Particle Dynamics & DL_POLY

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STFC DARESBURY LABORATORY
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EPSRC Pioneering research and skills
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NATURAL ENVIRONMENT RESEARCH COUNCIL
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CoSeC Computational Science Centre for Research Communities

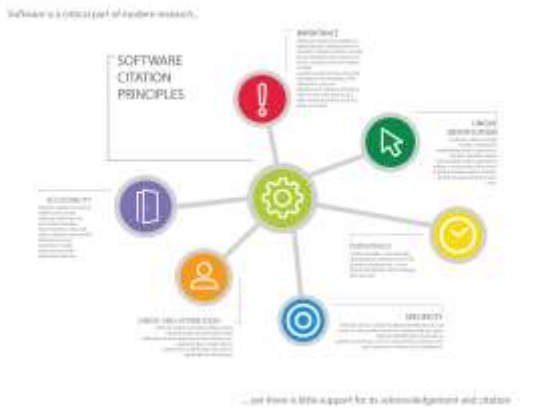
Daresbury Laboratory

Who We Are

RSE
RESEARCH SOFTWARE ENGINEERS ASSOCIATION

FORCE11
The Future of Research Communications and e-Scholarship

Software Sustainability Institute

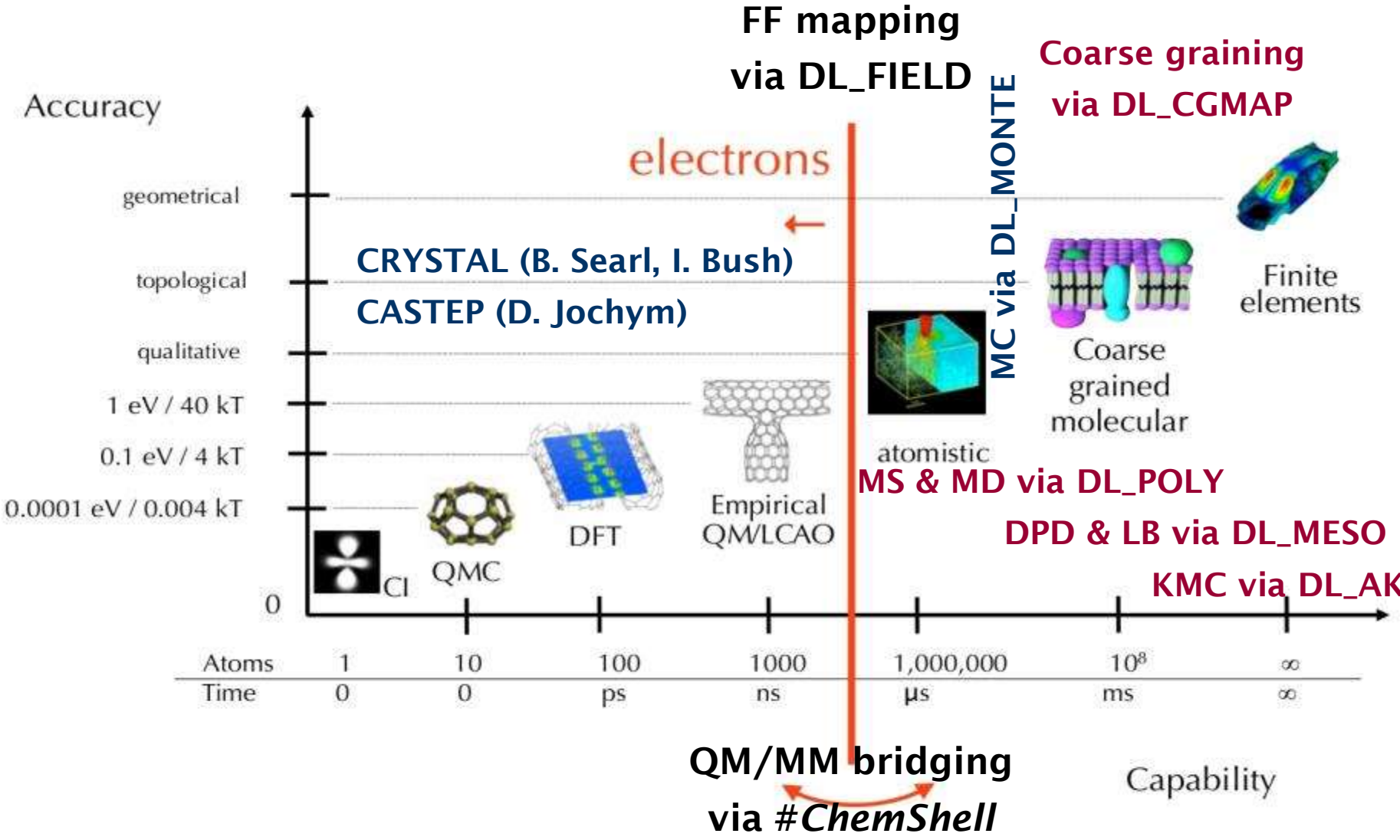


Importance
Identification
Persistence
Specificity
Credit
Accessibility

You can support and work with us advancing and utilising our methodologies by:

- citing appropriately our software packages
- collaborating and publishing research with us

Multiple Scales of Materials Modelling



Part 0

The DL_Software Packages

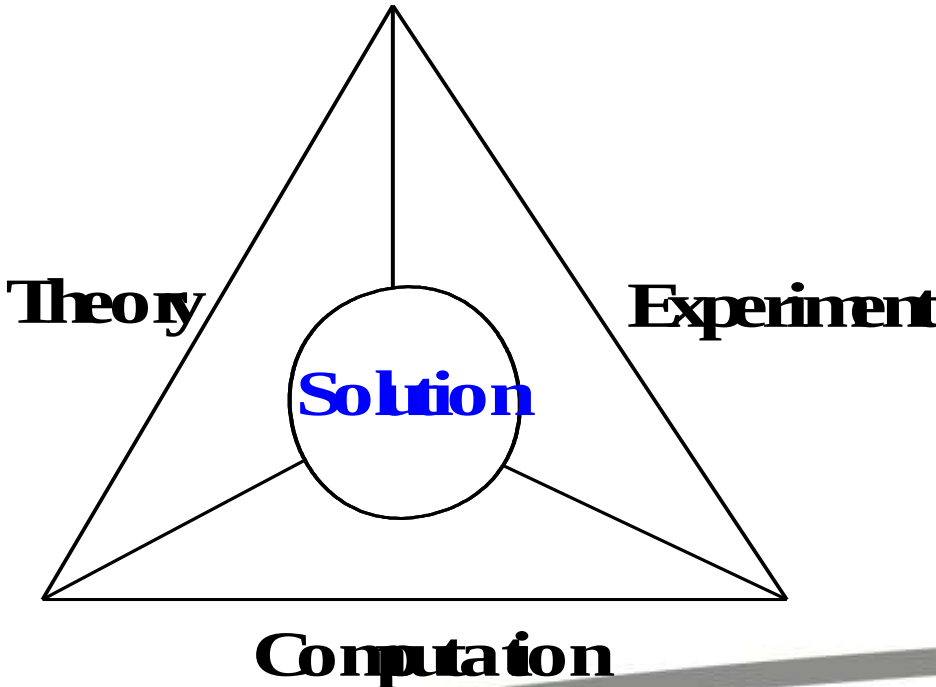
DL_Software

Enabling Discovery

Computer Modelling

Computer modelling is used to provide insight and understanding of how complex systems behave beyond what theory and experiment could deliver separately. It bridges theory and experiment by solving state equations numerically.

Computer simulations are used as an assisting tool by scientists and engineers to verify and/or predict experimental observations as well as test and/or tune theoretical models.



Computational Science

Computational Science is a generic term for any field of science where computer simulation is used in conjunction with theory and experiment to model various aspects of “reality” (observed or sought after phenomena), to provide solution to problems and answer to questions that often cannot be satisfactory explained by theory and experiment alone.

Within natural sciences one could outline a number of fields which generally resolve behaviour of nature (the physical world surrounding us) on different time- and length-scales: Physics, Chemistry, Materials and Engineering.

Modelling & Simulation

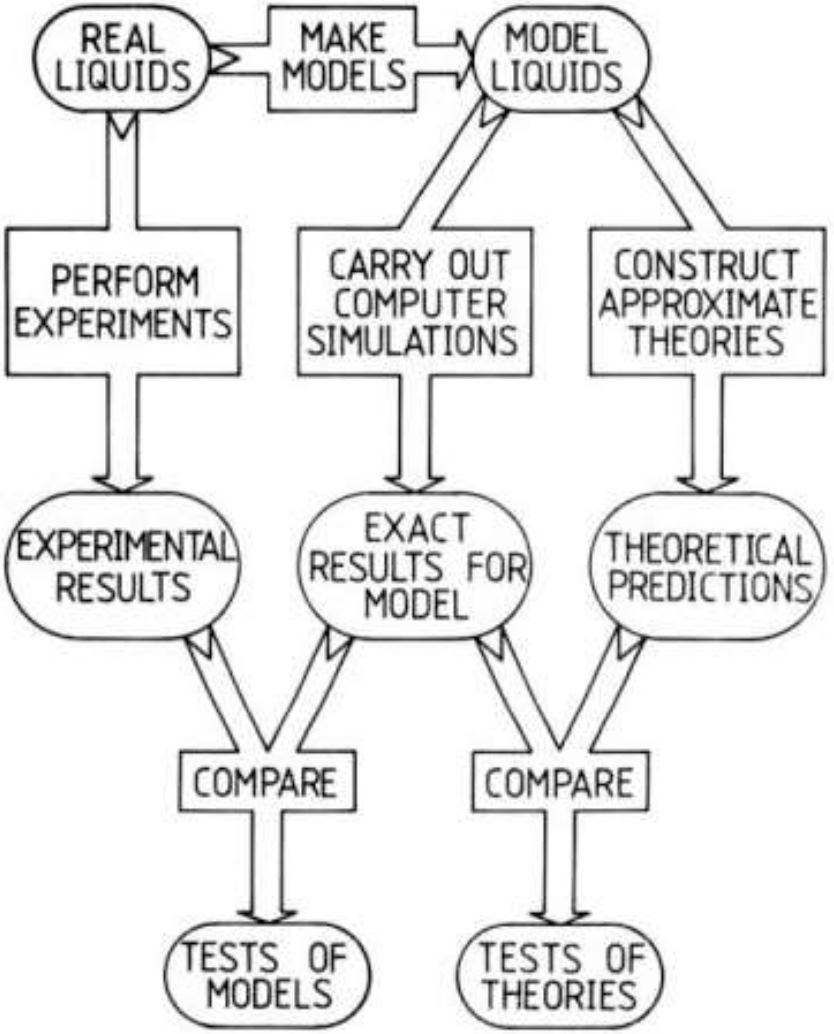
Allen & Tildesley

Two primary roles:

- **Test models which explain experiments**
- **Test theoretical predictions**

Driving forces:

- **Computers are fast enough for numerical experiments**
- **Most models are too complicated for purely theoretical reasoning**
- **There are phenomena which can not be observed directly by experiments**



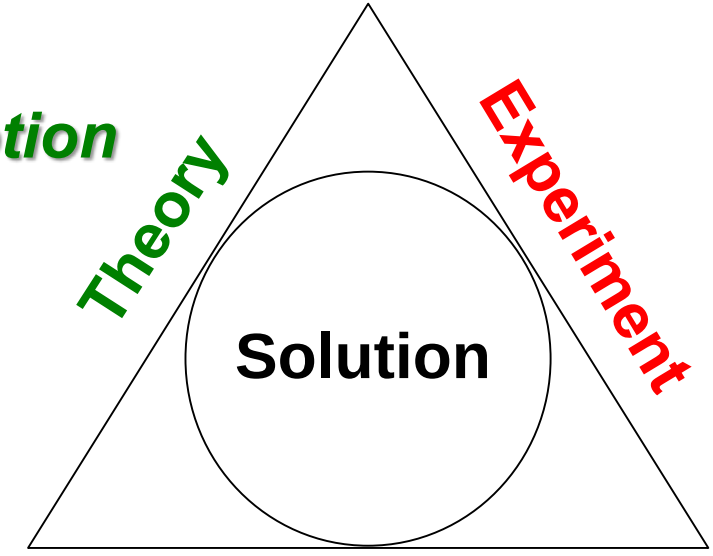
Micro/Meso-scopic/Celestial Evolution

Newton's Laws of Motion

force = mass * acceleration

t = time
v = velocity
r = position

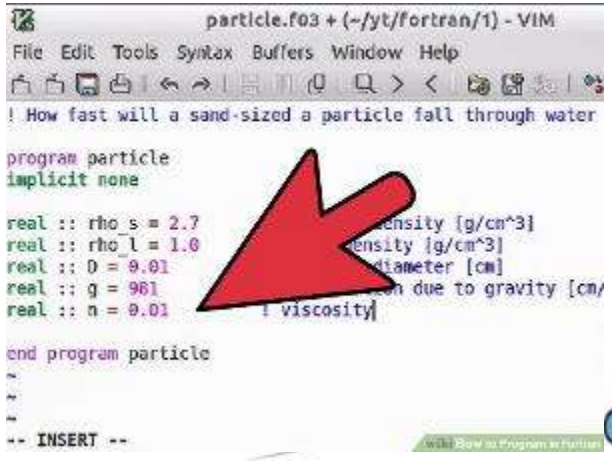
$r = r_0 + v * t + f * t^2 / m$



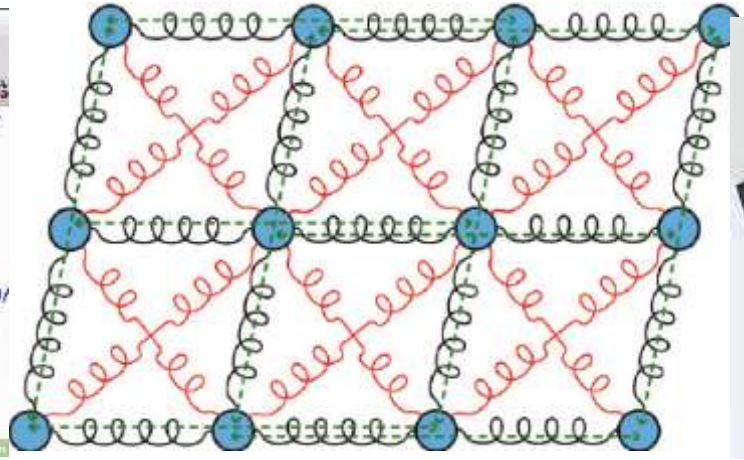
Computation

Instruments

Software (maths)

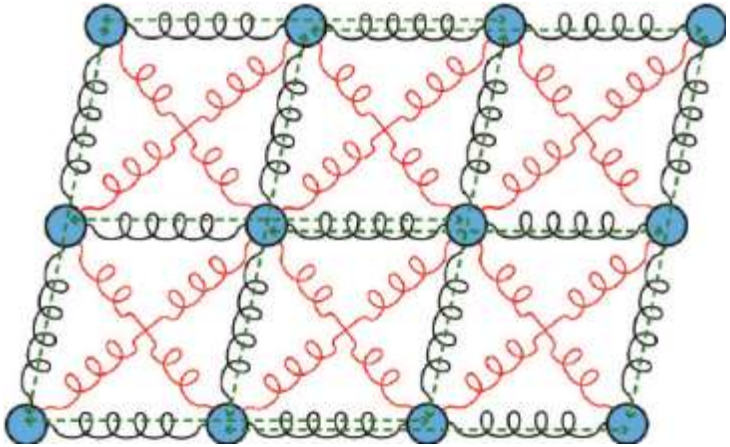


Model (forces)

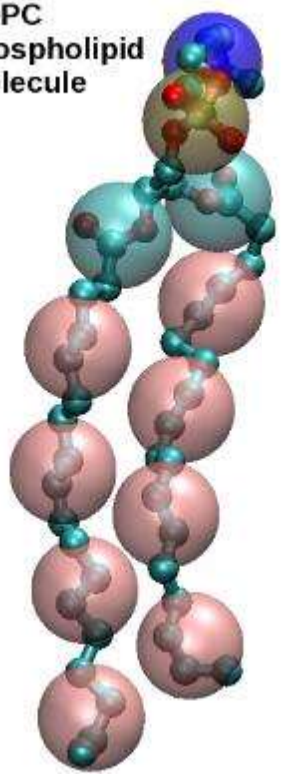


Computer (crunch)

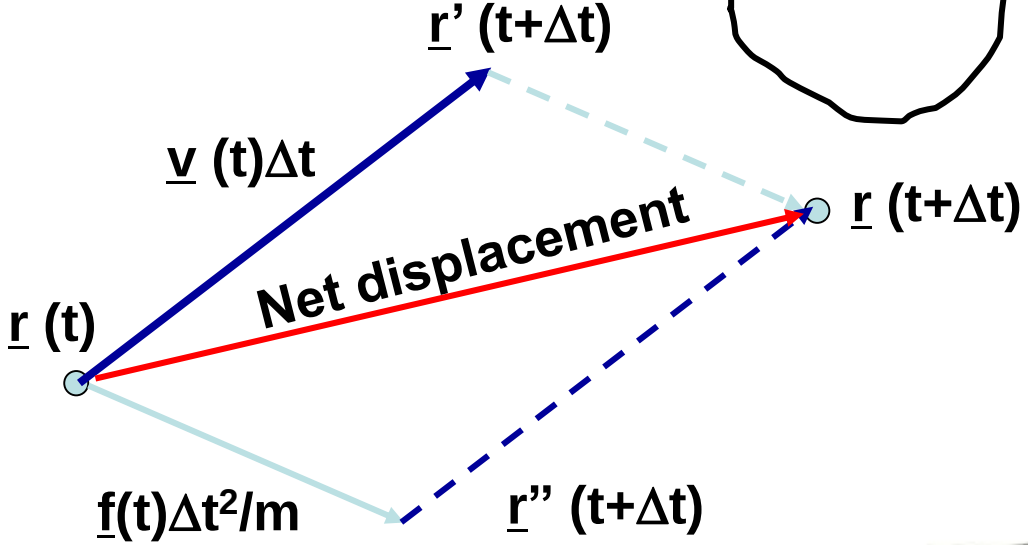
The DL_POLY Vehicle



DOPC phospholipid molecule



A



B

r (t), v(t), f(t) ⟶ r (t+Δt), v(t+Δt), f(t+Δt)

Science & Technology Facilities Council

UK Research and Innovation

Build to Perform

on supercomputers, mobiles, laptops...

