of change of the coefficient  $\zeta$  is given by

$$\frac{d\zeta}{dt} = \frac{1}{Q} \left( \sum_i^N m v_i^2 - 3Nk_B T_0 \right) \left( -\zeta \frac{d\zeta}{dt} \right), \quad (0.4)$$

where  $Q$  describes the strength of the coupling between the system and the heat bath.

There is a modified Hamiltonian from which the equations of motion can be derived.

## Force Field Models

The Lennard-Jones potential acts pairwise

$$V(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)$$

The force is zero when  $r = 2^{\frac{1}{6}}\sigma$  and then  $V = -\epsilon$ . The quantities  $\sigma$  and  $\epsilon$  are fitting parameters chosen to match the lattice constant  $a$  and cohesive energy  $u$  of the material. The bulk modulus  $B$  can also be found in terms of  $\sigma$  and  $\epsilon$ . For an fcc lattice  $u = -8.5\epsilon$ ,  $a = 1.541\sigma$  and  $B = \frac{75\epsilon}{\sigma^3}$ .

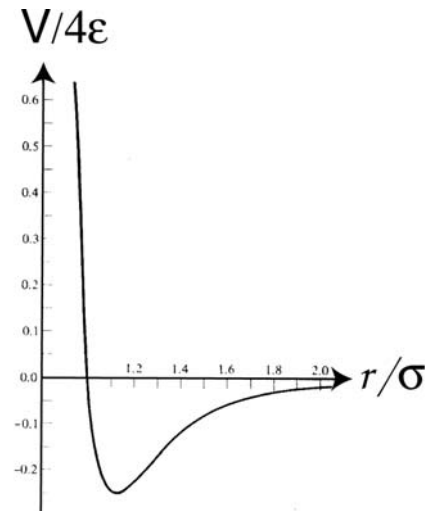


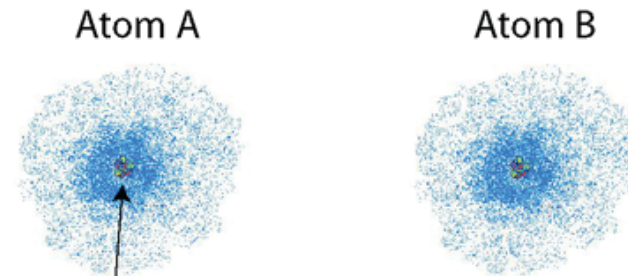
Table 1: Values of the fitting constants for the rare gases

element	Ne	Ar	Kr	Xe
$\epsilon$ (eV)	0.0031	0.0104	0.0140	0.0200
$\sigma$ ( $\text{\AA}^3$ )	2.74	3.40	3.65	3.98
$r_0$ ( $\text{\AA}$ ) expt.	3.13	3.75	3.99	4.33
$r_0$ ( $\text{\AA}$ ) theory	2.99	3.71	3.98	4.34
$u_0$ (eV) expt.	-0.02	-0.08	-0.11	-0.17
$u_0$ (eV) theory	-0.027	-0.089	-0.12	-0.172
$B$ ( $10^9$ pascals) expt.	1.1	2.7	3.5	3.6
$B$ ( $10^9$ pascals) theory	1.81	3.18	3.46	3.81

## The Lennard-Jones Pair-potential



# Screened Coulomb Potential Functions



$\exp(-r/a)$  ---screening function

Nucleus with charge  $Ze$  "screened" from the nucleus of atom B by the surrounding electron cloud.

## The original Bohr Model (1948)

$$V = Z_A Z_B e^2 \frac{\exp(-r/a)}{4\pi\epsilon_0 r}$$

was used to determine the penetration depth of ions in solids. Here  $a$  is called the screening length. This is related to the Bohr radius  $a_0$ .

## The origin of the ZBL potential

$$V = V_{nn} + V_{en} + V_{ee} + V_k + V_a$$

$V_{nn}$  — electrostatic PE between nuclei

$V_{ee}$  — electrostatic PE between electron distributions

$V_{en}$  — electrostatic PE between each nucleus and the other electron distribution

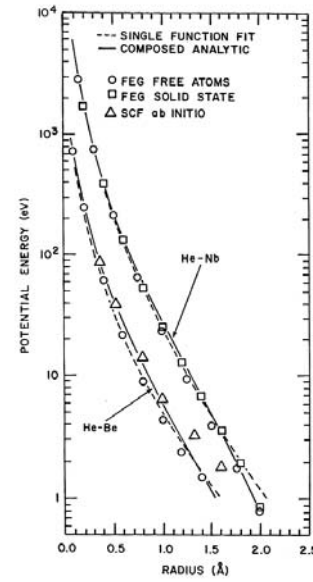
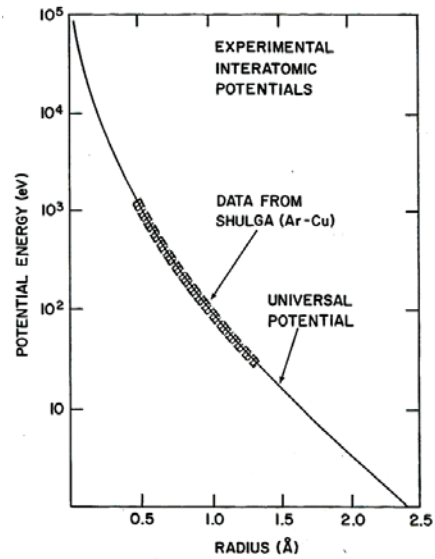
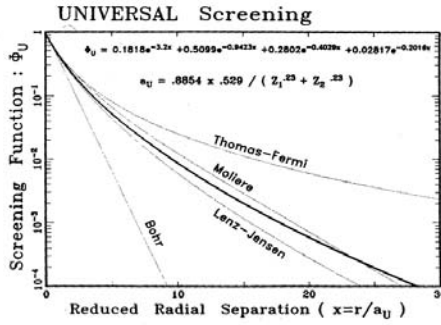
$V_k$  — increase in the KE of the electrons in the overlap region due to Pauli exclusion (free electron gas model)

$V_a$  — increase in the exchange energy of these electrons

$V(r)$  calculated for 522 representative ion pairs and the resulting data fit to a formula.

$$\chi_M(x) = 0.18175 \exp(-3.1998x) + 0.50986 \exp(-0.94229x) \\ + 0.28022 \exp(-0.4029x) + 0.028171 \exp(-0.20162x)$$

# The ZBL Screened Coulomb Potential Functions



# Fixed charge pairwise ionic potentials

- Used for MgO, spinels and bixbyite simulations

$$\phi(r_{ij}) = \begin{cases} ZBL & r_{ij} < r_a; \\ g(r_{ij}) = e^{(f_1 + f_2 r_{ij} + f_3 r_{ij}^2 + f_4 r_{ij}^3 + f_5 r_{ij}^4 + f_6 r_{ij}^5)} & r_a \leq r_{ij} < r_b; \\ A_{ij} \exp\left(-\frac{r_{ij}}{p_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + V_{coul}(r_{ij}) & r_b \leq r_{ij} < r_c; \\ h(r_{ij}) \times \left(A_{ij} \exp\left(-\frac{r_{ij}}{p_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}\right) + V_{coul}(r_{ij}) & r_c \leq r_{ij} < r_0; \\ V_{coul}(r_{ij}) & r_{ij} \geq r_0, \end{cases}$$

$$h(r_{ij}) = \begin{cases} 1 & r_{ij} < r_c; \\ \frac{1}{2} \left(1 + \cos \pi \frac{r_{ij} - r_c}{d}\right) & r_c \leq r_{ij} < r_0; \\ 0 & r_{ij} \geq r_0, \end{cases}$$

*ionic potential are remarkable good compared to DFT results for bulk materials*

# Variable charge ionic potentials

Pioneered for MD simulations by Rappé and Goddard and van Duin (ReaXFF) and Streitz and Mintmire

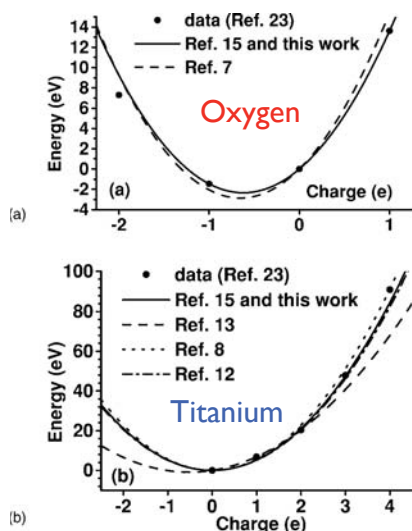


FIG. 2. Atomic self-energy of ion (a) O, (b) Ti as a function of charge.