Powerful & Versatile

to handle obstacles on unchartered terrain in unknown conditions

Multifunction Control

to navigate safely & securely in all circumstances

Science & Technology Facilities Council

UK Research and Innovation

Comfortable

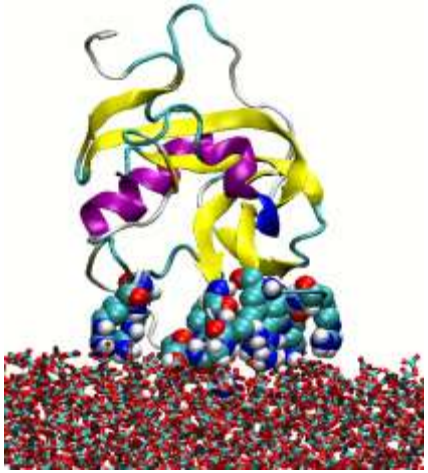
for STEM researchers to use for everyday's tasks

Informative & Responsive

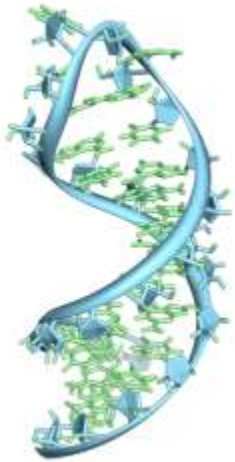
to indicate why, where & how a problem occurred

As Functional as a Sports Utility Vehicle

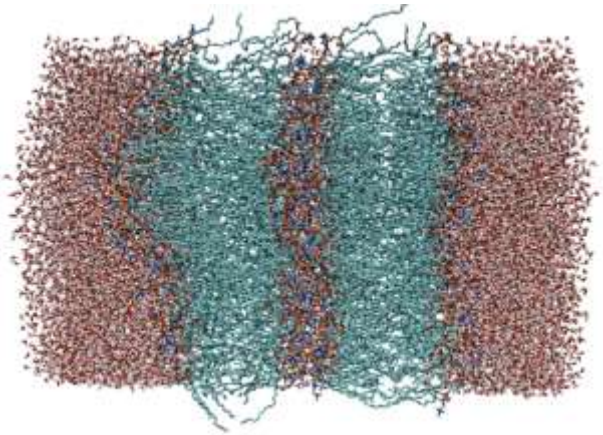
Examples of Model Systems



Proteins
solvation & binding

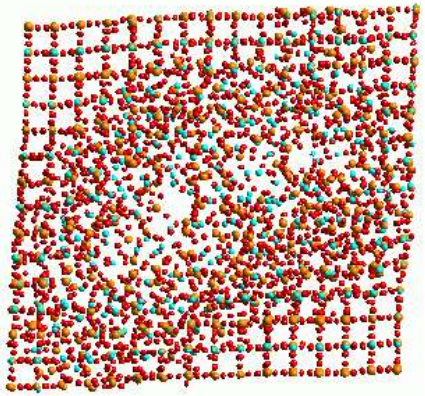


DNA strands
dynamics

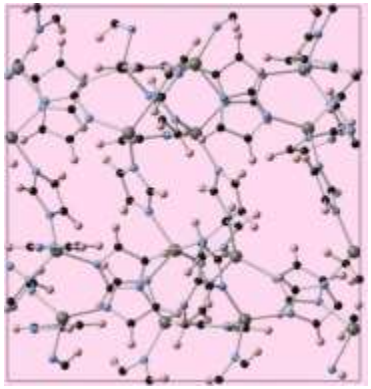


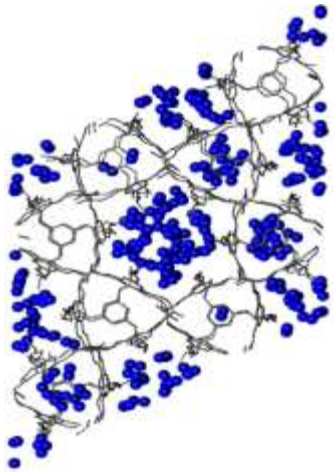
Membranes' processes

Drug polymorphs
& discovery

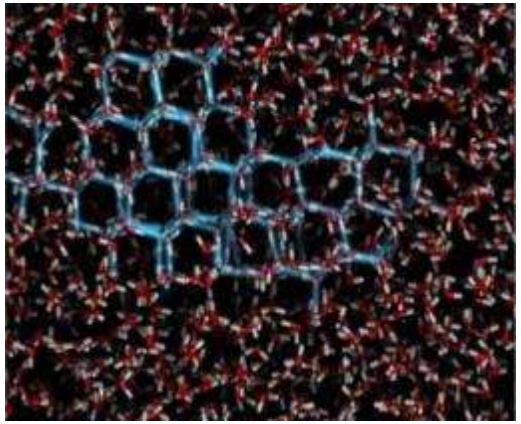


Crystalline & Amorphous
Solids – damage and recovery





Dynamic processes in
Metal-Organic & Organic Frameworks



Dynamics at Interfaces &
of Phase Transformations

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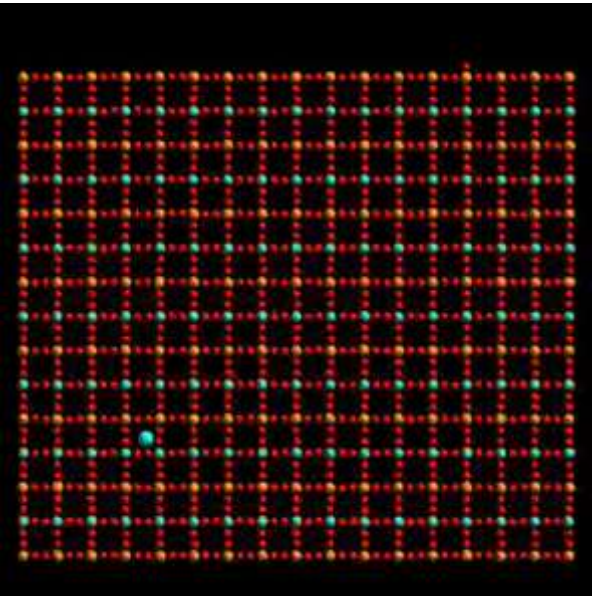
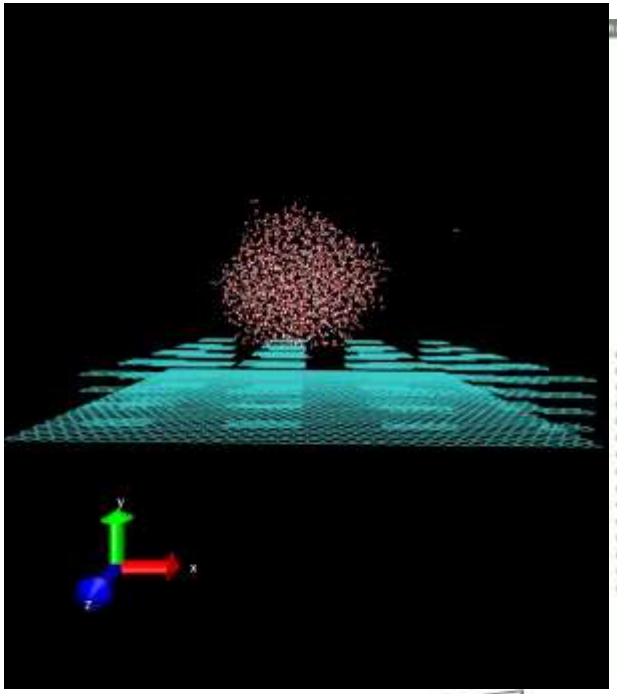
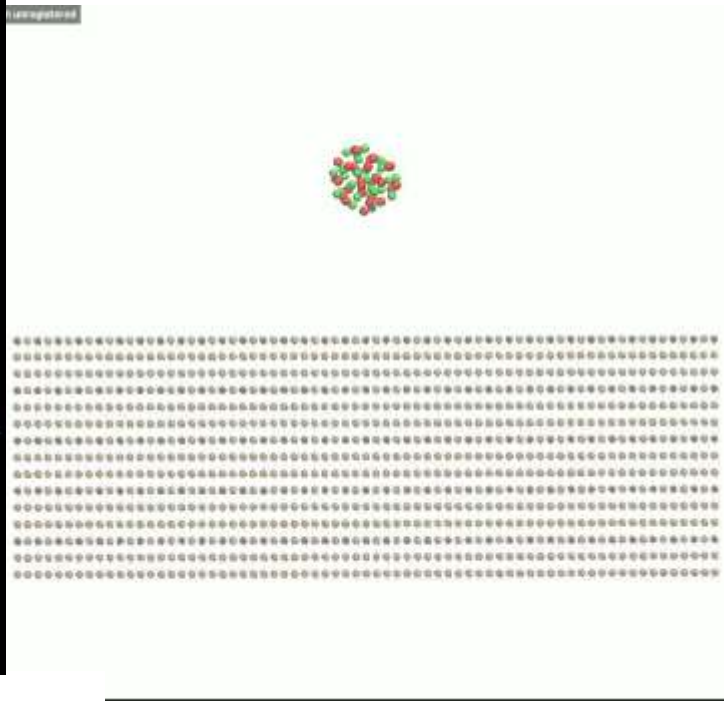
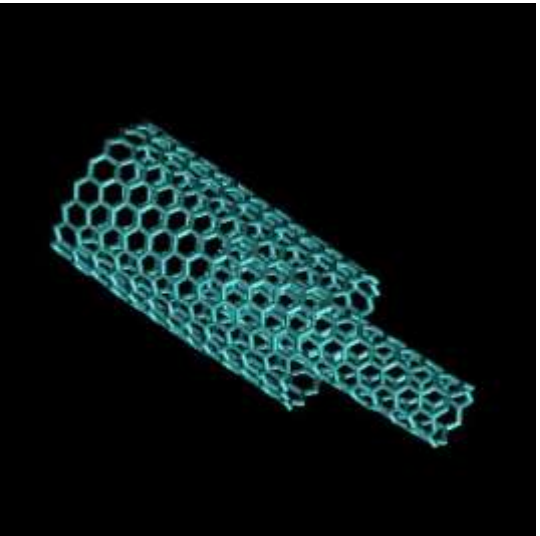
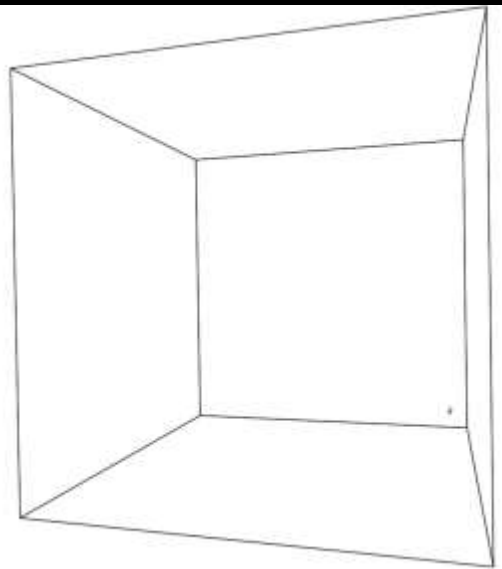
Examples of Videos

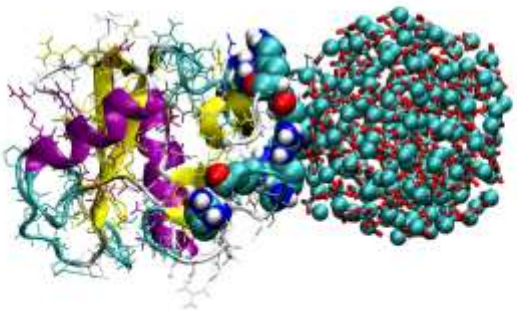












DL_FIELD
A force field and model development tool for DL_POLY

Dr Chin W. Yong
Computational Chemistry, Daresbury Laboratory

Science & Technology Facilities Council
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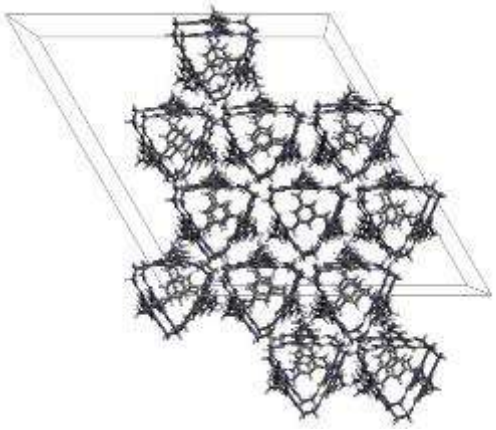
DL_FIELD uses:

Important application tool to enhance the usability of DL_POLY MD simulation package and to facilitate the use of a wide range of advance features included in the DL_POLY program.

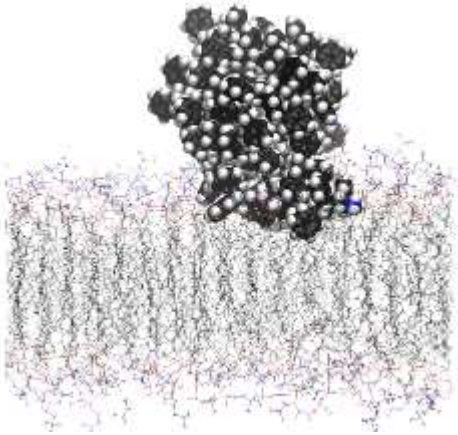
Force field model conversion tool – produces CONFIG, FIELD files for DL_POLY runs.

Software infrastructure for users to easily simulate a wide-range of different types molecular models with minimum effort, while giving choice to adjust force field models.

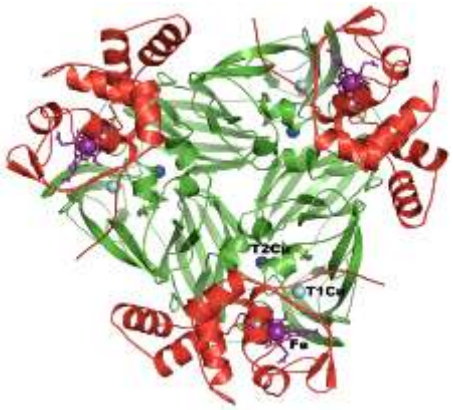
Selected model examples using DL_FIELD



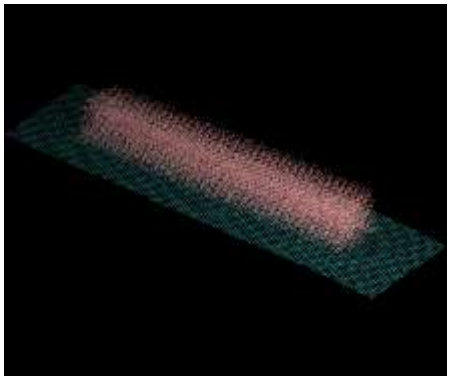
Organic cages

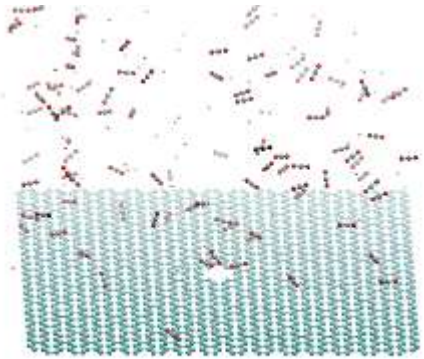


Polymer nanoparticle
On POPC membrane

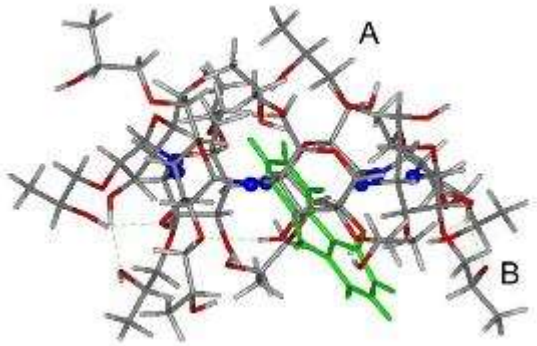


RpNiR - Complex multi-domain, multi-metal centers protein





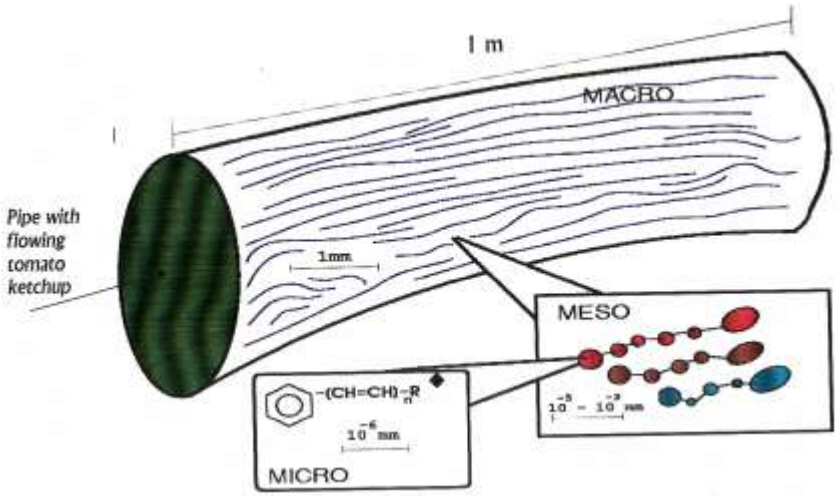
Nanocomposite materials involving graphene



Carbohydrates and complex drug molecules

Accessing the Mesoscale via DL_MESO

- Modelling at mesoscale
  - Between atomistic and fluid dynamics length/time scales
  - Both atom-like and fluid-like behaviours important
  - Bottom-up (coarse-graining) or top-down approaches valid



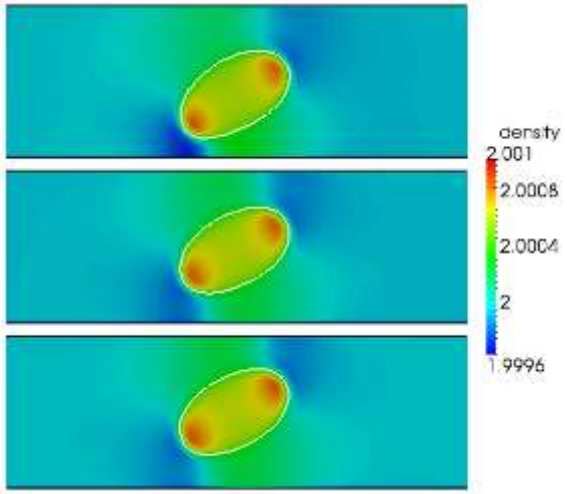
Source: Prof. PV Coveney,
Centre for Computational Science, UCL

- DL_MESO: mesoscopic modelling software suite
  - **Authored by Dr Michael Seaton**
  - Created for CCP5, base code for UKCOMES, used extensively by industry
  - Contains serial/parallel codes for different techniques (LBE, DPD)
  - Currently on version 2.6 (released November 2015)
  - 800 academic users (20% from UK) from variety of backgrounds (chemistry, physics, engineering etc.)