Fixed charge :  $Ti^{qt}$  ;  $O^{qo}$  ;  $qt = +4$ ;  $qo = -2$ ;

Variable charge :  $qt$  and  $qo$  depend on the local environment.

Minimise Total QEq at each step

$$E_{QEq} = \sum_i E_i + \sum_i \sum_{j \neq i} E_{ij}^{elec}$$

Ion self-energy:

$$E_i = E_i(0) + \chi_i^0 q_i + \frac{1}{2} J_i^0 q_i^2$$

↑  
Electronegativity

↑  
Hardness

Rappe, A.; Goddard, W. A. J. Phys. Chem. 1991, 95, 3358-3363

F.H Streitz and J. Mintmire Phys. Rev. B 50, 11996-12003 (1994)

Halil et al PRB 73 165406 (2006) D. Raymond, A van Duin et al Surface Science 602 (2008) 1020-1031

# Other potentials...covalent materials

Tersoff type bond order potentials..Si, Ge, C, GaN, multicomponent Si-C-H (Brenner, Beardmore)

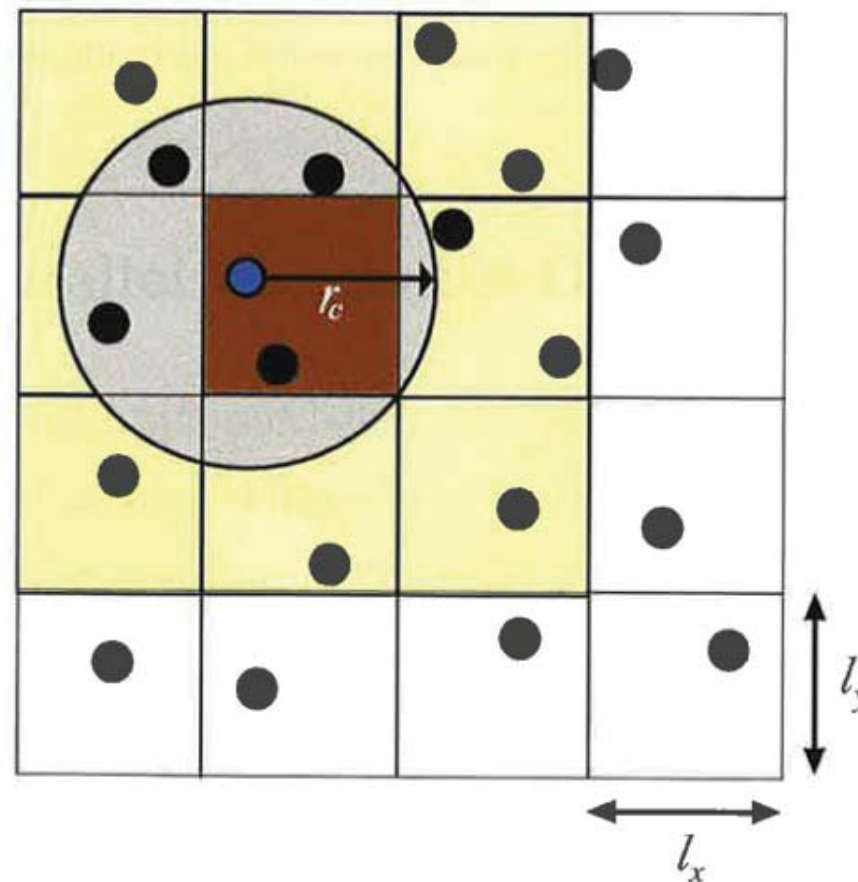
$$V(r_i) = \sum \sum (f_R(r_{ij}) + b_{ij} f_A(r_{ij}))$$

Stillinger-Weber type 3-body potentials..Si, CdTe

$$V(r_i) = \sum (V_{ij}(r_{ij}) + \sum V_{ijk}(r_{ij}, r_{ik}, r_{jk}))$$

***If each atom were to interact with every other atom in the system the force evaluations would scale as  $N^2$  for pair potentials. This is unacceptably slow.***

# Boxing and the use of neighbour lists for short-ranged potentials



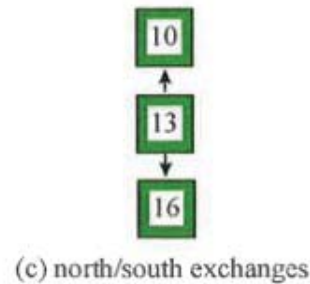
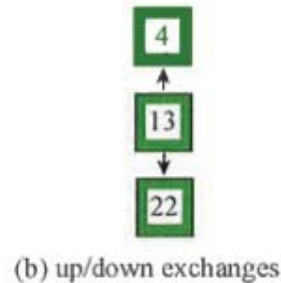
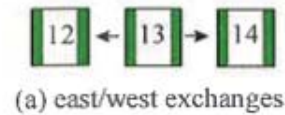
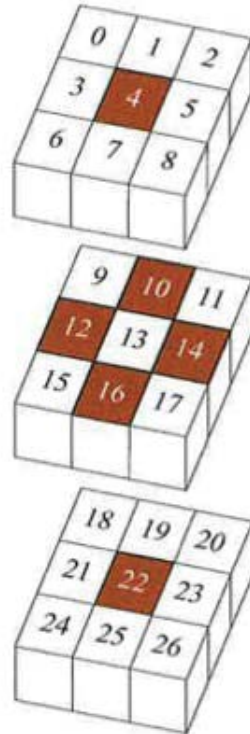
The potential cut-off is  $r_c$ . Atoms in the brown and adjacent boxes are stored in a neighbour list. For a system of  $N$  atoms, the number of force evaluations at each times step is  $N \times$  average number of neighbours (usually a small number relative to  $N$ ),

***i.e. force evaluations scale linearly with the number of atoms.***

# Parallelisation : Spatial decomposition and multiscale modelling

*Length scales can be extended through the use of more and more processors*

MPI is the standard parallel language



Here the force evaluations on atoms in each box are evaluated on separate processors. An atom in box 13 needs information from the 26 surrounding boxes. Data exchange is required so the communication time between processors needs to be small compared to the time of the force evaluations. Typically ~50,000 atoms per processor is optimal. So a one million atom simulation requires >~20 processors.



# Coulomb sum evaluation

Coulomb sums lead to *conditionally* convergent series and are *long-ranged*  
e.g.  $\ln(2.0) = 1 - 1/2 + 1/3 - 1/4 + 1/5 - 1/6 + 1/7 - 1/8 \dots = 0.6931\dots$

*we need to take ~20,000 terms to get 4 figure accuracy*

Two methods commonly used:

(1) Ewald summation for periodic systems  
(scales as  $N \cdot \log N$ )

(2) Fast multipole method for non-periodic systems (Greengard and Rhoklin)  
(scales linearly with  $N$ )

You can also truncate the ionic potential. This is a relatively good approximation for systems that are charge neutral in the cut-off region ;

e.g. ReaXFF truncates at 1 nm

The Fennel approximation does this smoothly

# **Length and time scales to be bridged in atomistic molecular dynamics (MD) simulations**

## *Time scales to be bridged*

*Integration time step  $\sim 1 \times 10^{-15}$  s in an MD simulation*

*On a modern computer with say 2000 atoms we can advance time by around 10 fs in 1 real second of computing time. 1 second would take  $10^9$  years.*