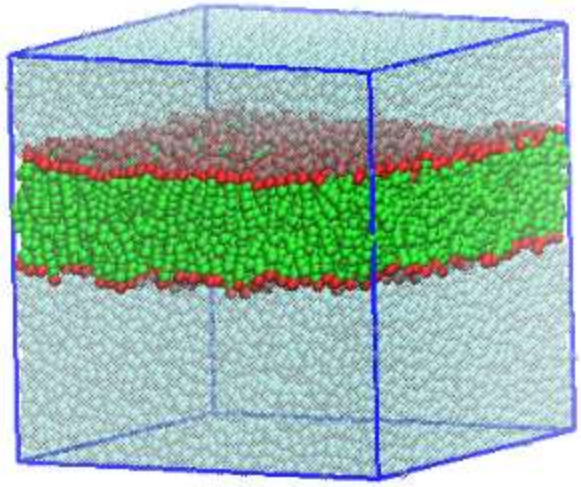
DL_MESO: Overview

Developer: michael.seaton@stfc.ac.uk

- Lattice Boltzmann Equation (LBE)
  - Statistical mechanics representation of fluid as gas particles: automatically gives Navier-Stokes (correct fluid) behaviour
  - Intuitive modelling of boundary conditions and interactions between multiple fluids
  - Inherently parallelisable using domain decomposition



- Dissipative Particle Dynamics (DPD)
  - Soft particles with pairwise thermostat: give Gallilean invariance and correct fluid behaviour
  - Close to classical molecular dynamics: particles can be coarse grains and represent (sections of) molecules with different interactions
  - Well suited to domain decomposition parallelism

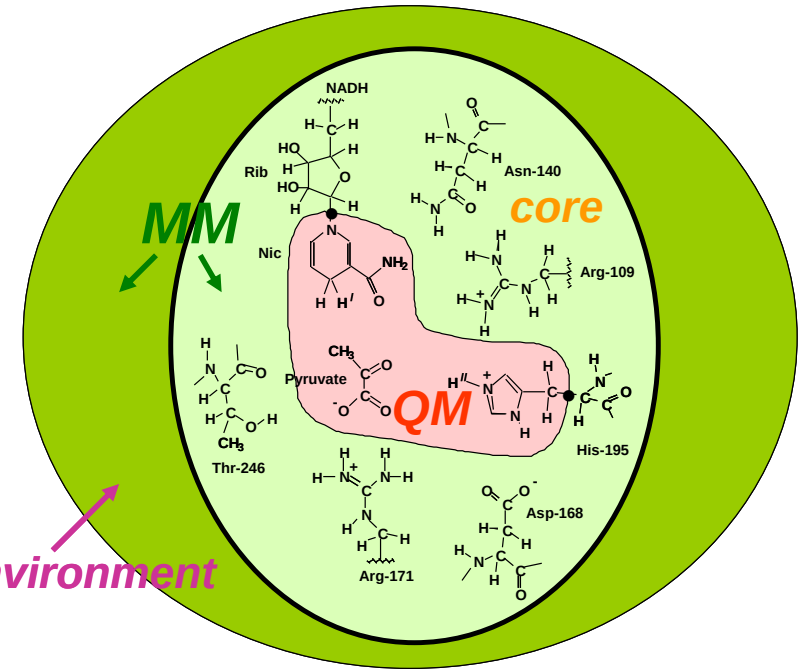


www.ccp5.ac.uk/DL_MESO

ChemShell

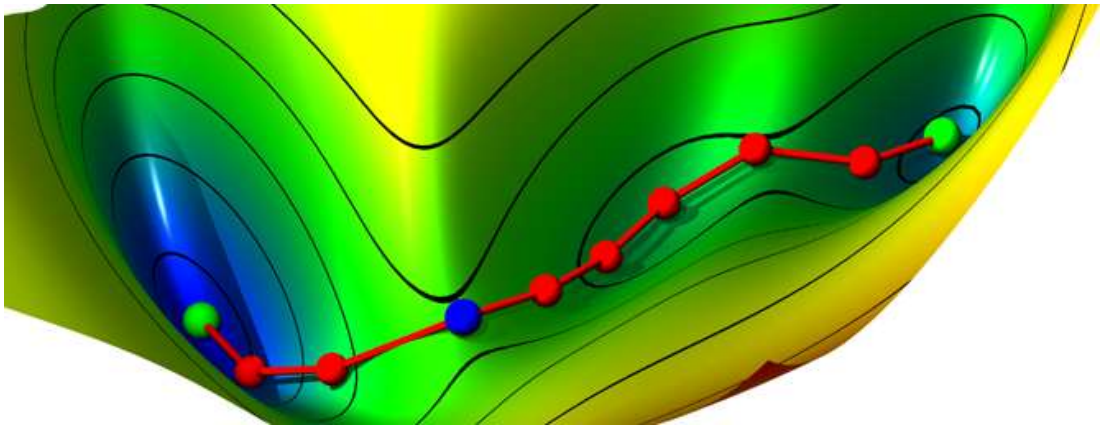
DL developers:
thomas.keal@stfc.ac.uk
you.lu@stfc.ac.uk

- Multiscale QM/MM simulations
- Wide range of interfaces to external QM and MM codes
  - inc. GAMESS-UK & DL_POLY
- ChemShell provides QM/MM driver and high-level tasks (optimisation, dynamics…)
- Parallelisation via MPI
- Controlled by scripts written in Tcl



DL-FIND

- Open source geometry optimisation library written in Fortran
- Standard optimisation driver for ChemShell
- Supports minimisation, transition state optimisation, reaction path optimisation, global optimisation, …
- Special algorithms for efficient QM/MM optimisation



J. Kästner, J.M. Carr, T.W. Keal, W. Thiel, A. Wander, P. Sherwood, *J. Phys. Chem. A,* **113**, 11856, (2009)

DL_MONTE
A general purpose parallel Monte Carlo program

Dr John Purton
Dr Andrey Brukhno

Daresbury Laboratory

Dr James Grant
Dr Tom Underwood

University of Bath

Science & Technology Facilities Council
UK Research and Innovation

Why Monte Carlo

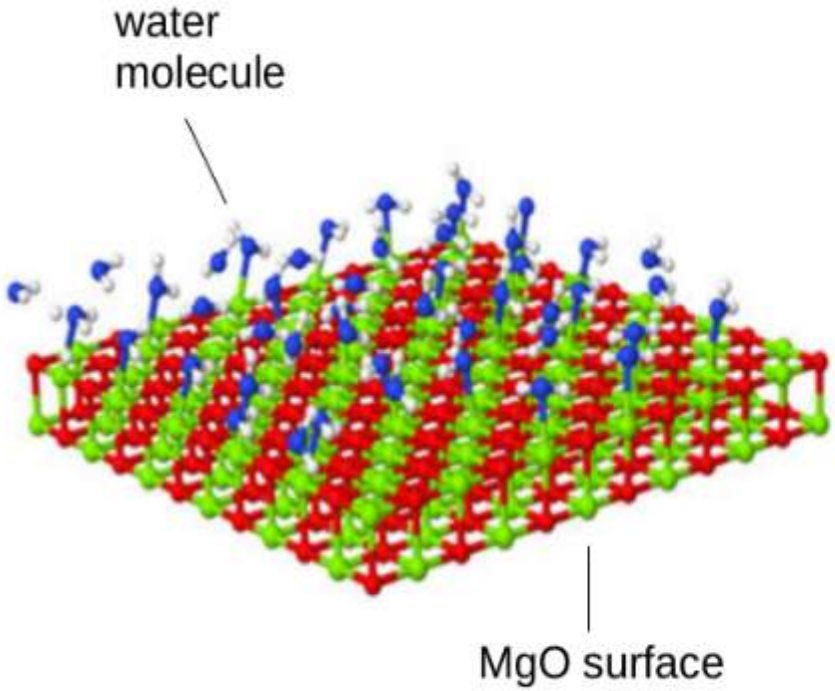
- A technique to explore “equilibrium” and answer “hypothetical” questions by throwing dice and using the Metropolis scheme for numerical integration

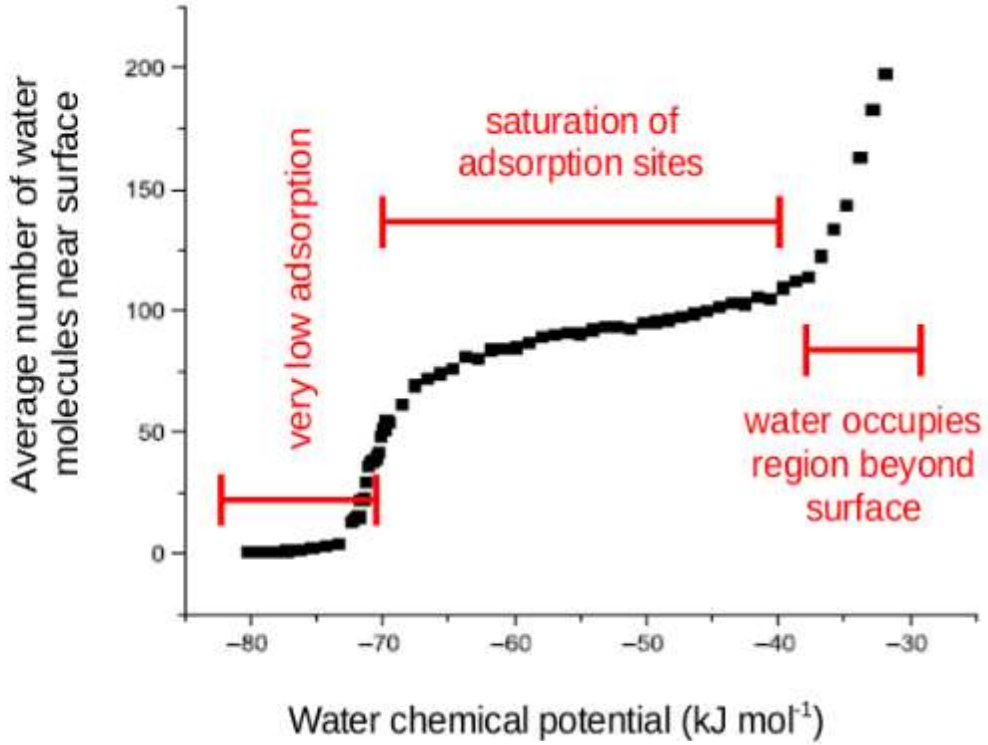
- Advantages of MC
  - atom/molecule insersions/deletions/mutations → chemical equilibrium
  - ”artistic” moves and pathways to skip energy barriers → metastability & coexistence
  - efficient biased exploration of configuration space → thermodynamic equilibrium
  - powerful riding free-energy landscapes → transition states & rare events
  - Metropolis scheme is simple conceptually & inexpensive algorithmically
  - easy to exploit parallelism (HPC)

- MC lacks time & forces (major players in MD)
  - no mapping onto real time scale -> no kinetics
  - no momenta / real forces -> might suffer from slow motion in dense systems
  - efficient MC implies an imaginative and knowledgeable developer

H2O adsorption on MgO surface

- Grand Canonical Ensemble - maintaining chemical potential





$$P_i = min\{1, exp[B + (E^{N+1} - E^N)/kT]/(N+1)\}$$

$$P_d = min\{1, Nexp[-B + (E^N - E^{N-1})/kT]\}$$

$$\mu = k_B T(B + ln\Lambda^3/V)$$

$$\Lambda = h/\sqrt{(2\pi k_B T m)}$$

J.A. Purton, J.C. Crabtree & S.C. Parker (2013) DL_MONTE: a general purpose program for parallel Monte Carlo simulation, Molecular Simulation, 39:14-15, 1240-1252, DOI: 10.1080/08927022.2013.839871

DL_AKMC

Developers: john.Purton@stfc.ac.uk
david.gunn@stfc.ac.uk

- Kinetic Monte Carlo (KMC) - simulates state-to-state kinetics of a rare event system. Rare events correspond to the thermal activation of atoms from one energy basin to another on the potential energy surface. If the rates of these transitions are known, KMC can be used to simulate kinetics over long time scales.
- Adaptive Kinetic Monte Carlo (aKMC) is a method for determining all of the transitions from each state on the fly, eliminating the need to use a pre-defined rate-list.

DL_AKMC:

- Uses MD-type potentials (e.g. Buckingham, Tersoff, EAM etc.)
- Dimer method for finding transition states, from DL_FIND
- DL_POLY-type input files
- Simulation times reaching the level of seconds
- Runs on small workstations and large HPCs

Uses:

- Diffusion across/to surfaces and bulk
- Surface growth
- Defect mobility and clustering
- Simulation of infrequent event kinetics

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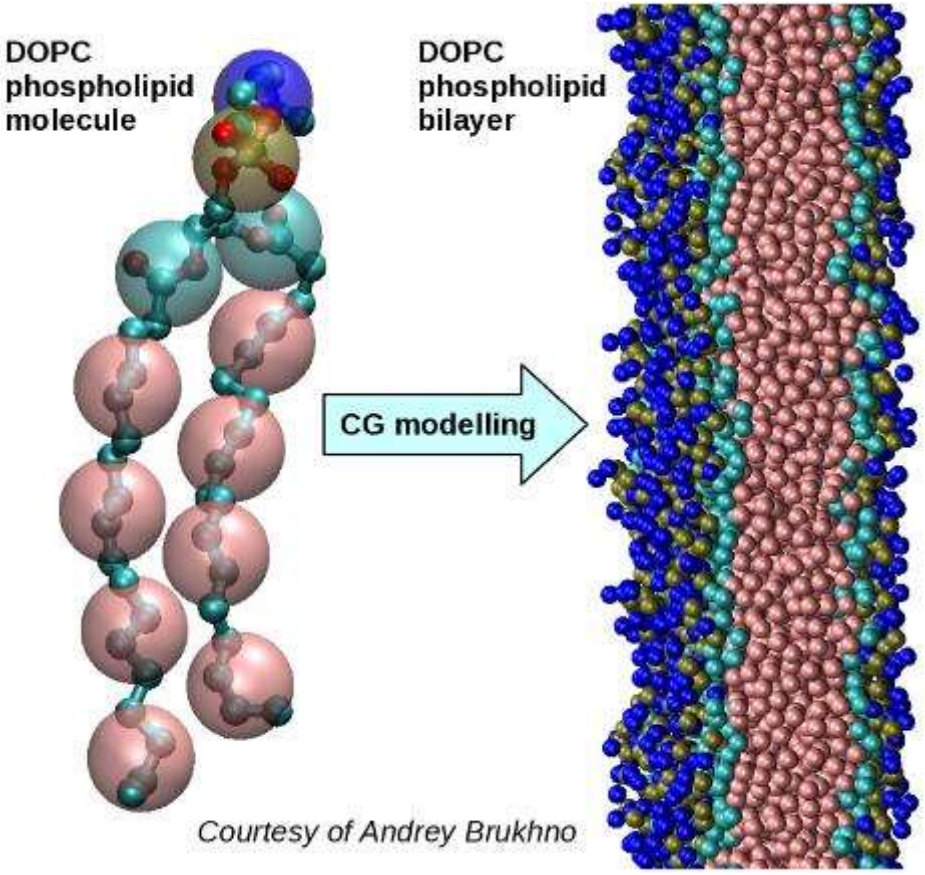
DL_CGMAP

- **Objectives**

  – provide the CCP5 community with state-of-the-art CG utilities
  – enable user-defined, numerically optimised coarse-grain models to be simulated by DL_POLY, DL_MESO, DL_MONTE
  – truly multiscale simulations with the use of DL_POLY



Dr Andrey Brukhno in collaboration with CCG and VOTCA team (work originated at the University of Bath) ***www.ccp5.ac.uk/projects/ccp5_cg.shtml & www.votca.org***

Part 1

The Molecular Dynamics Method

Recommended Books

Elements of Molecular Dynamics W. Smith, 2017 (WWW)

Statistical Mechanics: Theory and Molecular Simulation Mark Tuckerman, Oxford Graduate Texts, (FE 2010, SE 2016)

Computer Simulation of Liquids M.P. Allen & D.J. Tildesley, Oxford (FE 1998, SE 2017)

The Art of Molecular Dynamics Simulation D.C. Rapaport, Cambridge University Press (2004)

Understanding Molecular Simulation Daan Frenkel & Berend Smit, Academic Press, (FE 1996, SE 2010)

Theory of Simple Liquids J.-P. Hansen and I.R. McDonald, Academic Press (1986).

Classical Mechanics H. Goldstein+ (FE 1950, SE 1980, TR 2001)

Molecular Modelling, Principles & Applications A.R. Leach, Pearson Prentice Hall (SE 2001)

Statistics & Warnings

- Just because you see something in a simulation does NOT mean it is real! There are a lot of approximations (numerical & statistical errors) and assumptions (ergodicity, potentials holding beyond state points fitted for – T, P, pH; no quantum effects at low temperature, no ionisation processes, charges are fixed, etc.).

- Equilibrium properties are all about statistics! However, systems may be subject to trapping (in phase space) due to circumstances as initial conditions.

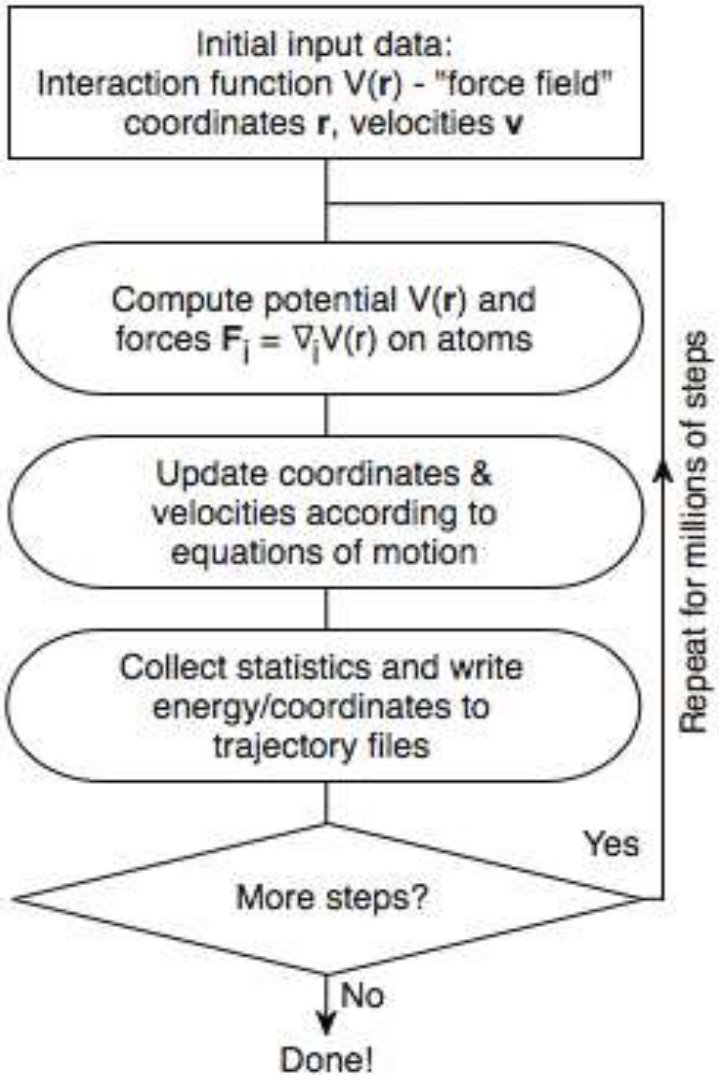
- When you've seen it 10 times it's significant - a single event is often not! This relates to how long is long for simulations.