## *Length scales to be bridged:*

*2000 atoms  $\sim 3\text{nm} \times 3\text{nm} \times 3\text{nm}$*

*2m atoms  $\sim 30\text{nm} \times 30\text{nm} \times 30\text{nm}$  (Parallel computing)*

## *Radiation damage phenomena*

*Dose rates maybe 1000's of dpa over a reactor lifetime so impossible using MD alone*

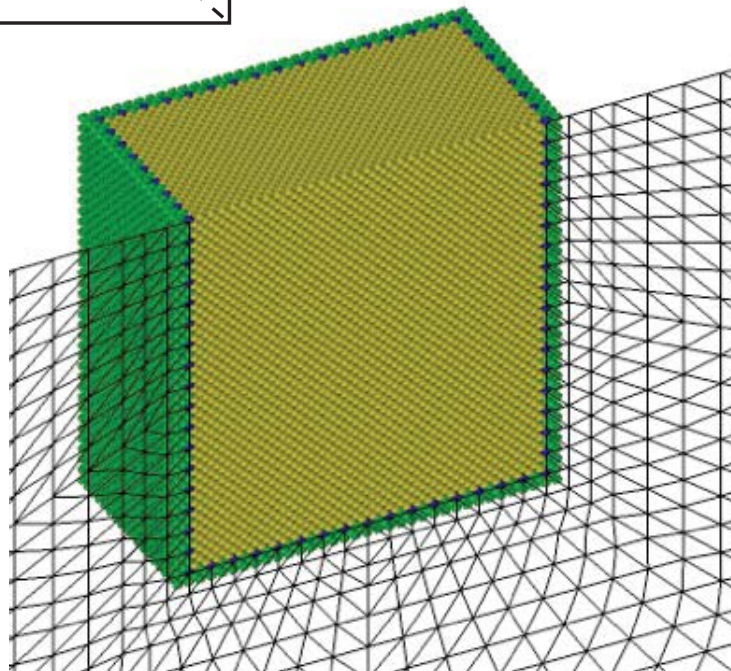
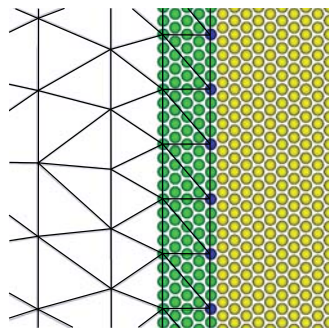
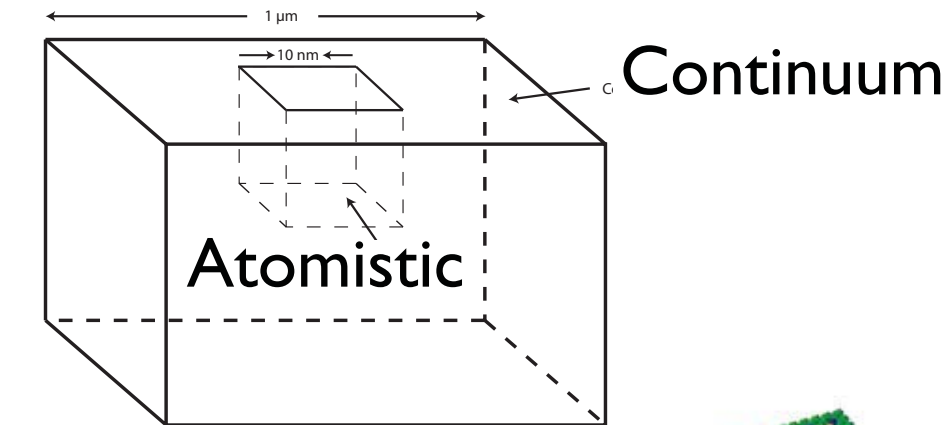
## *Thin Film Growth*

*Rates are monolayers per second  $\sim$  time bridging a long way off with MD*

# ***Bridging Length Scales in atomistic simulations***

- Use DFT calculations, system sizes  $\sim 100$ 's of atoms to parameterise classical potentials for MD simulations (DFT-MD)
- Parallel Computing
  - Solve Newton's laws of motion numerically with forces derived from the parameterised potentials
  - Assuming  $10^{27}$  atoms per cubic metre, i.e.  $10^9$  per cubic micron. With  $10^5$  atoms per processor in a typical MD simulation you need  $10^4$  processors to simulate atomistically 1 cubic micron of material.
- Embed an atomistic region in a continuum (MD-FE)

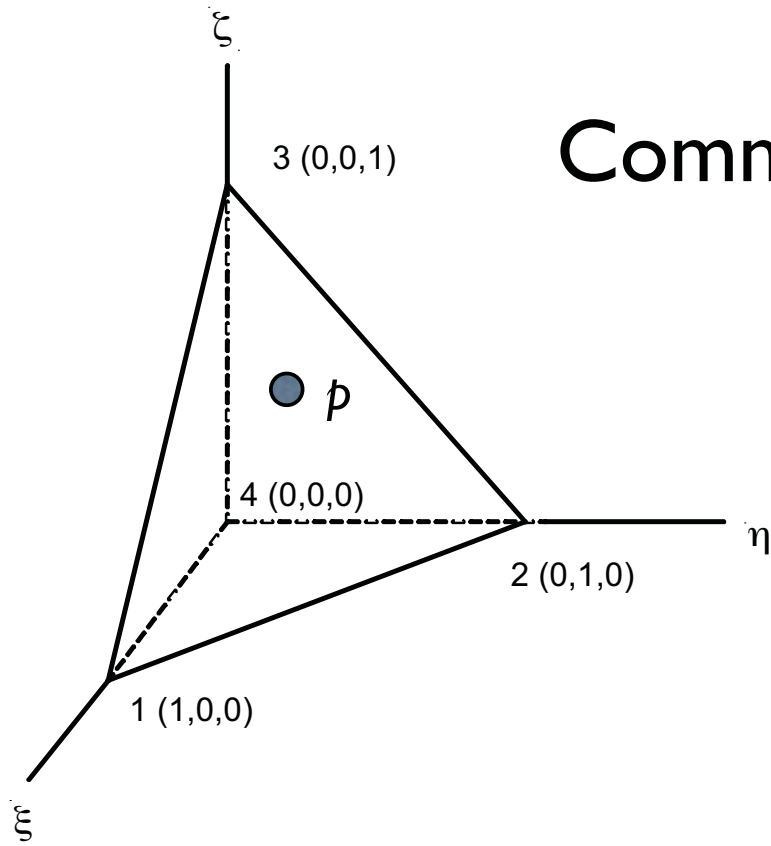
# Atomistics to finite elements



- This extends the system size without the same increase in computational cost.
- The MD region is embedded in a FE mesh.
- Imaginary atoms (green and blue) make up the neighbours of real atoms.
- The first layer of elements overlaps with the imaginary atoms.

E. Mcgee, S.D. Kenny and R. Smith Int. J. Mater. Res. 98 430 (2007)

# Communication FE to MD



- Linear interpolation is used to position imaginary atoms according to nodal displacements.
- An atom  $p$  with fractional coordinates  $(\xi_p, \eta_p, \zeta_p)$  has displacements  $(u_p, v_p, w_p)$ .
- These equations keep the fractional coordinates constant.
- This provides feedback from the FE model to the MD region.