- You should always try to calculate error estimates for predicted properties!

Molecular Dynamics: Definitions

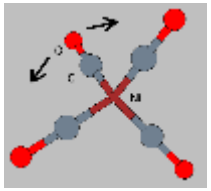
- Theoretical tool for modelling the detailed microscopic behaviour of many different types of systems, including; gases, liquids, solids, polymers, surfaces and clusters.
- In an MD simulation, the classical equations of motion governing the microscopic time evolution of a many body system are solved numerically, subject to the boundary conditions appropriate for the geometry or symmetry of the system.
- Can be used to monitor the microscopic mechanisms of energy and mass transfer in chemical processes, and dynamical properties such as absorption spectra, rate constants and transport properties can be calculated.
- Can be employed as a means of sampling from a statistical mechanical ensemble and determining equilibrium properties. These properties include average thermodynamic quantities (pressure, volume, temperature, etc.), structure, and free energies along reaction paths.

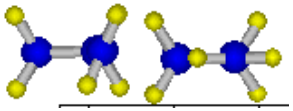
Molecular Dynamics in a Nutshell

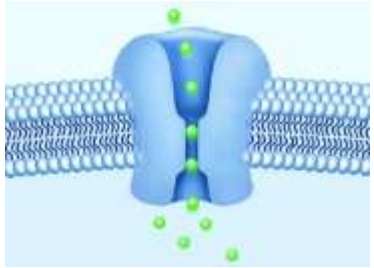


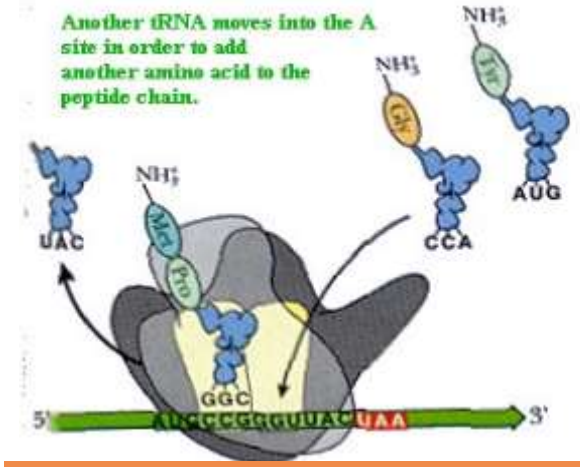
- **MD is the solution of the classical equations of motion for atoms and molecules to obtain the time evolution of a system.**
- **It is applied to many-particle systems since a general analytical solution is not possible. Thus one must resort to numerical methods and computers.**
- **It does classical mechanics only since a fully fledged many-particle time-dependent quantum method is not yet available.**
- **It uses a Maxwell-Boltzmann averaging process for thermodynamic properties (i.e. time averaging).**

Time and Length Scales









Biological Experiments

10^{-15}s 10^{-12}s 10^{-9}s 10^{-6}s 10^{-3}s 10^{0}s 10^{3}s

Coarse-grained models

(Whole proteins, viruses)

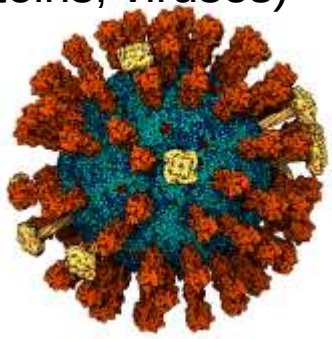
Molecular dynamics

(Atomic detail)

QM simulations

(Electrons)

(MD is fast!)

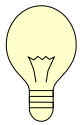


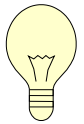
Science & Tech Facilities Council

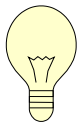
Molecular Dynamics for Beginners

MD simulations are used for:

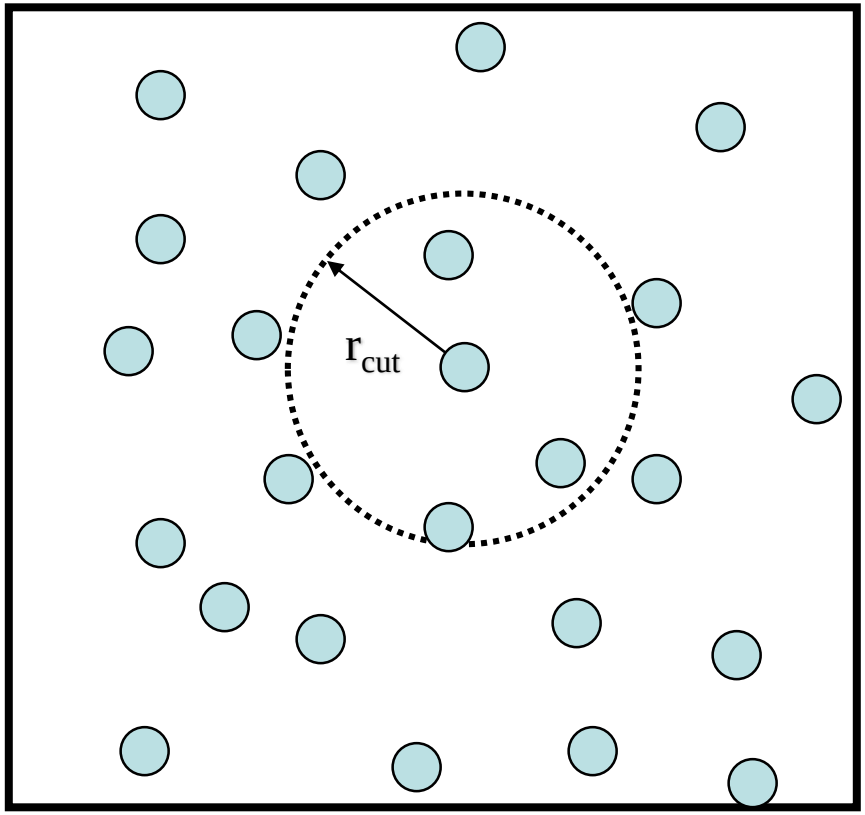
- Microscopic insight: we can follow the motion of a single molecule (glass of water)
- Investigation of phase change (NaCl)
- Understanding of complex systems like polymers (plastics – hydrophilic and hydrophobic behaviour)







Example: Simulation of Argon



Pair Potential:

$$V(r_{ij}) = 4\varepsilon\left\{\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right\}$$

Lagrangian:

$$L = K(\dot{\vec{v}}) - U(\vec{r})$$

$$L(\vec{r_i}, \vec{v_i}) = \frac{1}{2}\sum_{i=1}^{N} m_i v_i^2 - \sum_{i=1}^{N-1}\sum_{j<i}^{N} V(r_{ij})$$

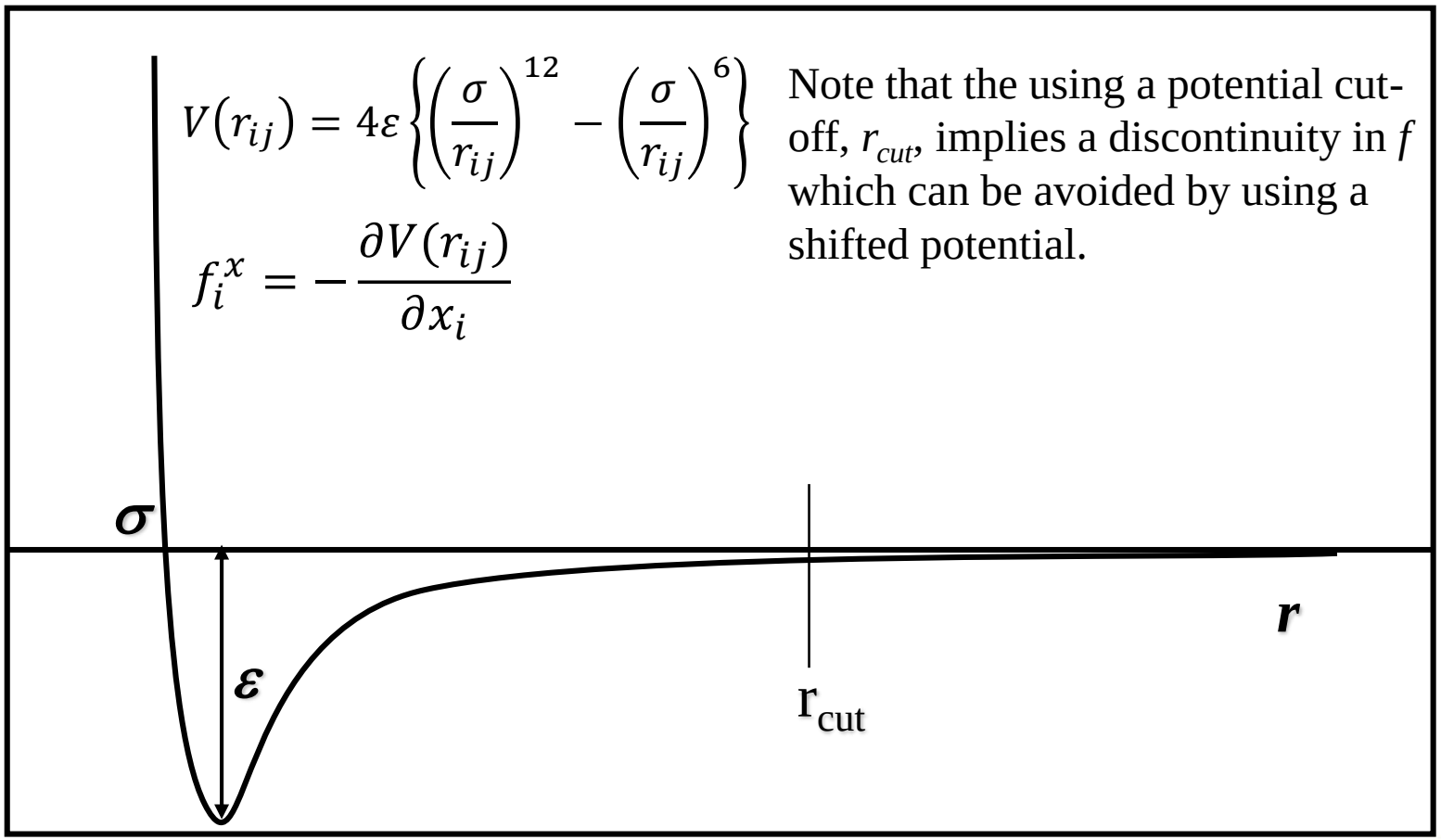
Lennard-Jones Potential

Models the Pauli exclusion principle (repulsive) at short distances & the van der Waals forces (attractive) at long ones

$$V(r_{ij}) = 4\varepsilon\left\{\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right\}$$

$$f_i^x = -\frac{\partial V(r_{ij})}{\partial x_i}$$

Note that the using a potential cut-off, r_{cut}, implies a discontinuity in f which can be avoided by using a shifted potential.



Pair-wise radial distance

Equations of Motion

Lagrange Equation – time evolution

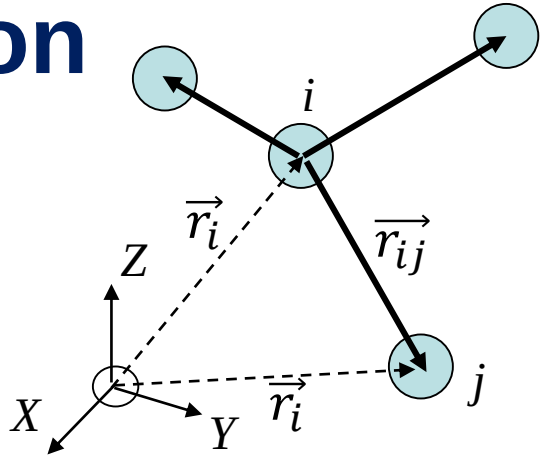
$$\frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{v}_i}\right) = \frac{\partial L}{\partial r_i}$$

$$m_i \vec{a}_i = \vec{F}_i$$

$$\vec{F}_i = \sum_{i=1}^{N} \vec{f}_{ij}$$

$$\vec{f}_{ij} = -\vec{\nabla}_i V(r_{ij})$$

Force Evaluation – particle interactions



Pair force:

$$f^x_{i(j)} = -\frac{\partial V(r_{ij})}{\partial x_i} = -\frac{\partial V(r_{ij})}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial x_i}$$

$$\overrightarrow{r_{ij}} = \overrightarrow{r_j} - \overrightarrow{r_i}$$

$$r_{ij} = \left[(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2\right]^{\frac{1}{2}}$$

$$\frac{\partial r_{ij}}{\partial x_i} = -\frac{(x_j - x_i)}{r_{ij}} = \frac{r^x_{ij}}{r_{ij}}$$

Note this leads to equal and opposite forces on the two particles.

EoM Consequences

$$f_i = m_i \frac{\partial v_i}{\partial t}$$

The force on atom *i* for any given configuration can be calculated from the force-field. This equation relates force and acceleration.

$$\frac{\partial v_i}{\partial t} = \frac{f_i}{m_i}$$

So for any given configuration we know the acceleration of each particle.

$$v_i(\tau) = v_i(0) + \int_0^\tau \frac{dv_i}{dt} dt$$

If a particle has an initial velocity, $v_i(0)$, and moves under the action of this force for a time, τ, its velocity after the time, τ, will be given by integration.

$$r_i(\tau) = r_i(0) + \int_0^\tau v_i(t) dt$$

Similarly the position of the particle after time, τ, is given by an integral of the velocity.

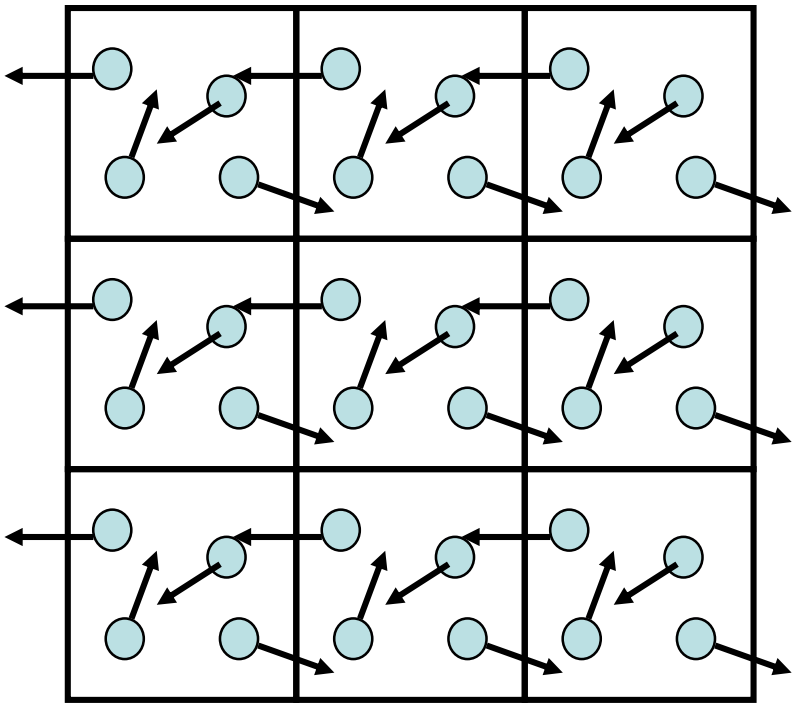
Unfortunately once the particles move the distances governing the potential change and so the forces are altered.

Molecular dynamics is about integrating these equations of motion such that the continuous trajectories are obtained numerically.

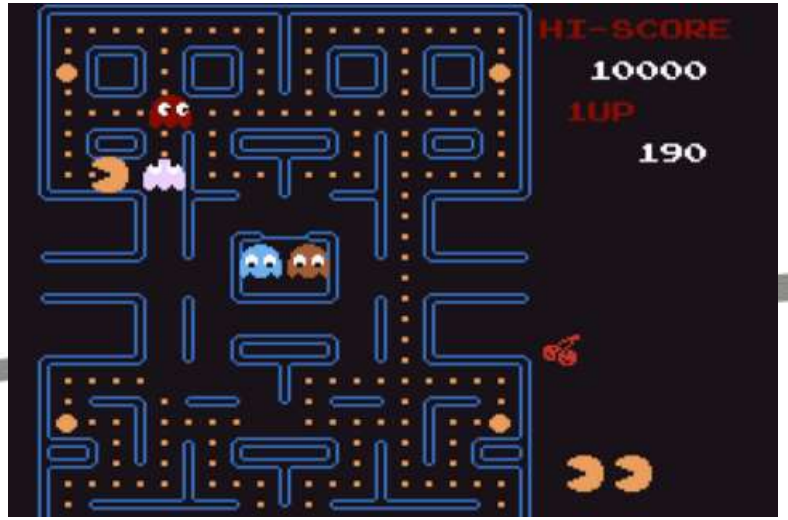
Boundary Conditions

- None – biopolymer simulations
- Stochastic boundaries – biopolymers
- Hard wall boundaries – pores, capillaries
- Periodic boundaries (PBC) – most MD simulations

2D cubic periodic



Why PBC: Our model systems are still too small especially with respect to Avogadro's number! To avoid surface over bulk domination effects we resort to periodic boundaries, pretending that boundaries do not exist (like in pacman)!

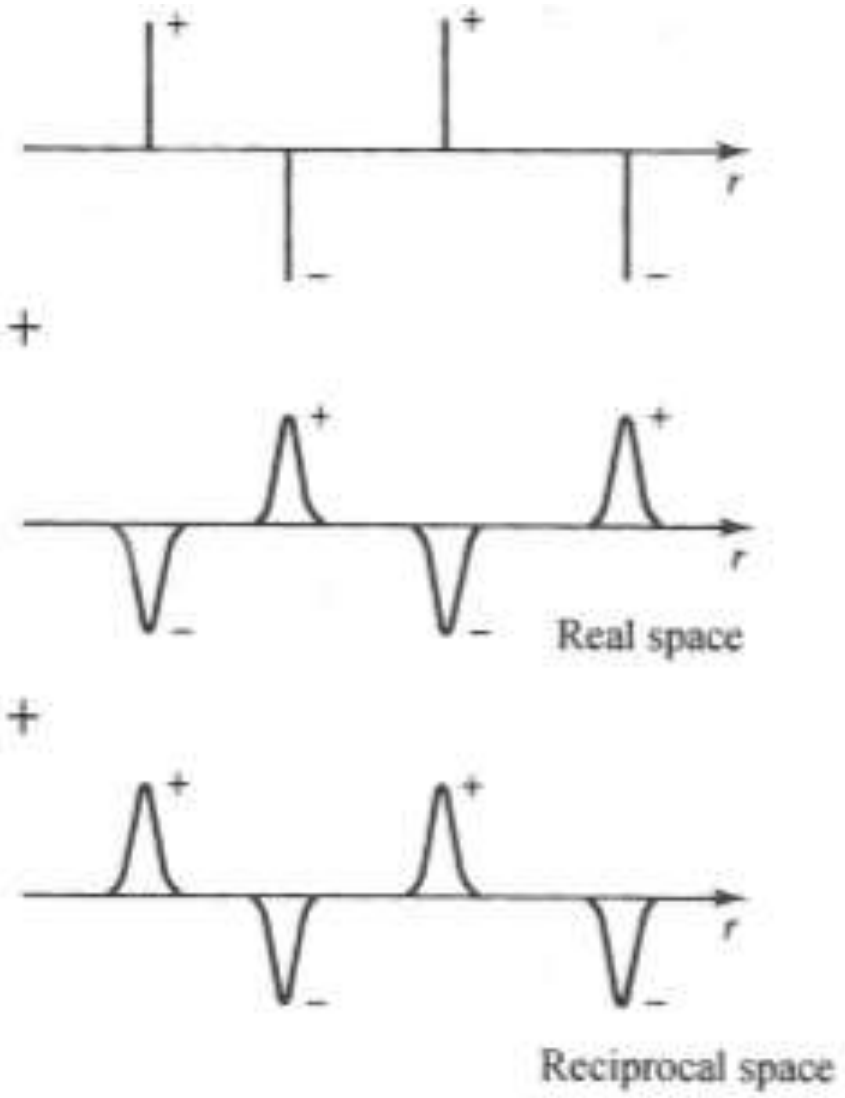


PBC Consequences

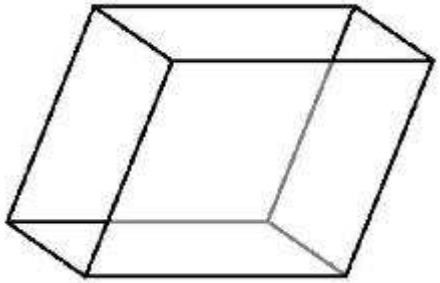
- The system no longer has a *surface*.
- The system becomes *pseudo-periodic* (used to advantage for Ewald sums). It is incorrect to impose cutoff on long range interactions. However, the Ewald method can deal with infinite number of periodic images – specifically Particle Mesh Ewald (PME)
- Correlations in space beyond *half cell width* (L/2) are artificial. For this reason, the cut-off r_{cut} is usually no greater than L/2.
- Correlations in time beyond t=L/c are (in principle) subject to *recurrence*. In practice this does not seem to be the case.
- Use with *Minimum Image* convention

Ewald Summation

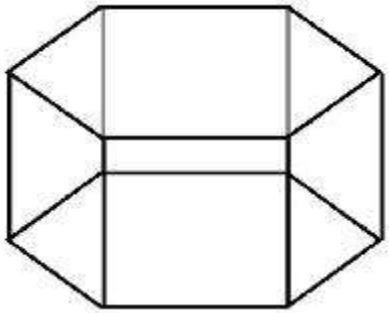
The method offers an elegant solution to solving the full electrostatic problem by splitting it in two parts – one in *real space* and one in *reciprocal space*. In real space, complying with the cutoff concept, a convenient screening function is added around all charges to make their interactions decay very fast at r_{cut}. The added screening functions can be subtracted in reciprocal space due to the periodic boundary condition by using *Fourier transforms.*



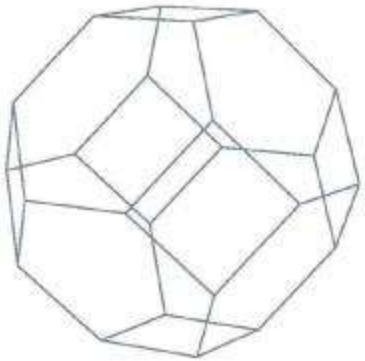
Periodic Boundary Conditions



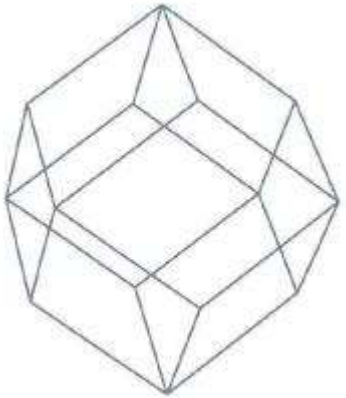
Triclinic



Hexagonal prism

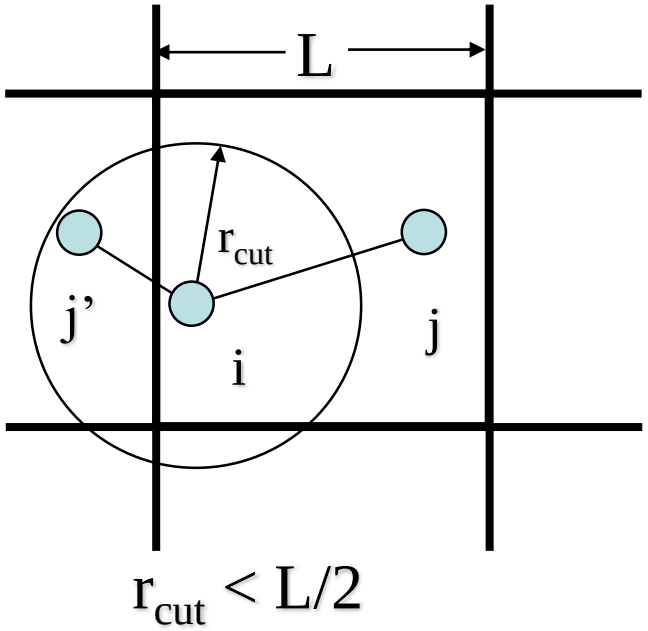


Truncated octahedron

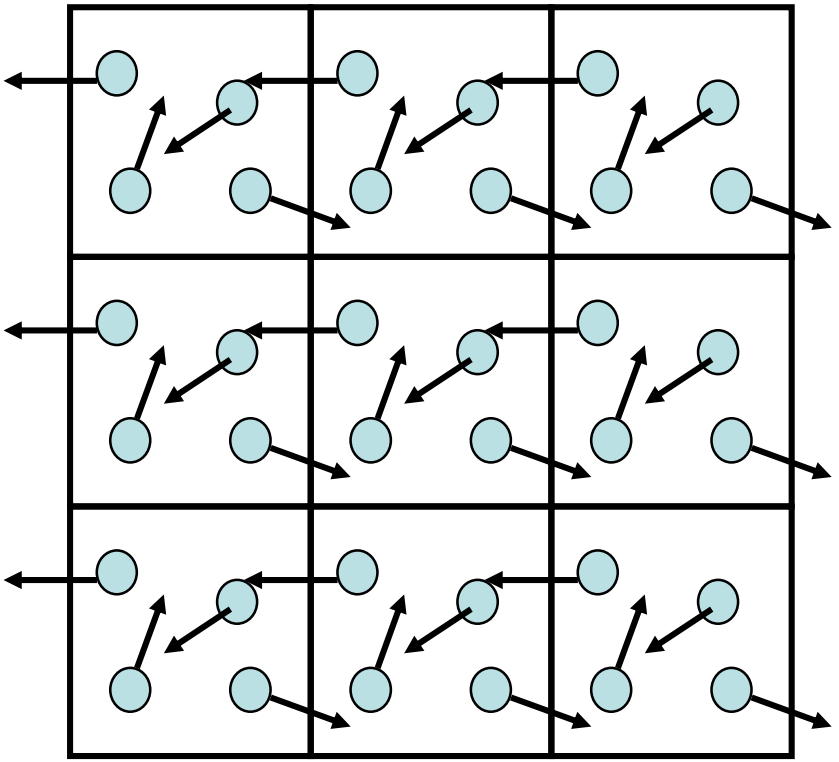


Rhombic dodecahedron

Minimum Image Condition (MIC)



2D cubic periodic



Use r_{ij}' not r_{ij}

$x_{ij} = x_{ij} - L * \mathrm{Nint}(x_{ij}/L)$

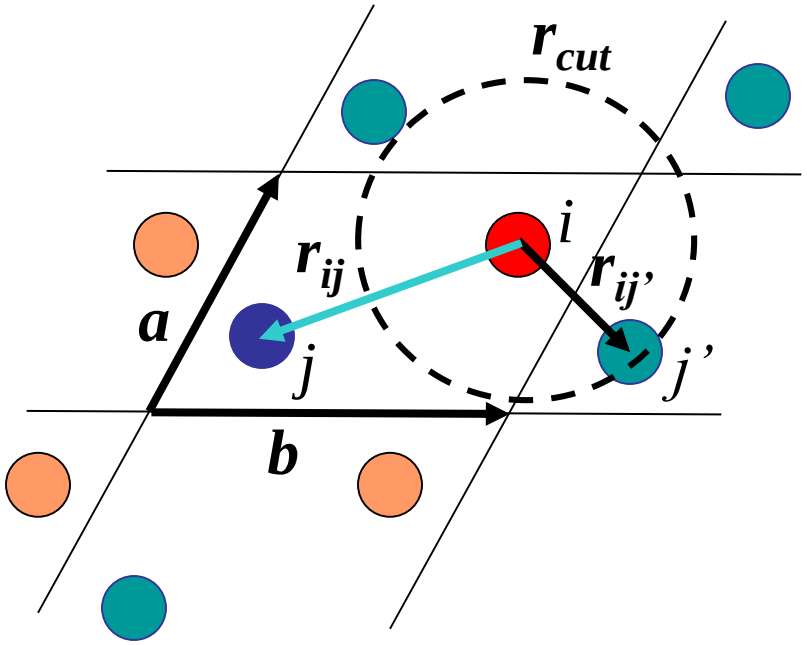
Nint(***a***)=nearest integer to ***a***

3D MIC

Use $\boldsymbol{r}_{ij}$, not $\boldsymbol{r}_{ij}$: To find $\boldsymbol{r}_{ij}$, work in fractional co-ordinates:

$$f_{aij} = a^* \bullet r_{ij} \qquad f_{bij} = b^* \bullet r_{ij} \qquad f_{aij} = c^* \bullet r_{ij}$$

(* indicates reciprocal space vectors)



These need to be in the range $-½ < f \leq ½$

$$f_{ij'} = f_{ij} - \mathrm{nint}\left(f_{ij}\right)$$

(nint(f)=nearest integer to f)

Then convert back to Cartesian:

$$\begin{pmatrix} r_{ij'x} \\ r_{ij'y} \\ r_{ij'z} \end{pmatrix} = \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix} \begin{pmatrix} f_{aij'} \\ f_{bij'} \\ f_{cij'} \end{pmatrix}$$

For van der Waals interactions use only the nearest images of atoms.

The minimum image convention limits the cut off used in the potential sum to half the shortest lattice parameter.

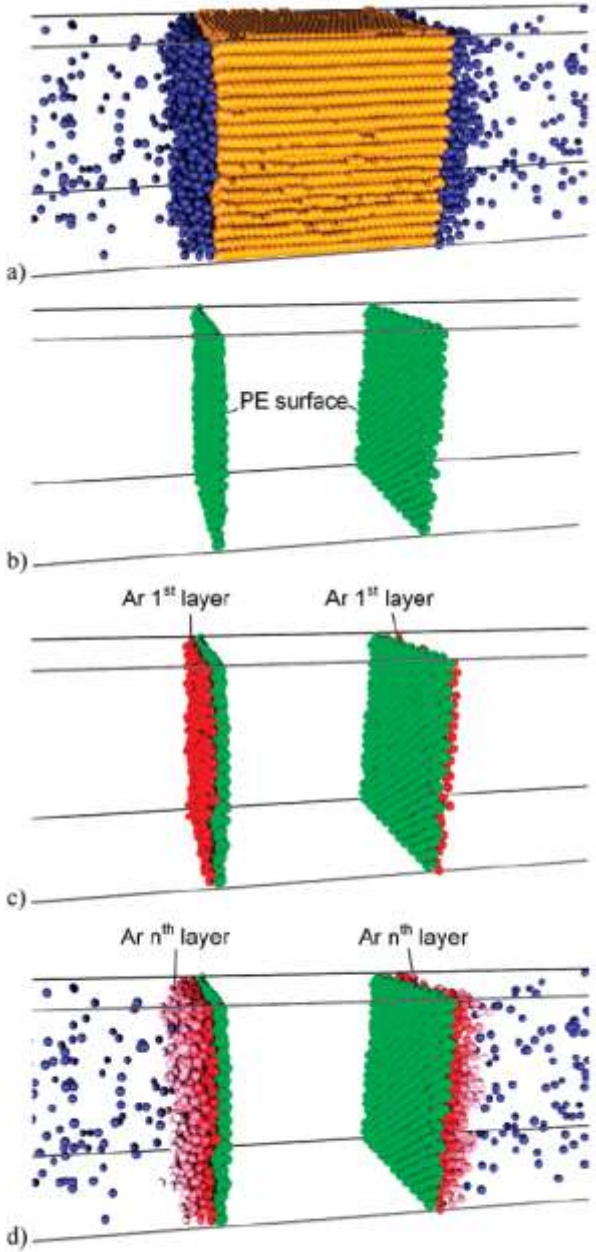


Figure 2. Snapshots of a condensation simulation at $T_{pg} = 80$ K and $\rho = 50$ g/dm^3 after 5 ns. (a) Complete polymer film with condensed argon and a part of the argon vapor phase. (b) Surface layers of polyethylene. (c) Polyethylene surface layer and first argon layer. (d) Polyethylene surface layer with first and all subsequent argon layers. Each layer has a different grayscale (red shade).

Lennard-Jones Spheres (Argon)

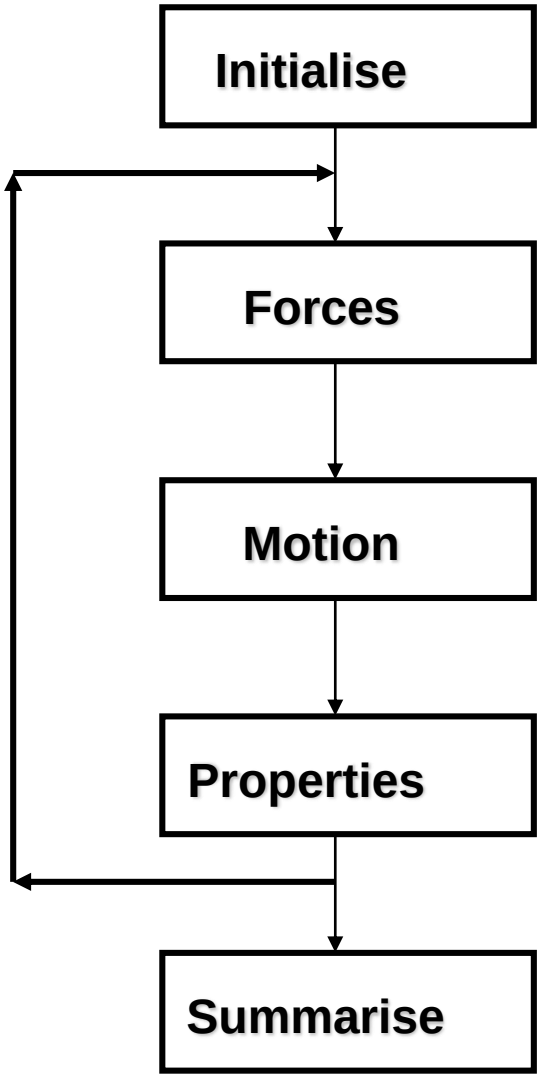
Provides a relatively simple system in which the ideas of using molecular dynamics to study kinetics and thermodynamics of physical processes can be tested.

Here is a simulation of Ar condensation at the surface of a polyethylene film is simulated.

System size: Film consists of 374 chains, 70 sites each.
Vapor phase: 5000 argon atoms.
Run times: 1 ns equilibration of components. 12 ns run times.