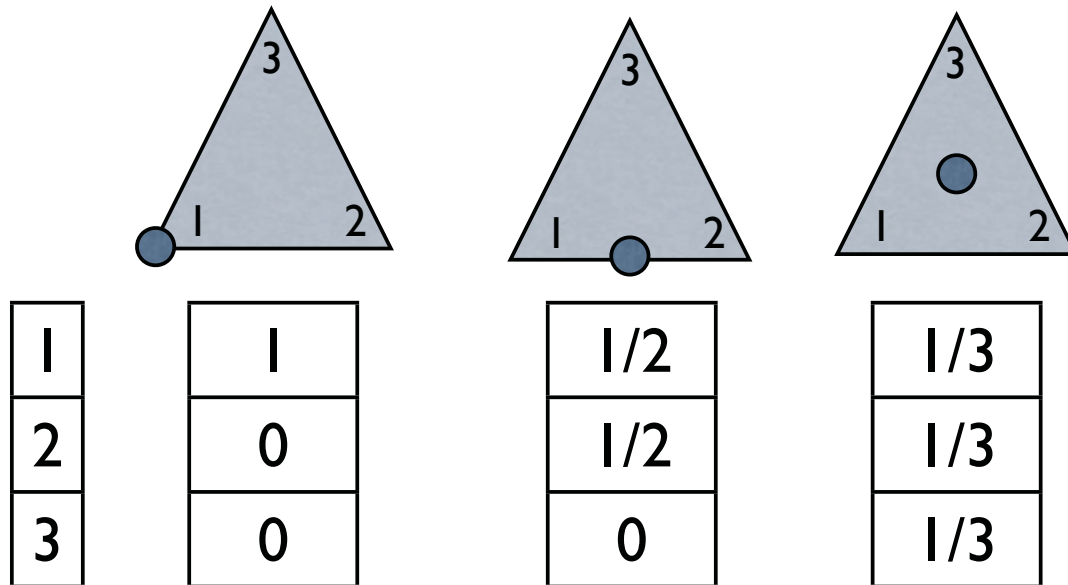
$$u_p = u_{14}\xi_p + u_{24}\eta_p + u_{34}\zeta_p + u_4$$

$$v_p = v_{14}\xi_p + v_{24}\eta_p + v_{34}\zeta_p + v_4$$

$$w_p = w_{14}\xi_p + w_{24}\eta_p + w_{34}\zeta_p + w_4.$$

# Communication

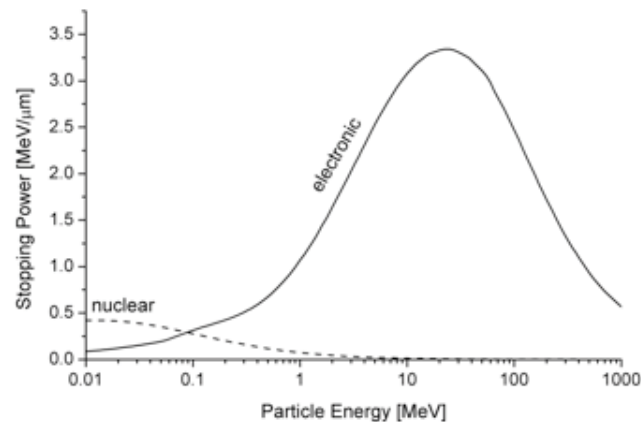
## MD to FE



$$F_{nde} = \sum_{i=1}^{n_a} N_{nde} |_i F_i$$

- Forces are present on imaginary atoms due to real atoms.
- The forces are assigned to nodes according to shape function values.
- The nodal force is then used in the dynamical FE update.
- FE calculations on one processor; spatial decomposition for the atomic system

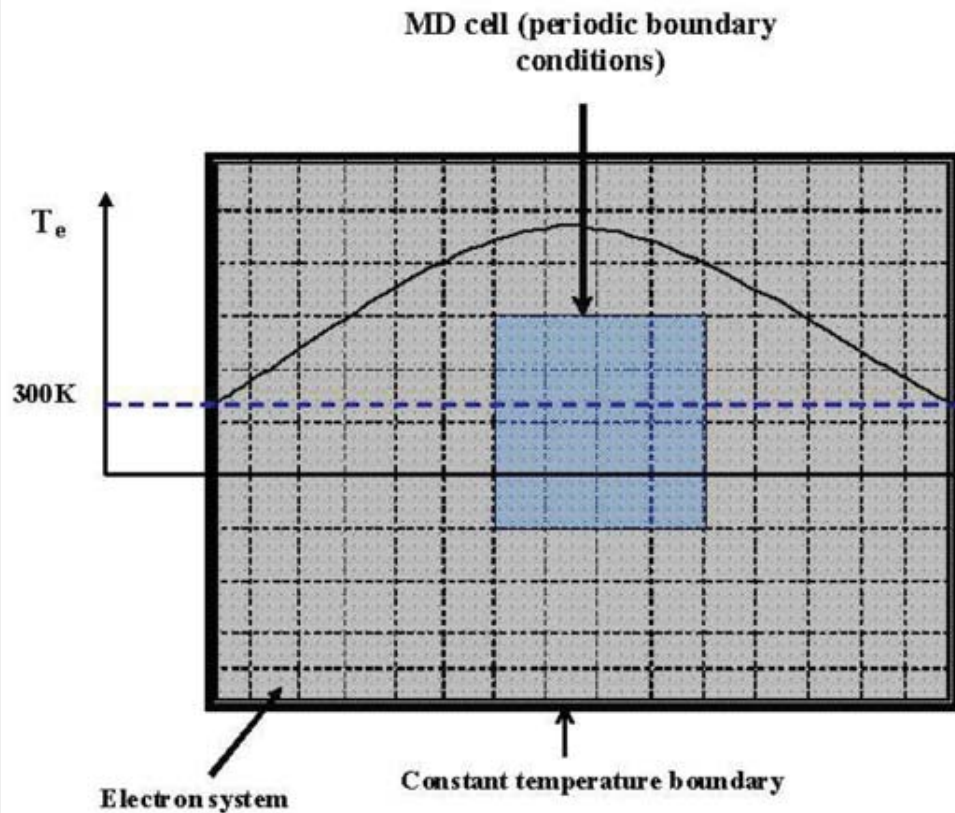
# Electronic energy loss (non-Hamiltonian)



Simplest models due to Lindhard, Scharff and Shiott, also Firsov.

Implemented in MD easily by rescaling the positions and velocities at each time step or by the introduction of a damping coefficient ( $-\gamma \times \text{velocity}$ ) extracted from the models.

# 2-Temperature model



$$C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla \cdot (\kappa_e(\nabla T_e)) - g[T_e - T_a]$$

$$C_a(T_a) \frac{\partial T_a}{\partial t} = \nabla \cdot (\kappa_a(\nabla T_a)) + g[T_e - T_a]$$

$$m_i \ddot{\mathbf{r}}_i = \underbrace{\mathbf{F}_i(t)}_1 - \underbrace{\gamma \dot{\mathbf{r}}_i}_2 + \underbrace{\tilde{\mathbf{F}}}_3$$

$$\langle \tilde{\mathbf{F}}(t') \tilde{\mathbf{F}}(t) \rangle = 2\gamma_1 k_B T_e(x, y, z) \delta(t' - t)$$

Rutherford and Duffy JPCM for metals currently being extended for insulators but conductivities and specific heats are not known with accuracy.



# Analysis Tools

Defect Identification in crystallographic systems:

Interstitials :An atom that is greater than a distance  $r_{int}$  from a lattice site. Typically  $r_{int}$  is chosen as  $\sim$  one third of the nearest neighbour distance.

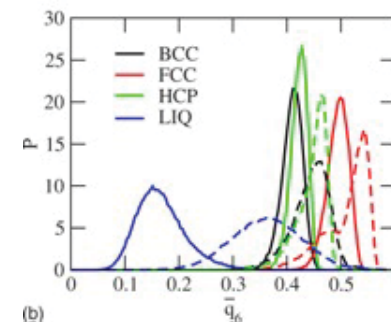
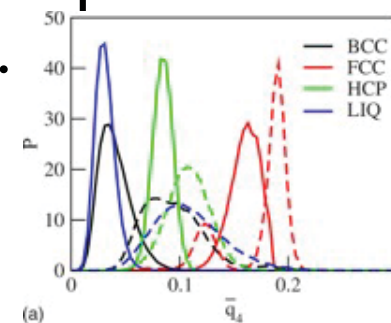
Vacancy :A lattice site that has no atom within a distance  $r_{int}$ .

q4 Parameter :A parameter based on evaluating the spherical harmonics  $Y_{lm}(r_{ij})$  for each neighbouring atom  $j$  of  $i$ .

Lechner and Dellago J. Chem Phys. 129 114707 (2008)

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\mathbf{r}_{ij}).$$

$$q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |q_{lm}(i)|^2}.$$



# Visualisation Tools

Lots of free software

Pov-Ray : <http://www.povray.org/>

PDB visualisers : <http://www.bernstein-plus-sons.com/software/rasmol/>

Write your own with vtk.