R. Rozas & T. Kraska, *J. Phys. Chem. C*, **111**, 15784, (2007).

Key Stages in MD Simulation



- ***Set up initial system***

positions of atoms and initial velocities (3D Boltzmann distributed)

- ***Calculate atomic forces***

based on potential model

- ***Calculate atomic motion***

via an integration algorithm

- ***Calculate physical properties***

basically collect instantaneous data for statistical purposes

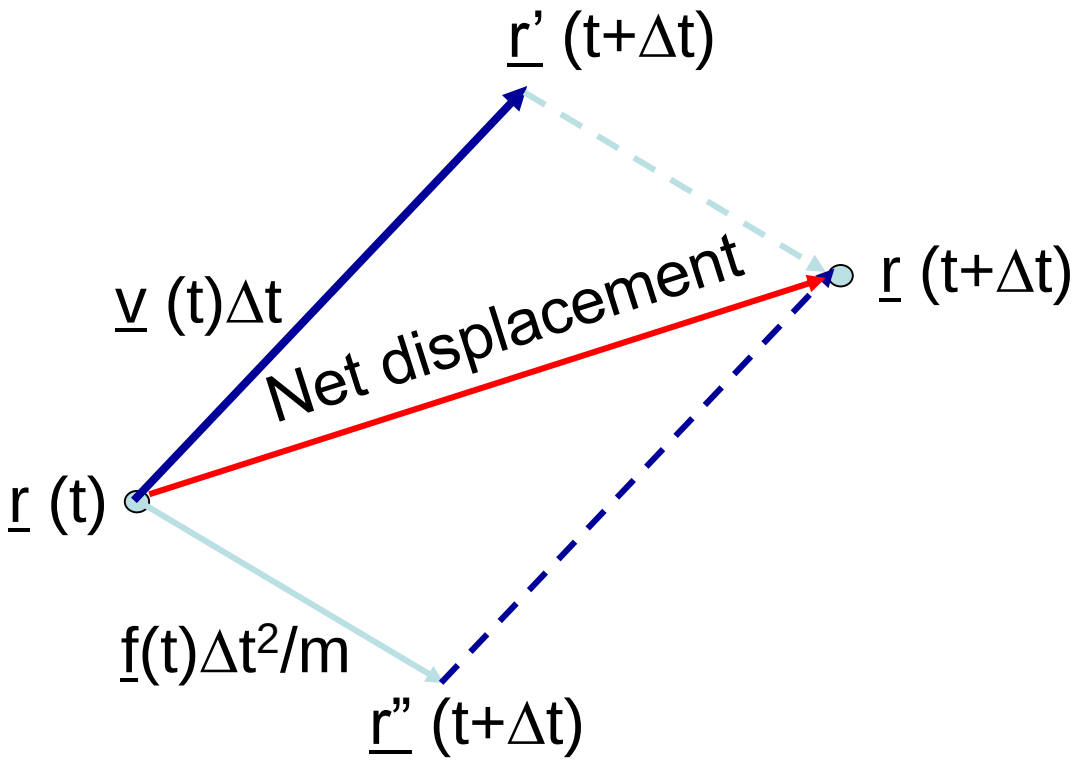
- ***Repeat !***
- ***Produce final summary***

Integration Algorithms

Essential Requirements:

- Computational speed
- Low memory demand
- Accuracy
- Stability (energy conservation, no drift)
- Useful property – time reversibility
- Extremely useful property – symplecticness = time reversibility + long term stability (warranting bounded errors in time)

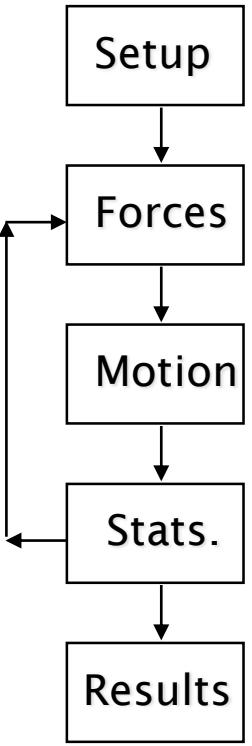
Integration: Essential Idea



$[\underline{r}\,(t), \underline{v}(t), \underline{f}(t)] \longrightarrow [\underline{r}\,(t+\Delta t), \underline{v}(t+\Delta t), \underline{f}(t+\Delta t)]$

Simulation Cycle & Integration Schemes

Taylor expansion: $r_{n+1} = r_n + \Delta t\, v_i(t) + \frac{\Delta t^2}{2!}\frac{f_n}{m} + \frac{\Delta t^3}{3!}\dddot{r}_i(t)\Delta t^3 + O(\Delta t^4)$



Set up initial system

Calculate forces

Calculate motion

Accumulate statistical data

Summarise simulation

Leapfrog Verlet (LFV)

0. $r_i(t), v_i\left(t - \frac{1}{2}\Delta t\right)$

1. $f_i(t)$ – calculated afresh

2. $v_i\left(t + \frac{1}{2}\Delta t\right) = v_i\left(t - \frac{1}{2}\Delta t\right) + \Delta t \frac{f_i(t)}{m_i}$

3. $r_i(t + \Delta t) = r_i(t) + \Delta t\, v_i\left(t + \frac{1}{2}\Delta t\right)$

3'. SHAKE (r_i, v_i, f_i)

3". $v_i(t) = \frac{v_i\left(t - \frac{1}{2}\Delta t\right) + v_i\left(t + \frac{1}{2}\Delta t\right)}{2}$

Velocity Verlet (VV)

1.0. $r_i(t), v_i(t), f_i(t)$

1.1. $v_i\left(t + \frac{1}{2}\Delta t\right) = v_i(t) + \frac{\Delta t}{2}\frac{f_i(t)}{m_i}$

1.2. $r_i(t + \Delta t) = r_i(t) + \Delta t\, v_i\left(t + \frac{1}{2}\Delta t\right)$

1.2'. SHAKE (r_i, v_i, f_i)

2.0. $f_i(t + \Delta t)$ – calculated afresh

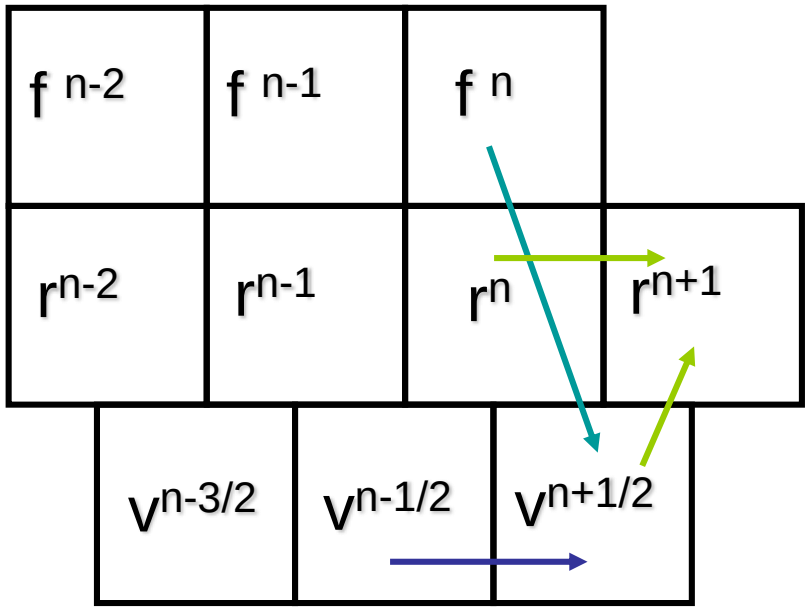
2.1. $v_i(t + \Delta t) = v_i\left(t + \frac{1}{2}\Delta t\right) + \frac{\Delta t}{2}\frac{f_i(t+\Delta t)}{m_i}$

2.1'. Rattle (v_i)

Leapfrog Verlet Integration

$$\vec{v}_i^{n+1/2} = \vec{v}_i^{n-1/2} + \frac{\Delta t}{m_i}\vec{f}_i^{n} + O(\Delta t^3)$$

$$\vec{r}_i^{n+1} = \vec{r}_i^{n} + \Delta t \vec{v}_i^{n+1/2} + O(\Delta t^4)$$



Application in Practice

$$\vec{v}_i^{n+1/2} = \vec{v}_i^{n-1/2} + \frac{\Delta t}{m_i}\vec{f}_i^{n}$$

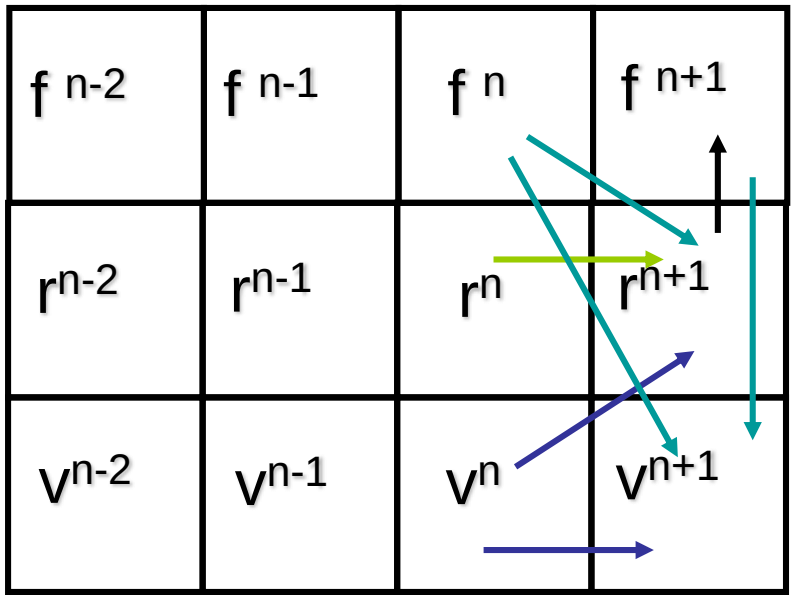
$$\vec{r}_i^{n+1} = \vec{r}_i^{n} + \Delta t \vec{v}_i^{n+1/2}$$

$$\vec{v}_i^{n} = \frac{\vec{v}_i^{n-1/2} + \vec{v}_i^{n+1/2}}{2}$$

Velocity Verlet Integration

$$\vec{r}_i^{n+1} = \vec{r}_i^n + \Delta t \vec{v}_i^n + \frac{\Delta t^2}{2m_i} \vec{f}_i^n + O(\Delta t^4)$$

$$\vec{v}_i^{n+1} = \vec{v}_i^n + \frac{\Delta t}{2m_i} \left(\vec{f}_i^n + \vec{f}_i^{n+1} \right) + O\left(\Delta t^2 \right)$$



Application in Practice

$$\vec{v}_i^{n+1/2} = \vec{v}_i^n + \frac{\Delta t}{2m_i} \vec{f}_i^n$$

$$\vec{r}_i^{n+1} = \vec{r}_i^n + \Delta t \vec{v}_i^{n+1/2}$$

$$\vec{v}_i^{n+1} = \vec{v}_i^{n+1/2} + \frac{\Delta t}{2m_i} \vec{f}_i^{n+1}$$

Considerations for MD

In the potentials we are using the force generated between a pair of atoms is equal and opposite. This means that the total momentum of the system cannot change, *i.e.*:

$$\sum_i m_i \vec{v}_i = 0$$

Similarly the centre of mass position should be fixed:

$$\vec{r}_{cm} = \frac{\sum_i m_i \vec{r}_i}{\sum_i m_i} \text{ since } \dot{\vec{r}}_{cm} = \frac{\sum_i m_i \dot{\vec{r}}_i}{\sum_i m_i}$$

Observations such as this allow checks that coding/integration are working!

In MD we have two contributions to the energy.

1) Kinetic energy, which sets the temperature:

$$KE(t) = \frac{1}{2}\sum_i m_i |\vec{v}_i(t)|^2$$

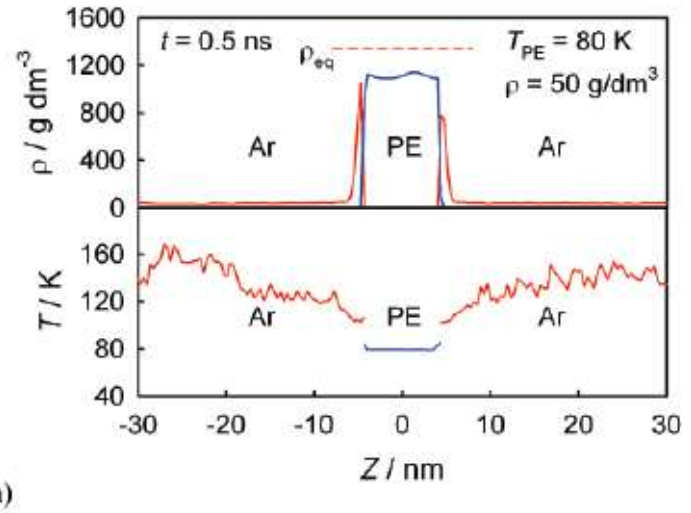
2) Potential energy, which is dependent on the atomic configuration according to the force-field:

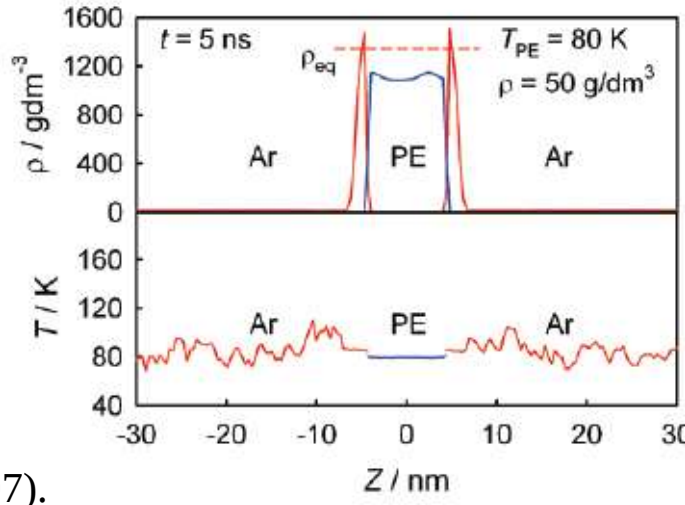
$$PE(t) = \sum_i \sum_{j>i} V_{ij}\left(r_{ij}(t)\right)$$

The energy of the system is continually interchanging between potential and kinetic contributions (when all interactions are conservative, no external fields).

System Properties – Static (1)

- **Kinetic Energy:** $\langle K.E. \rangle = \left\langle \frac{1}{2} \sum_{i}^{N} m_i v_i^2 \right\rangle$
- **Temperature:** $T = \frac{2}{3} \frac{\langle K.E. \rangle}{N k_B}$
- **Configuration Energy:** $U_c = \left\langle \sum_{i}^{N-1} \sum_{j>i}^{N} V(r_{ij}) \right\rangle$
- **Pressure:** $PV = N k_B T - \frac{1}{3} \left\langle \sum_{i}^{N} \vec{r}_i \cdot \vec{f}_i \right\rangle$
- **Specific heat:** $\langle \delta(U_c)^2 \rangle = \frac{3}{2} N {k_B}^2 T^2 \left(1 - \frac{3}{2} \frac{N k_B}{C_v} \right)$





Data from: R. Rozas & T. Kraska, *J. Phys. Chem. C*, **111**, 15784, (2007).

System Properties – Static (2)

Structural Properties

- Pair correlation (Radial Distribution Function):

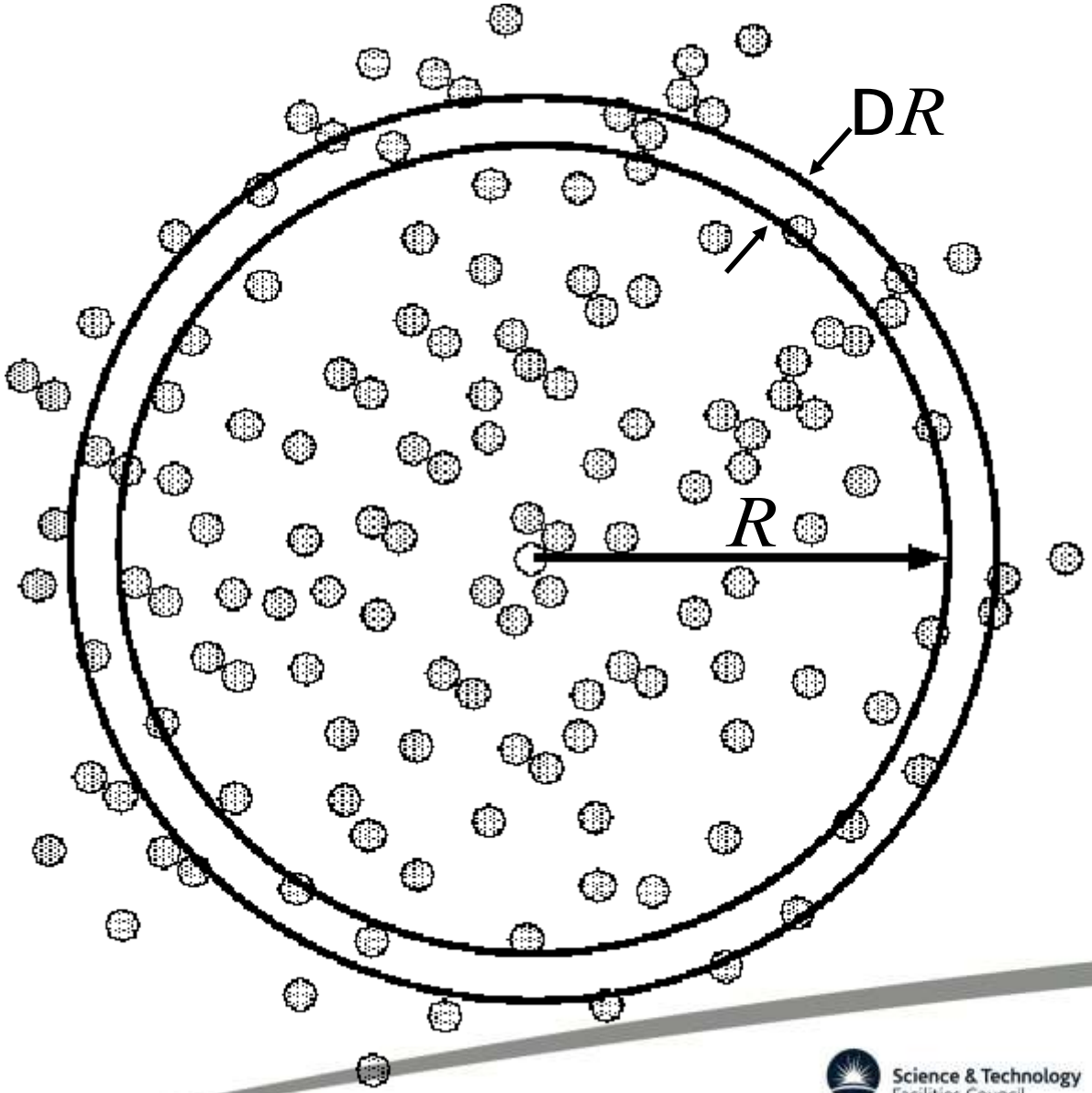
$$g(r) = \frac{\langle n(r) \rangle}{4\pi\rho r^2 \Delta r} = \frac{V}{N^2} \left\langle \sum_{i=1}^{N-1} \sum_{j \neq i}^{N} \delta(r - r_{ij}) \right\rangle$$

- Structure factor:

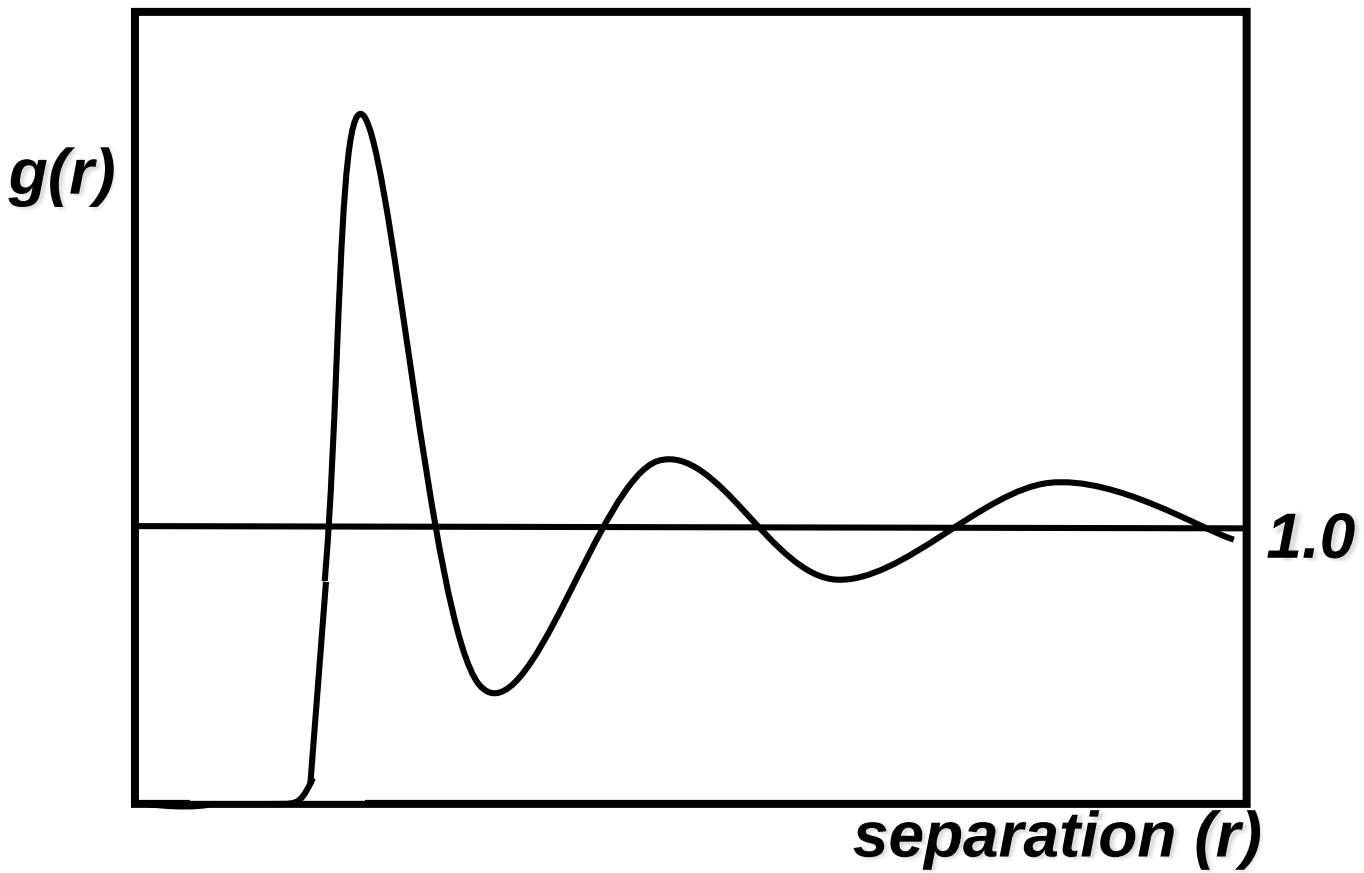
$$S(k) = 1 + 4\pi\rho \int_0^\infty \frac{\sin(kr)}{kr} (g(r) - 1)\, r^2 \, dr$$

- Note: *S(k)* available from X-ray diffraction

Radial Distribution Function (RDF)



Typical RDF



System Properties – Dynamic (1)

Single correlation functions:

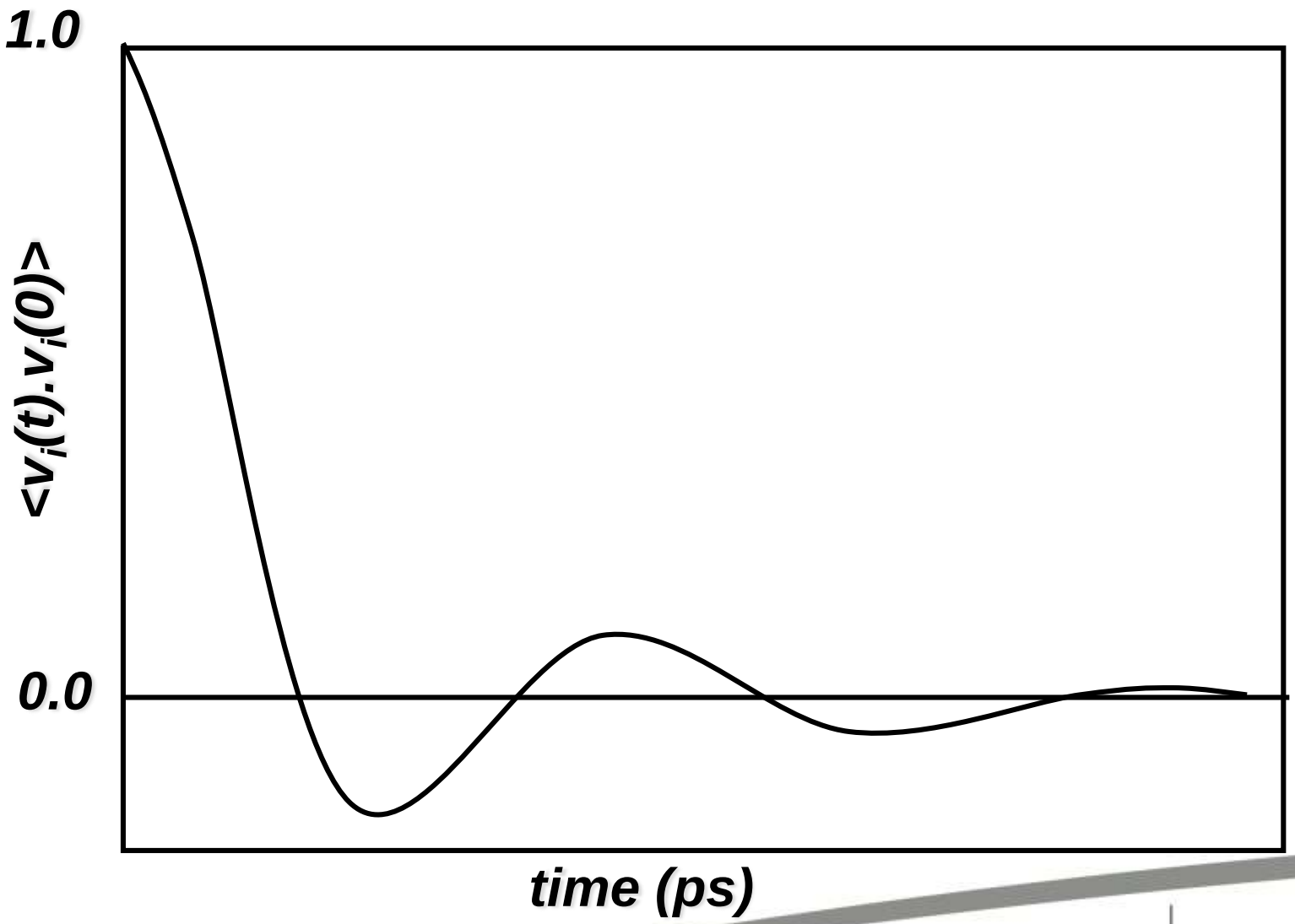
- **Mean squared displacement (Einstein relation)**

$$2Dt = \frac{1}{3}\left\langle |r_i(t) - r_i(0)|^2 \right\rangle$$

- **Velocity Autocorrelation (Green-Kubo relation)**

$$D = \frac{1}{3}\int_0^t \langle v_i(t) - v_i(0) \rangle \, dt$$

Typical VAF



System Properties – Dynamic (2)

Collective Correlation Functions: DL_POLY GUI

- General van Hove correlation function

$$G(\mathbf{r},t) = \frac{1}{N}\left\langle \sum_{i,j=1}^{N} \delta[r + r_i(0) - r_j(t)] \right\rangle$$

- van Hove self-correlation function

$$G_s(\mathbf{r},t) = \frac{1}{N}\left\langle \sum_{i}^{N} \delta[r - r_i(0) - r_i(t)] \right\rangle$$

- van Hove distinct correlation function

$$G_d(\mathbf{r},t) = \frac{1}{N}\left\langle \sum_{i}^{N}\sum_{j\neq i}^{N} \delta[r + r_i(0) - r_j(t)] \right\rangle$$

Uses of MD

Ensemble average:

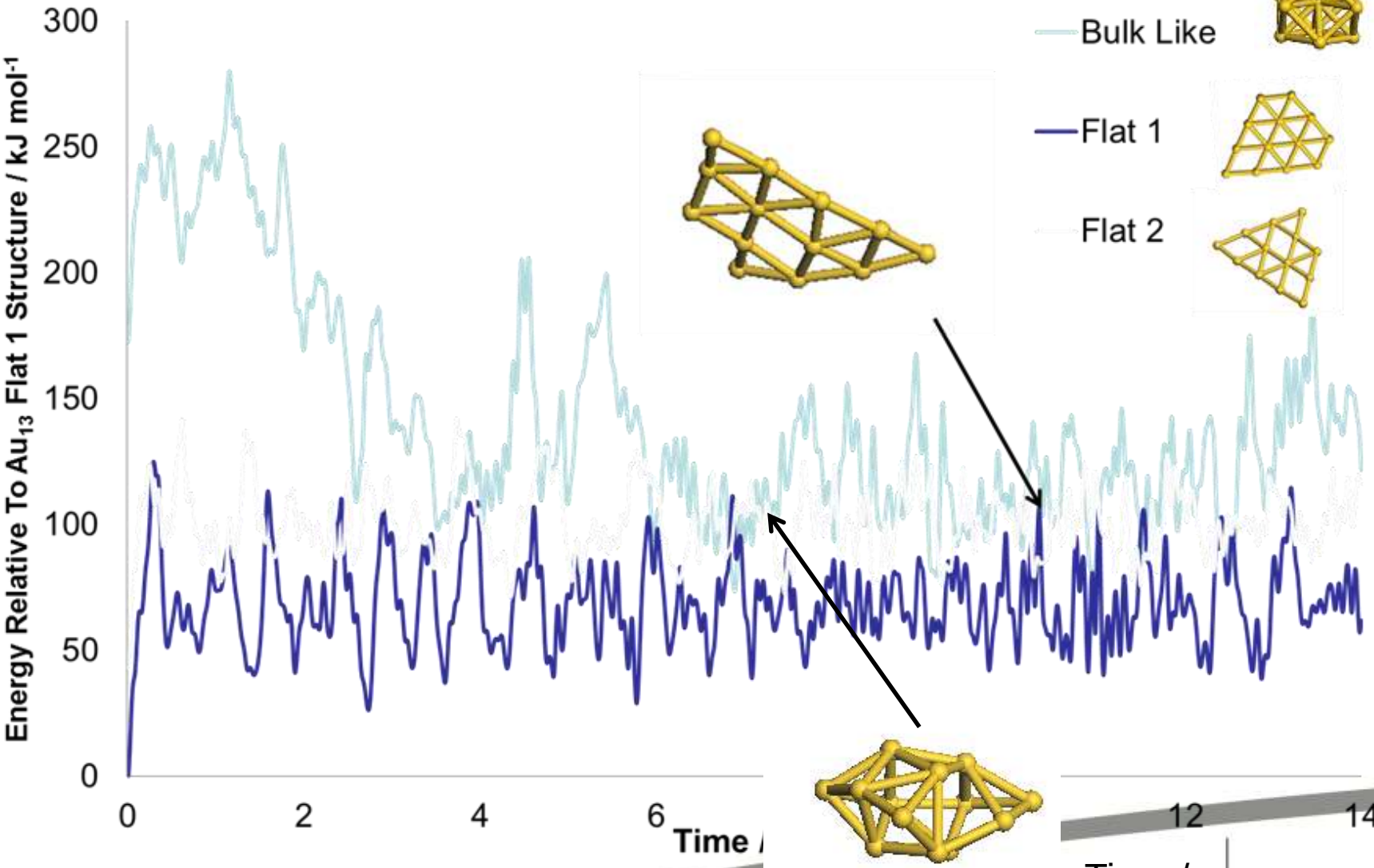
- **Free energy (of binding, solvation, interaction) differences**
- **Diffusion coefficients, viscosity, elastic constants**
- **Reaction rates, phase transition properties**
- **Protein folding times**
- **Structure refinement**

Non-equilibrium processes:

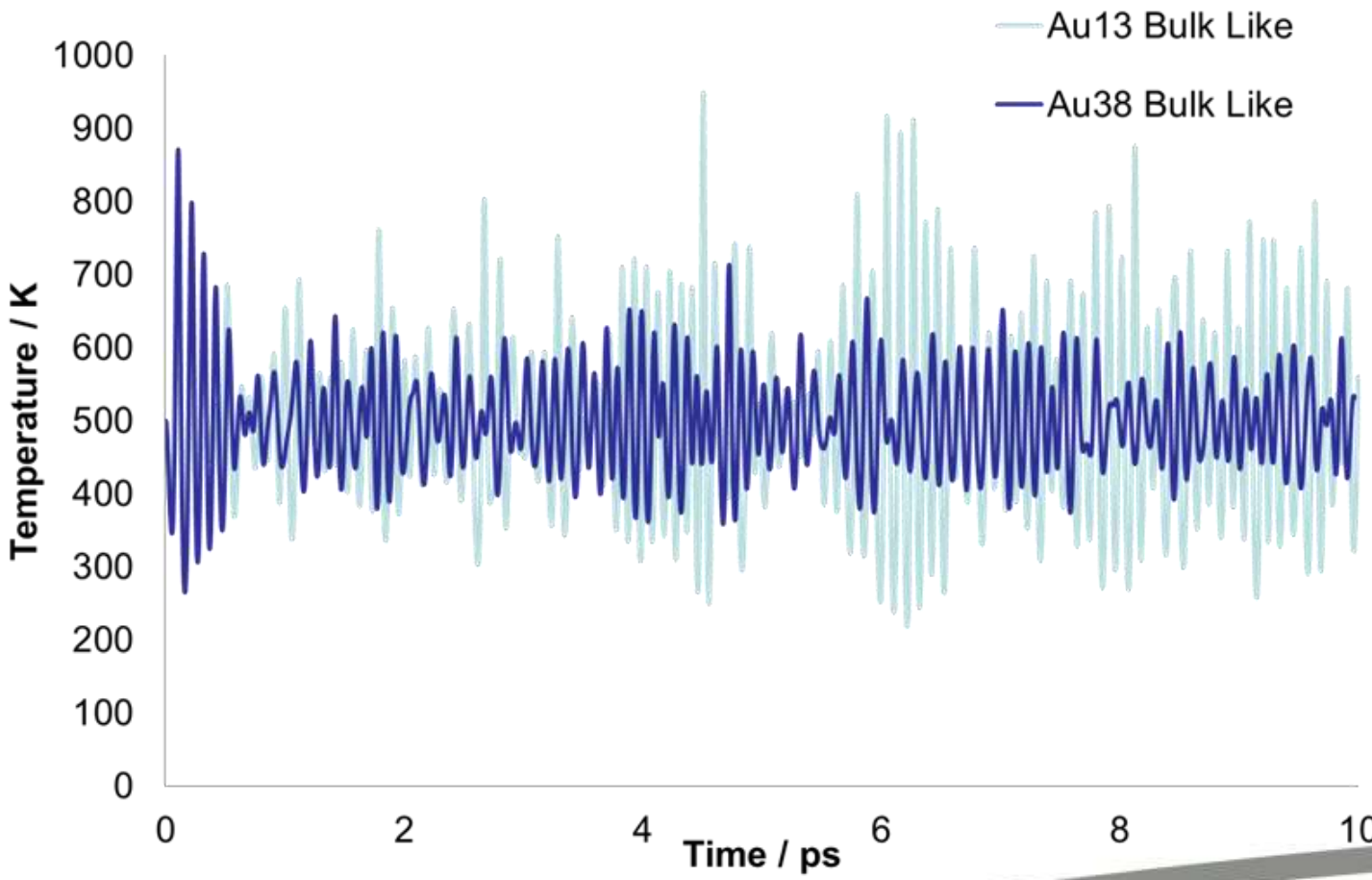
- **Energy Dissipation/Radiation damage**
- **Sound Propagation**
- **Surface coating**
- **Nucleation (meta-dynamics)**

Some properties can be obtained directly from neutron scattering

Au_{13} MD Runs


Energy Relative To Au13 Flat 1 Structure / kJ mol-1
300
250
200
150
100
50
0
0
2
4
6
12
14
Time / ps
Bulk Like
Flat 1
Flat 2

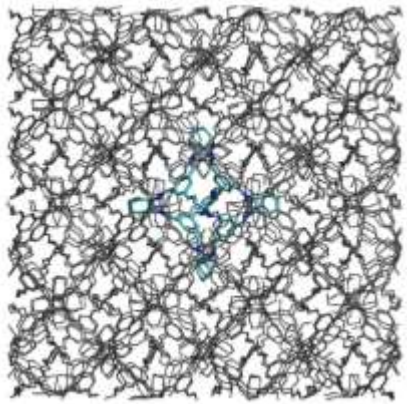
Temperature *vs* Time



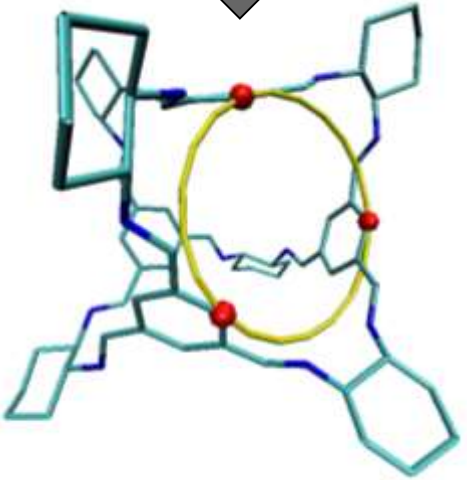
CC3 Research, Dan Holden & Abbie Trewin (Liverpool)

The first thing is to locate the PLD within **CC3**.

We know that **CC3** has a 3D diamondoid network.