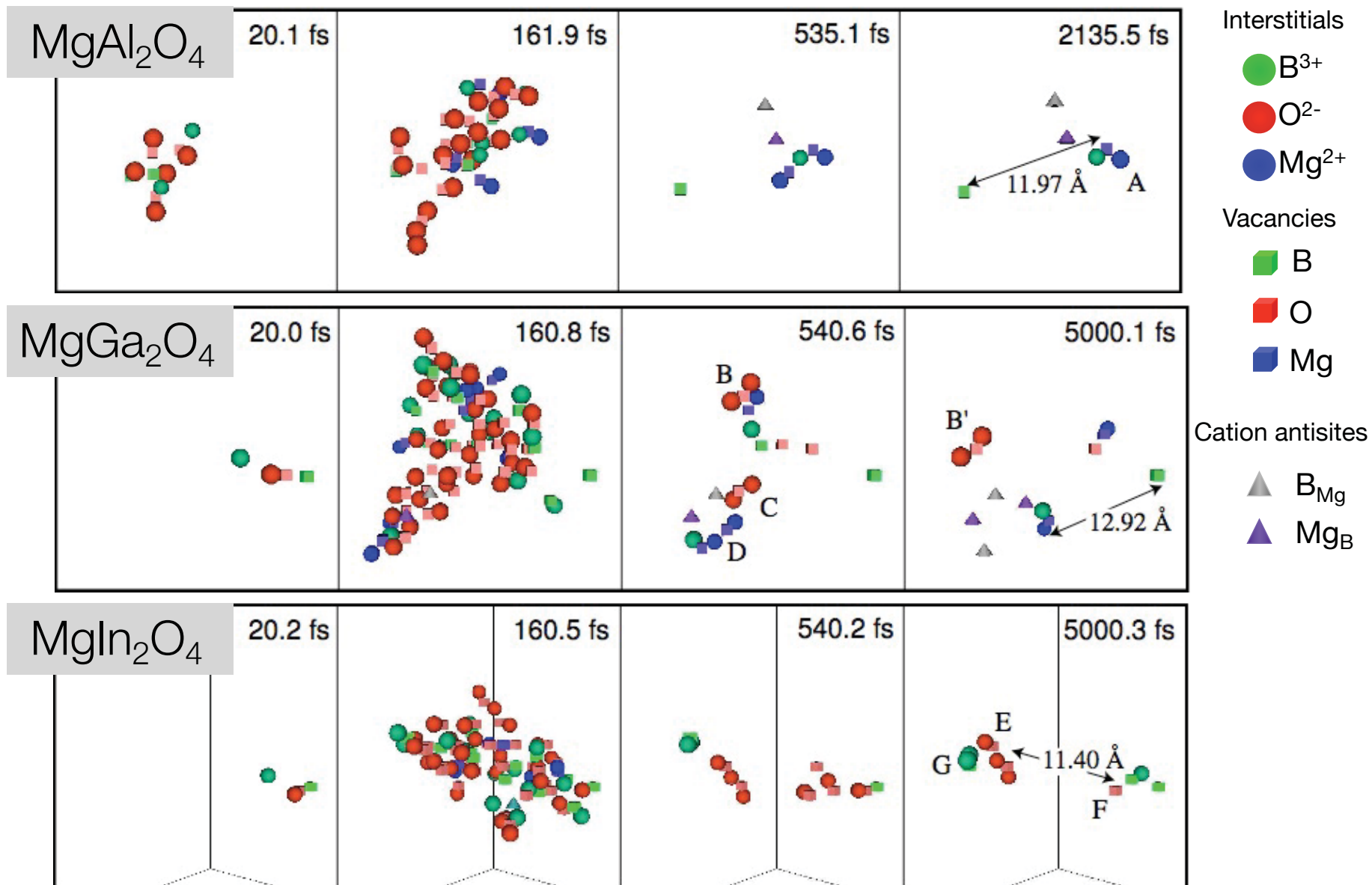
pdb file

```
HEADER  pKc =2.4  pKn =9.8          13-JUL-93
          COMPND  glycine  GLY  MW = 57
ATOM    1  N  GLY  I   -1.476  0.232  0.252  1.00  0.00
ATOM    2  CA GLY  I   -0.012  0.296  0.348  1.00  0.00
ATOM    3  C  GLY  I    0.596 -0.652 -0.648  1.00  0.00
ATOM    4  O  GLY  I   -0.124 -1.320 -1.368  1.00  0.00
ATOM    5  OXT GLY I    1.916 -0.760 -0.740  1.00  0.00
ATOM    6  H3  GLY I   -1.736 -0.252 -0.592  1.00  0.00
ATOM    7  HA2 GLY I    0.292  0.020  1.364  1.00  0.00
ATOM    8  HA1 GLY I    0.320  1.320  0.132  1.00  0.00
ATOM    9  H9  GLY I   -1.636 -0.236  1.132  1.00  0.00
ATOM   10  H1  GLY I   -1.916  1.136  0.272  1.00  0.00
          TER    II  GLY  I
          END
```

xyz file

```
8
1  7.17  4.42  3.45  0.0000  -4.2208  -0.6967
2  7.01  4.38  4.38  0.0000  -4.2208  0.3204
3  6.27  4.40  3.09  0.0000  -4.2208  0.3740
4  9.51  4.30  1.69  0.0000  -4.2208  -0.6906
5  9.61  5.23  1.47  0.0000  -4.2208  0.3181
6  8.74  4.29  2.27  0.0000  -4.2208  0.3830
7  2.87  1.04  2.93  0.0000  -4.2208  0.3233
8  0.93  1.34  2.54  0.0000  -4.2208  0.2552
```

# 0.4 keV cascade snapshots



# Defects in amorphous systems e.g. glasses

## Three possible approaches : but more work required

- Use Voronoi tessellation to study defects in amorphous structures
- Investigate by use of a short range ordering parameter  $c_{ij} = p_{ij}/p_{ij}^0 - 1$ , where  $p_{ij}$  is the probability of finding atoms  $i$  and  $j$  as neighbours and  $p_{ij}^0$  is the unirradiated probability
- Can also monitor the cascades by visualising the displaced atoms.

## Other considerations not mentioned

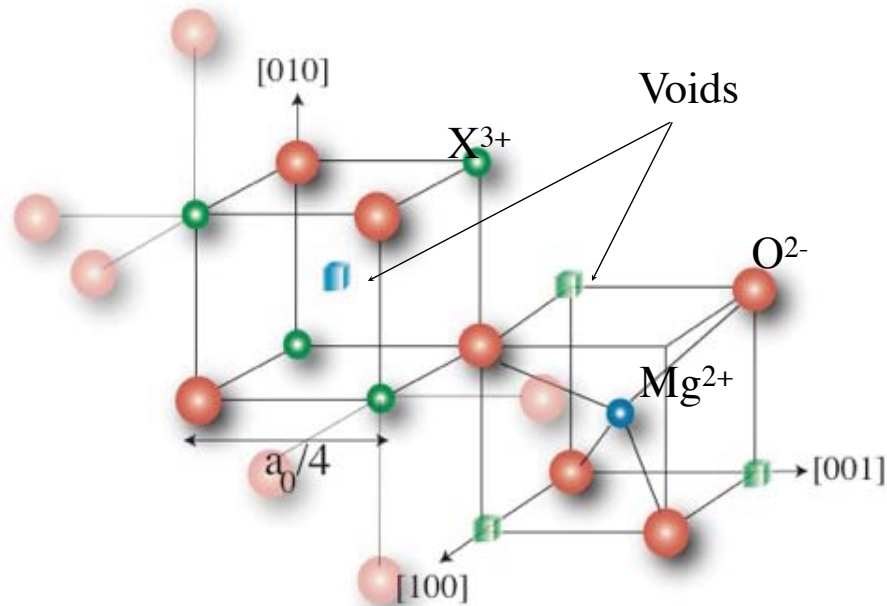
- Optimisation algorithms
  - Conjugate gradient, steepest descents, quasi-Newton
- Potential construction
  - Fitting methods e.g. neural networks
- Constant pressure MD and implementation of constraints
- ab initio methods
  - use hellman-Feynman theorem to determine forces

# Some Examples

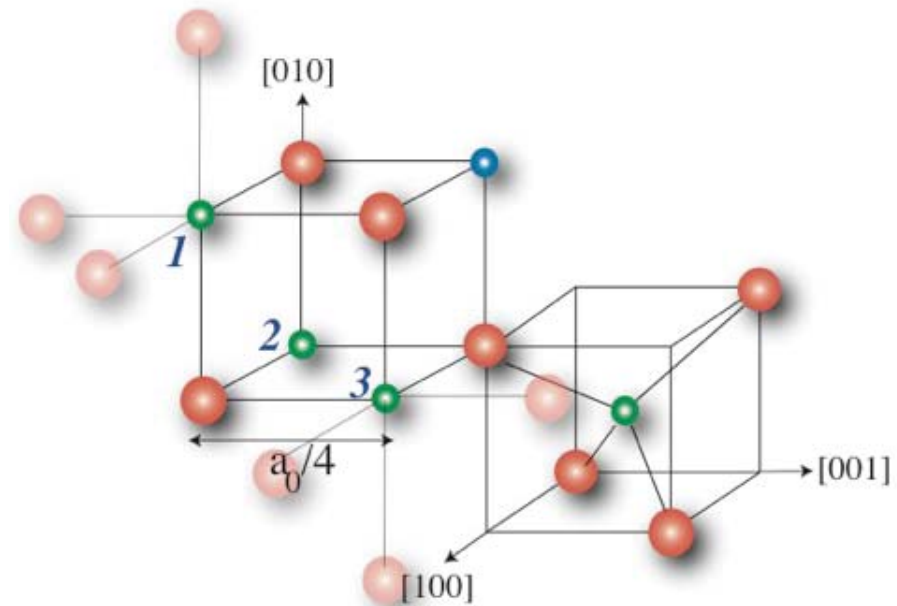


# Structure of spinel

Normal spinel



Inverse spinel

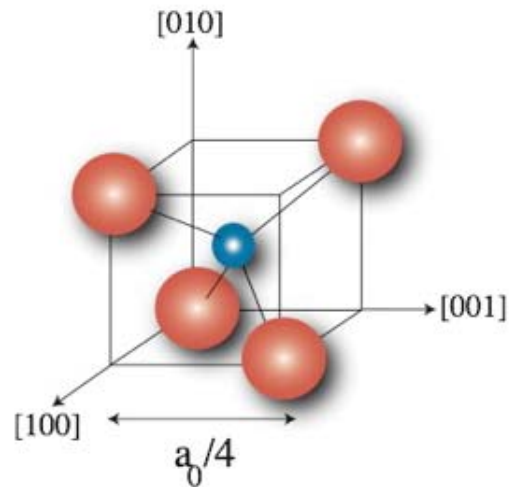


Unit cell: 8 formula units of MgX<sub>2</sub>O<sub>4</sub> (X= Al, Ga, In)

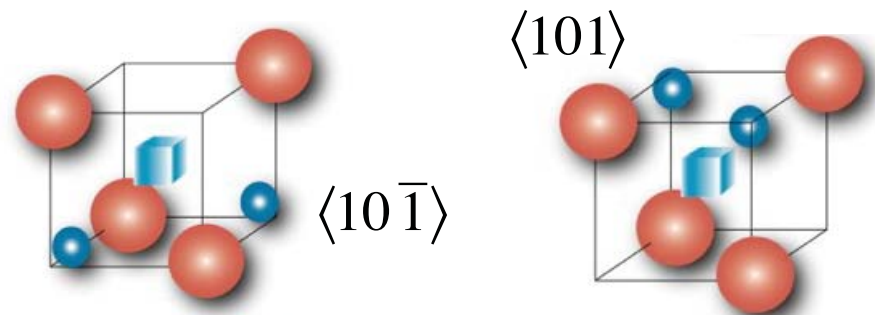
Spinel can exhibit appreciable **disordering** of cations within their structures - site exchange

# Defects in normal spinel, $\text{MgAl}_2\text{O}_4$

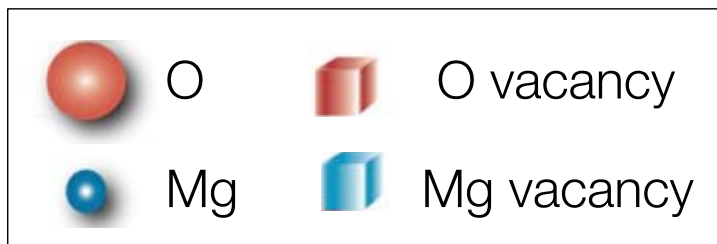
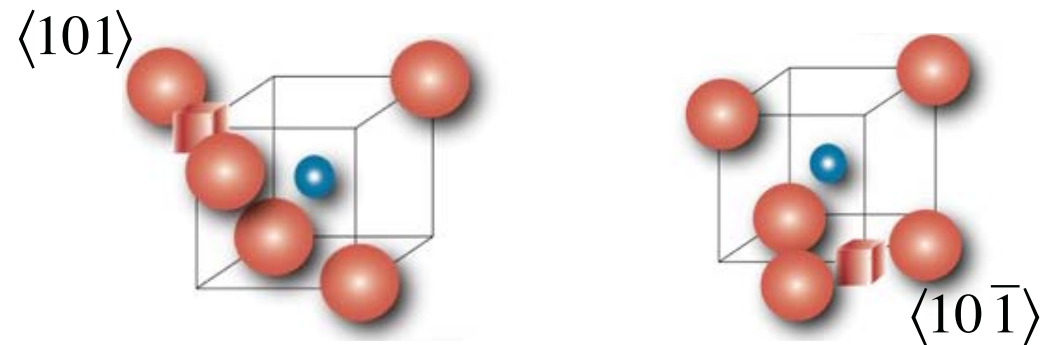
Perfect structure



Mg split interstitial



Anion split interstitial





# Example : 10 keV PKA cascade in magnesium aluminate spinel (fixed charge ionic potential)

Interstitials

● B<sup>3+</sup>

● O<sup>2-</sup>

● Mg<sup>2+</sup>

Vacancies

■ B

■ O

■ Mg

Cation antisites

▲ B<sub>Mg</sub>

▲ Mg<sub>B</sub>

# Example : 10 keV PKA cascade in magnesium aluminate spinel (fixed charge ionic potential)

MDtime = 0.00 fs  
Total Atoms = 988391  
Vacancies = 0  
Interstitials = 0  
Antisites = 0

Interstitials

- B<sup>3+</sup>
- O<sup>2-</sup>
- Mg<sup>2+</sup>

Vacancies

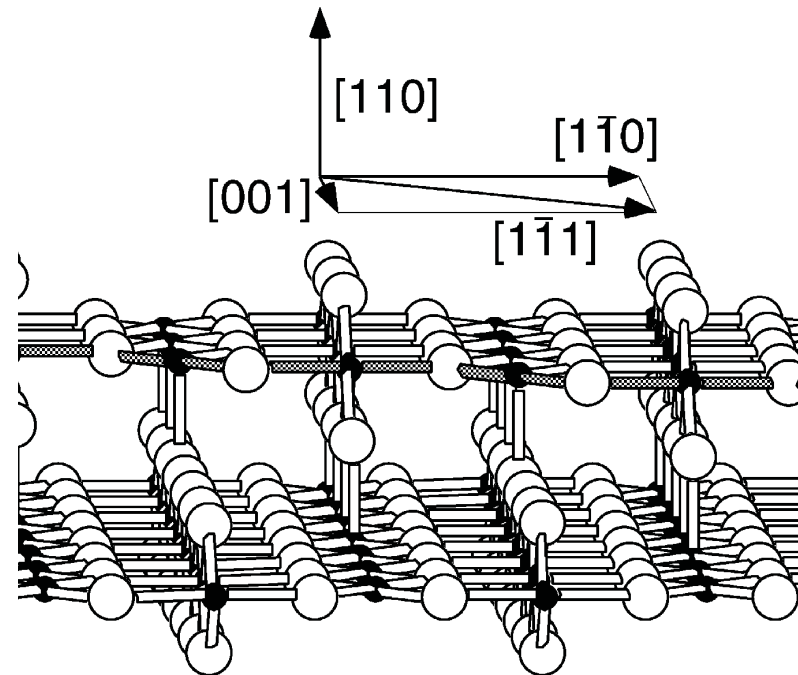
- B
- O
- Mg

Cation antisites

- ▲ B<sub>Mg</sub>
- ▲ Mg<sub>B</sub>

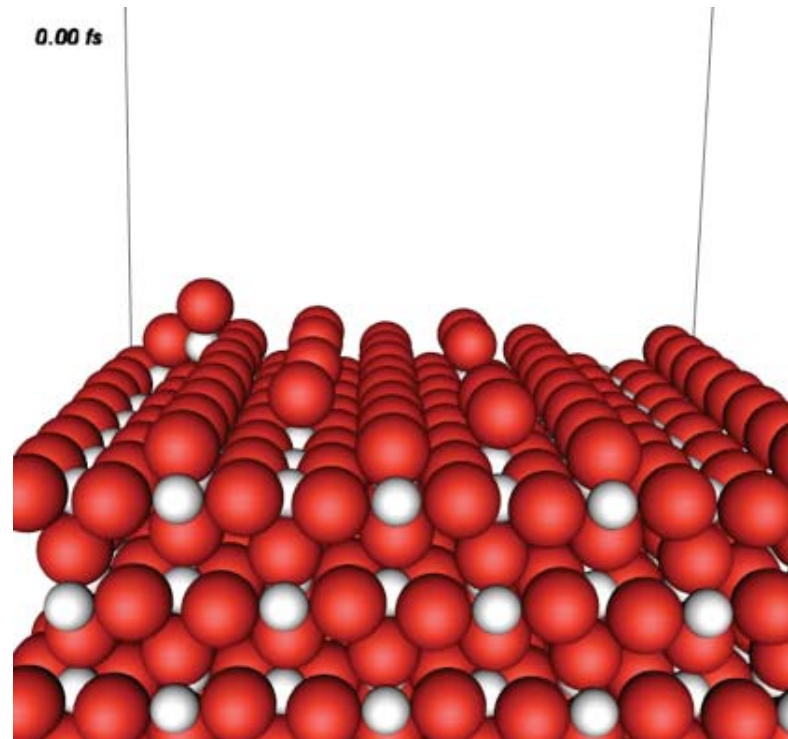
# Rutile (110) Surface

- Rutile (110) surface
  - 5-coord Ti atoms
  - 6-coord Ti atoms
  - 3-coord O atoms
  - 2-coord O atom “bridges” along [001]

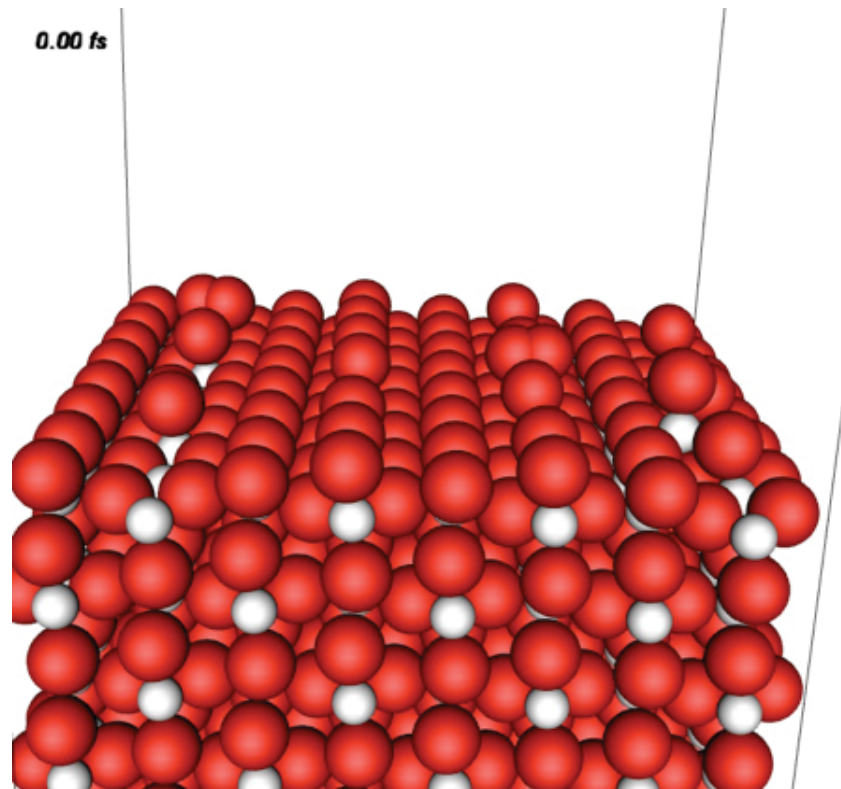


Diebold, Ulrich "The surface science of titanium dioxide" *Surface Science Reports* 48 pp. 53-229

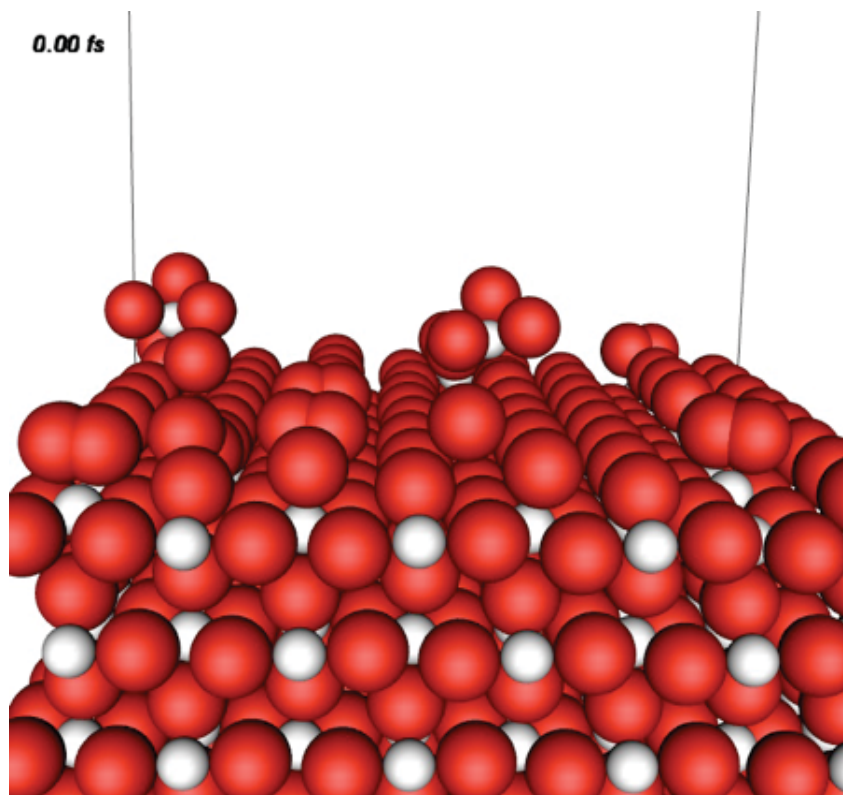
# Example: The oxidation of the $\text{TiO}_2$ rutile $\{110\}$ surface (variable charge potential)



○ dimer added to the trench

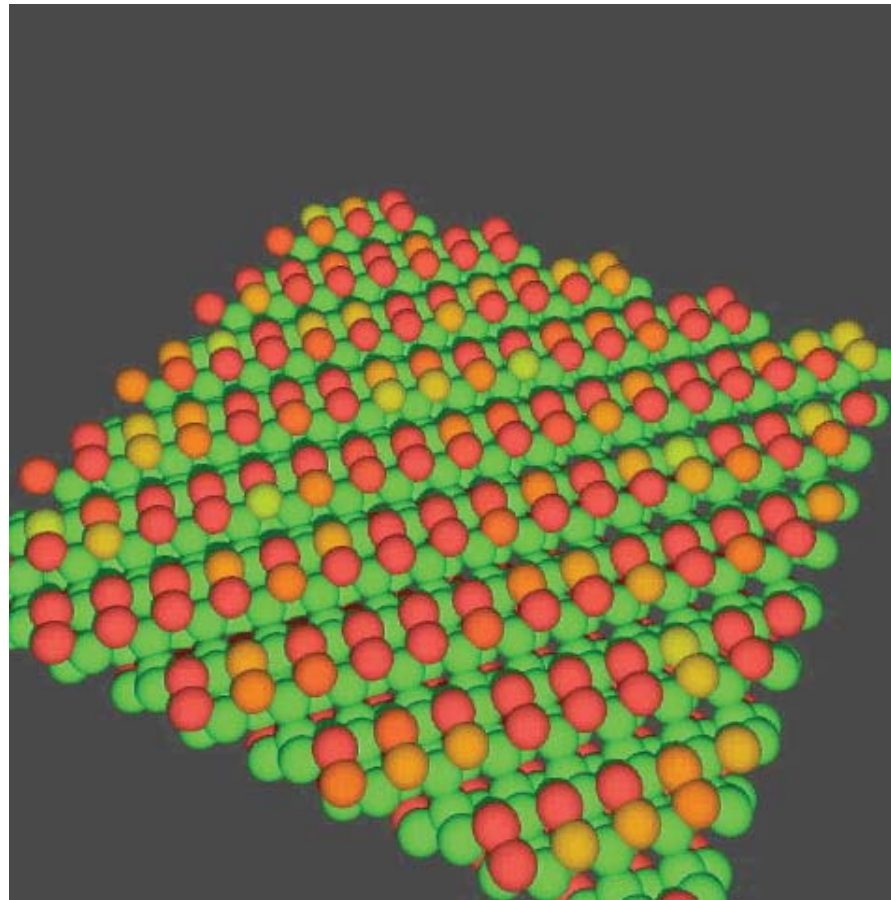


Ti extraction from a subsurface layer



Etching of the surface with more O addition

# MD deposition of C<sub>60</sub> onto Si{100} (2 × 1) at 600K (Tersoff-Brenner potential)



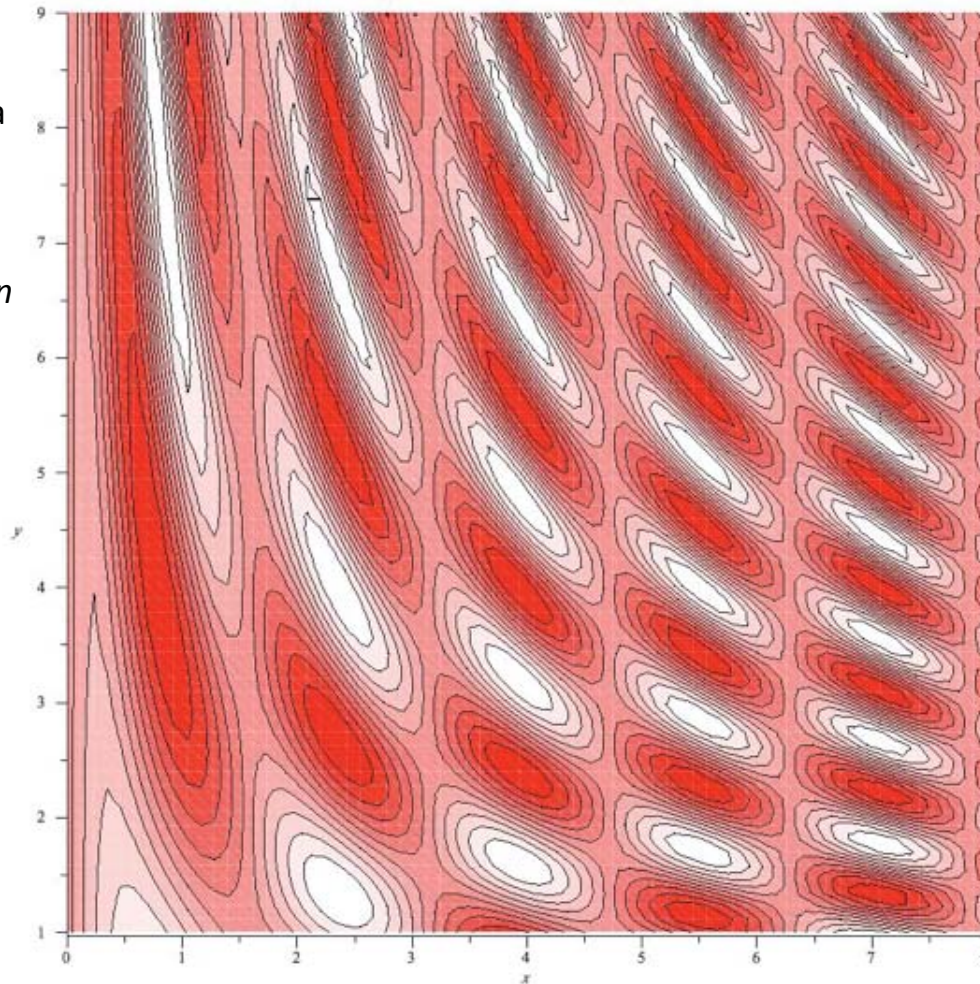
Question : What is physically unrealistic about this movie ?  
Answer : Unrealistic deposition rates



## Example : Particle moving in a 2-D potential field

deep red -- maxima  
light red -- minima

*The system gets trapped in the basin around a minimum and transits to the next basin over a saddle point*



$$V(x,y) = \sin(2x) \cos(xy)$$

$$x_0 = 3\pi/4$$

$$y_0 = 4.0$$



# Conclusions

MD simulations can now be run routinely on systems containing millions of atoms

Potentials are now so refined that they can model both the close interactions and the chemical bonding with reasonable accuracy

The length scale problem is almost solved by using parallel computing and embedding in a finite element region

The time scale problem is not yet solved but will be effectively solved within the next decade (see next lecture)

For a  $2 \times 2$  system where

$$M = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

The condition for symplecticity  $M^T J M = J$  gives

$$\begin{pmatrix} a & c \\ b & d \end{pmatrix} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

i.e.

$$\begin{pmatrix} 0 & ad - bc \\ bc - ad & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

i.e.  $\det M = 1$ .

## What is special about the Verlet algorithm

Consider the problem of simple harmonic motion. In Hamiltonian form this can be written

$$\mathcal{H} = \frac{1}{2}(p^2 + k^2q^2) \quad \dot{q} = p \quad \dot{p} = -k^2q$$

A second order Runge-Kutta method could be given by

$$k_1 = f(t_n, y_n), \quad k_2 = f(t_n + h, y_n + hk_1),$$
$$y_{n+1} = y_n + f(t_n + h, y_n + \frac{1}{2}h(k_1 + k_2))$$

Applying this method to the SHM problem gives

$$\begin{pmatrix} q_{n+1} \\ p_{n+1} \end{pmatrix} = \begin{pmatrix} 1 - \frac{1}{2}(hk)^2 & -hk^2 \\ -h & 1 - \frac{1}{2}(hk)^2 \end{pmatrix} \begin{pmatrix} q_n \\ p_n \end{pmatrix}$$

whereas the Verlet algorithm gives

$$\begin{pmatrix} q_{n+1} \\ p_{n+1} \end{pmatrix} = \begin{pmatrix} 1 - \frac{1}{2}(hk)^2 & h \\ -hk^2(1 + \frac{1}{2}(hk)^2) & 1 - \frac{1}{2}(hk)^2 \end{pmatrix} \begin{pmatrix} q_n \\ p_n \end{pmatrix}$$

For the R-K case  $\det M = 1 + \frac{1}{4}(hk)^4$

For the Verlet case  $\det M = 1$