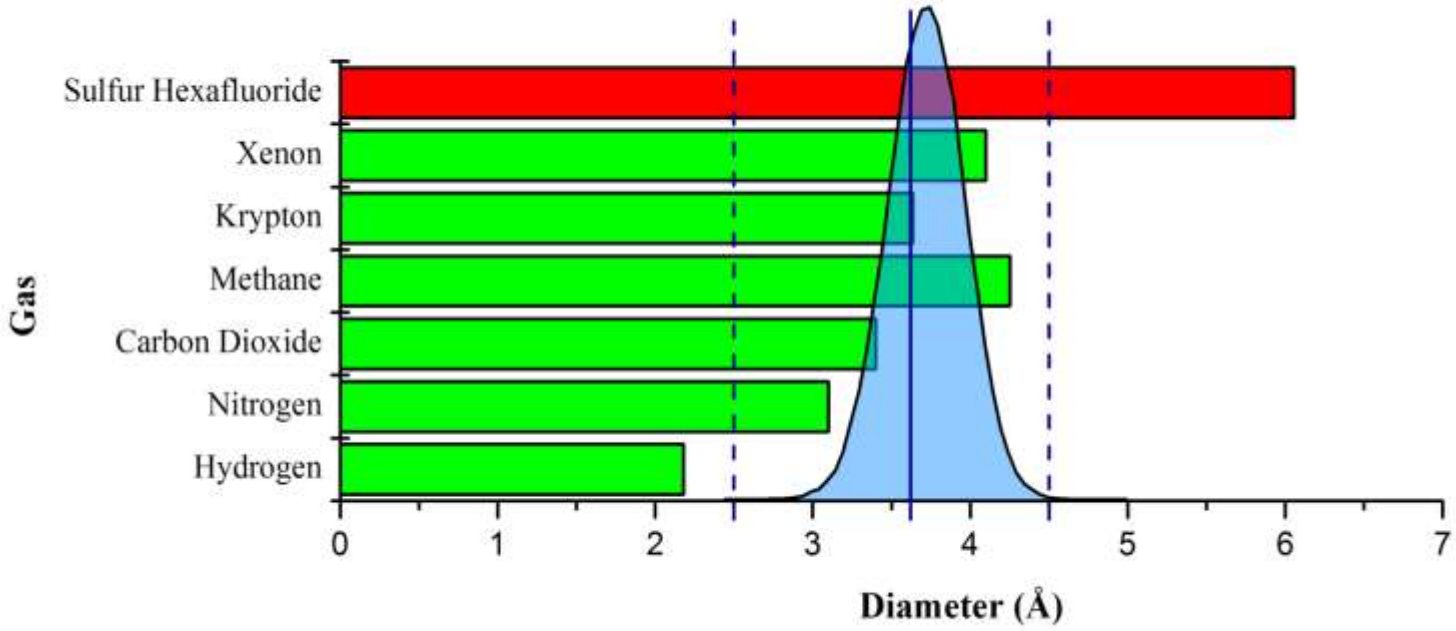
Use crystal structure of **CC3** to compare against 3D pore network. Established that the cage was limiting the PLD, therefore one cage isolated.



This cage was examined and the atoms involved in creating the narrow neck in the pore topology identified; the circumference of this circle was 3.62 Å – this is the PLD.

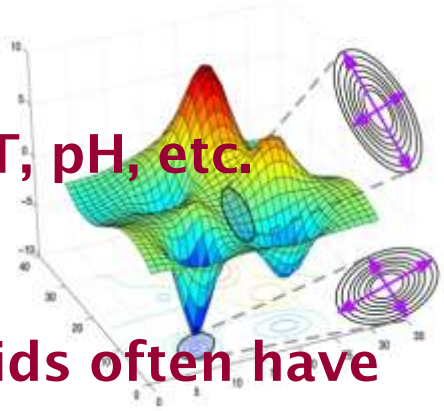
CC3 Research

The PLD could then be compared to the diameter of the gases:



This now suggests that all the gases, save SF_6, are small enough to diffuse through **CC3**.

Limitations of MD



- Parameters are imperfect and fit to particular P, T, pH, etc.
- Phase space is not sampled exhaustively
- Example: Free energies of solvation for amino acids often have errors ~1kJ/mol
- Likely impossible to calculate binding free energies more accurately than this
- Chemical bonds breaking and creation is not allowed
- Limited polarization effects; waters can reorient, but partial charges are fixed

However, MD simulations are cheaper than experiments as more easy to set up, repeat with changes to the models system, force-field and/or initial conditions and thus serve as an invaluable testing tool for scientists! It may be used cleverly to answer cheaply hypothetical and comparative questions!

How to Use MD

- Think first and then simulate
- Ask specific questions
    - Which of a set of molecules binds best?
    - Which material recovers better, faster under irradiation?
- Simulate 10 models: do they act the same?
- Try to answer A/B type questions:
    - Does a His-Arg mutation affect stability?
    - Does replacement of Zr with Pb in pyrochlores affect the recovery processes under ballistic bombardment?

Beyond Classical MD

The atomic scale is not always best choice when trying to access phenomena occurring on a larger time- or length scales. There ways to use MD strengths and modify the equations of motion and reduce the degrees of freedom as in Dissipative Particle Dynamics or just the do the latter use Coarse Grained MD. These simulations will be cheaper to run but some of the fine-grainness (chemistry and small scale details) will be lost as well as will the accurate timing. Particles will be a congregations of atoms and may even have a shape and interact via non-spherically symmetric potentials.

Another way to ask questions for rare processes and speed up time-scale (nucleation, vacancy hopping, defects annihilation, protein folding, crystal phases in emulsion formation) is to extend dynamics using advanced methodologies such as temperature accelerated dynamics, hyper-dynamics and meta-dynamics.

Think about what you want to get from the simulation: *predictions* or *explanations!*

Part 2

DL_POLY Project Background

DL_POLY Trivia

- General purpose parallel (classical) MD simulation software
- It was conceived to meet needs of CCP5 - The Computer Simulation of Condensed Phases (academic collaboration community)
- Written in modularised Fortran90 (NagWare & FORCHECK compliant) with MPI2 (MPI1+MPI-I/O) & fully self-contained
  - 1994 – 2010: DL_POLY_2 (RD) by W. Smith & T.R. Forester (funded for 6 years by EPSRC at DL). In 2010 moved to a BSD open source licence as DL_POLY_Classic.
  - 2003 – 2010: DL_POLY_3 (DD) by I.T. Todorov & W. Smith (funded for 4 years by NERC at Cambridge). Up-licensed to DL_POLY_4 in 2010 – free of charge to academic researchers and at cost to industry (*provided as source*).
- ~ 21,600 licences taken out since 1994 (~1,500 pa since 2007)
- ~ 4,500 *e*-mail list

Current Versions

Written in modularised free formatted F90 (+MPI) with rigorous code syntax (FORCHECK and NAGWare verified) and **no external library dependencies**

- **DL_POLY_4** (version 9)
  - **Domain Decomposition** parallelisation, based on domain decomposition (no dynamic load balancing), limits: up to $\approx 2.1 \times 10^9$ atoms with inherent parallelisation
  - Parallel I/O (amber netCDF) and radiation damage features
  - Free format (flexible) reading with some fail-safe features and basic reporting (but not fully fool-proofed)
- **DL_POLY_Classic** (version 1.10)
  - **Replicated Data** parallelisation, limits up to ≈30,000 atoms with good parallelisation up to 100 (system dependent) processors (running on any processor count)
  - Hyper-dynamics, Temperature Accelerated Dynamics, Solvation Dynamics, Path Integral MD
  - Free format reading (somewhat rigid)

DL_POLY on the Web

WWW:

http://www.ccp5.ac.uk/DL_POLY/

FTP:

ftp://ftp.dl.ac.uk/ccp5/DL_POLY/

COMM:

http:/www.jiscmail.ac.uk/DLPOLY/

Further Information

W. Smith and T.R. Forester
J. Molec. Graphics (1996), **14**, 136

W. Smith, C.W. Yong, P.M. Rodger
Molecular Simulation (2002), **28**, 385

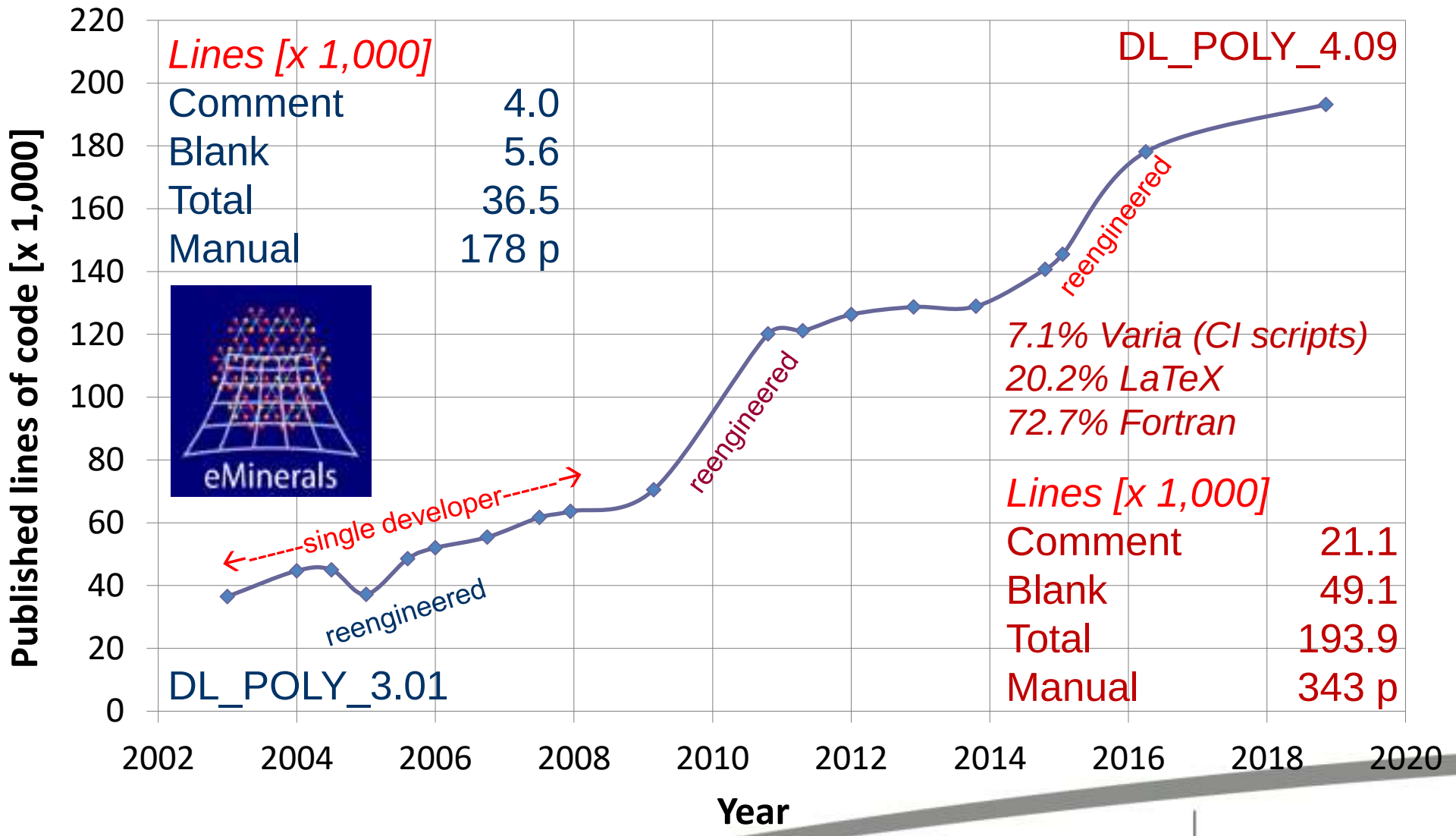
I.T. Todorov, W. Smith, K. Trachenko, M.T. Dove
J. Mater. Chem. (2006), **16**, 1611-1618

W. Smith (Guest Editor)
Molecular Simulation (2006), **32**, 933

I.J. Bush, I.T. Todorov and W. Smith
Comp. Phys. Commun. (2006), **175**, 323-329

W. Smith
Elements of MD

DL_POLY_DD Project Evolution



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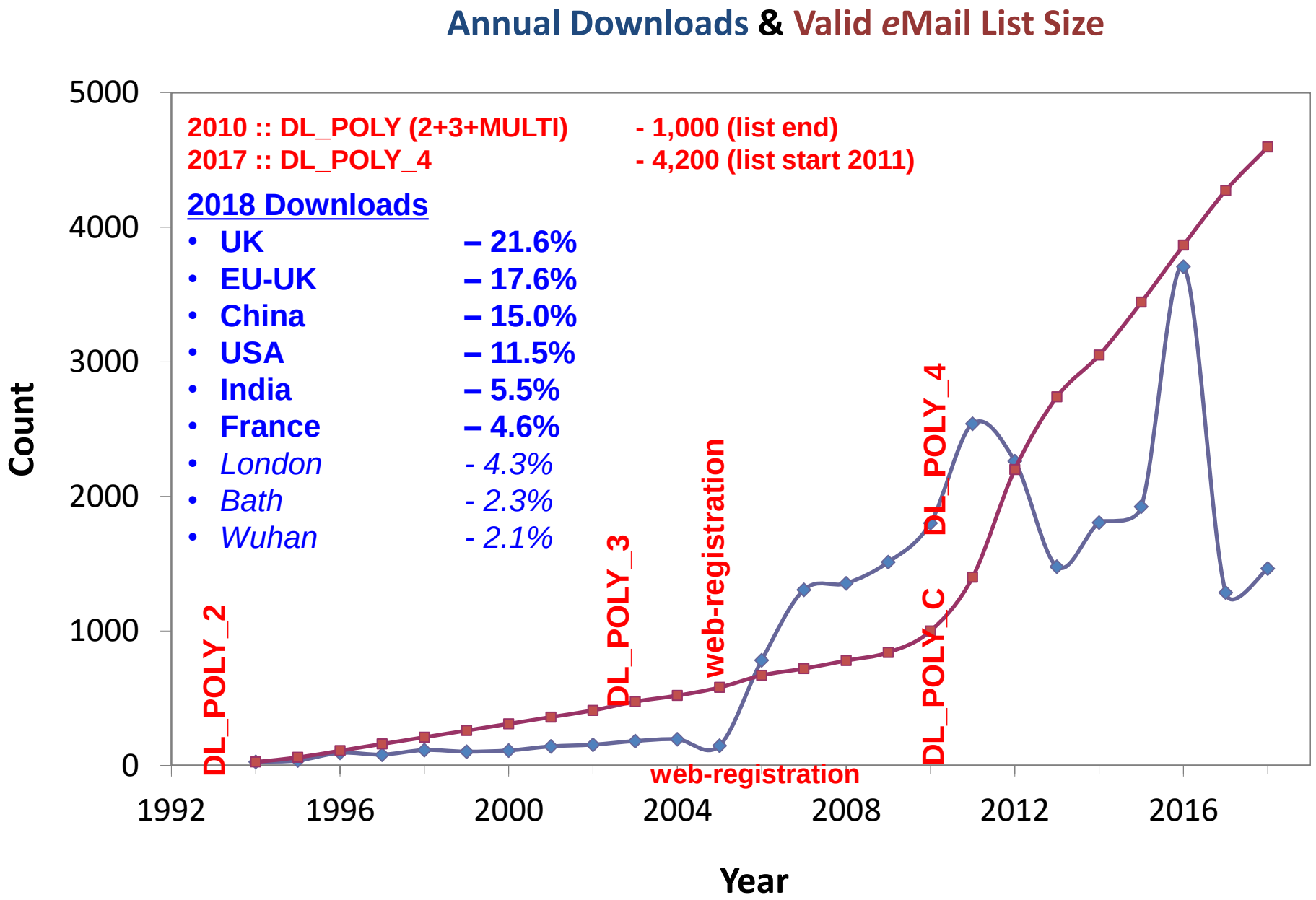
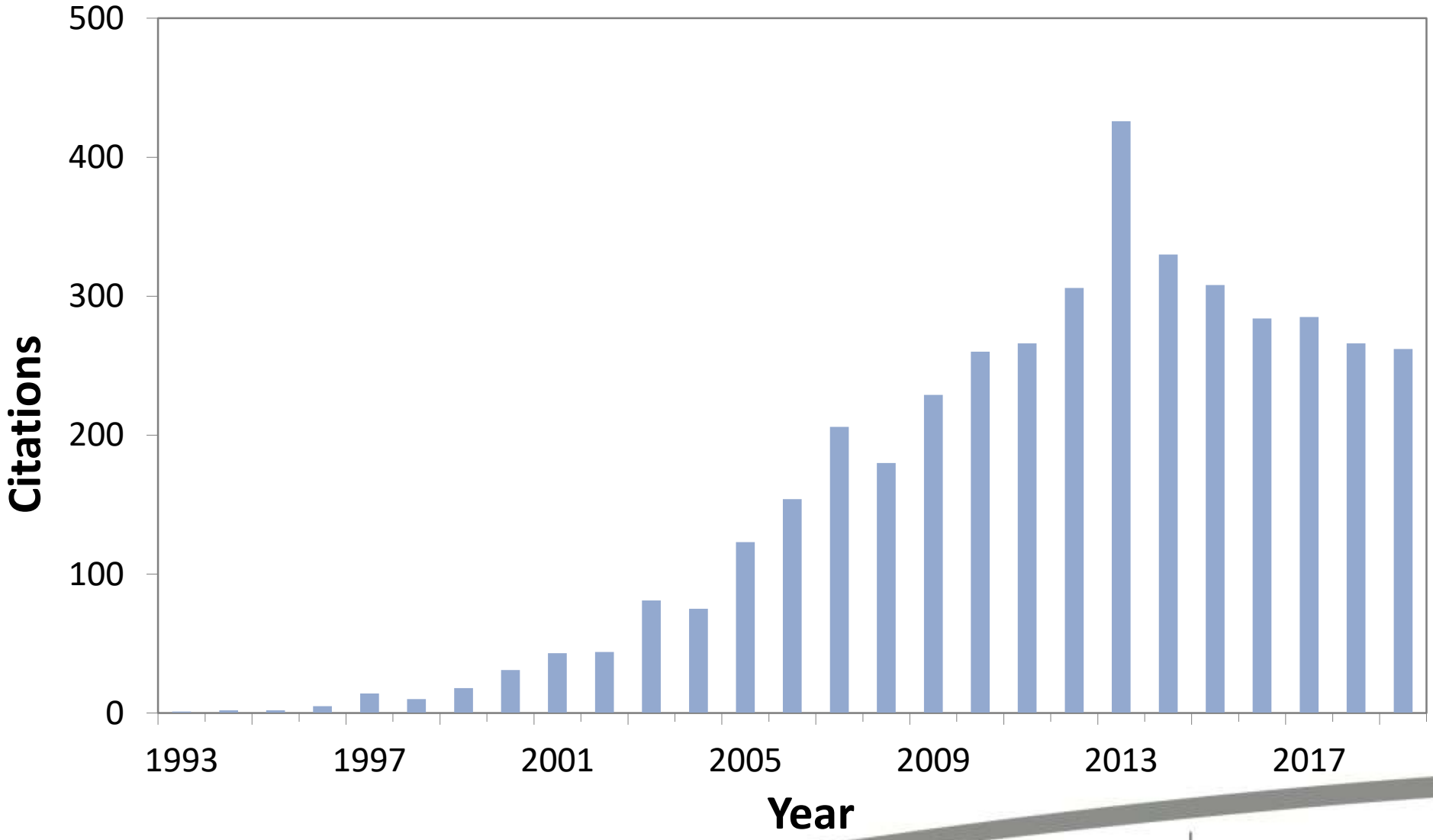
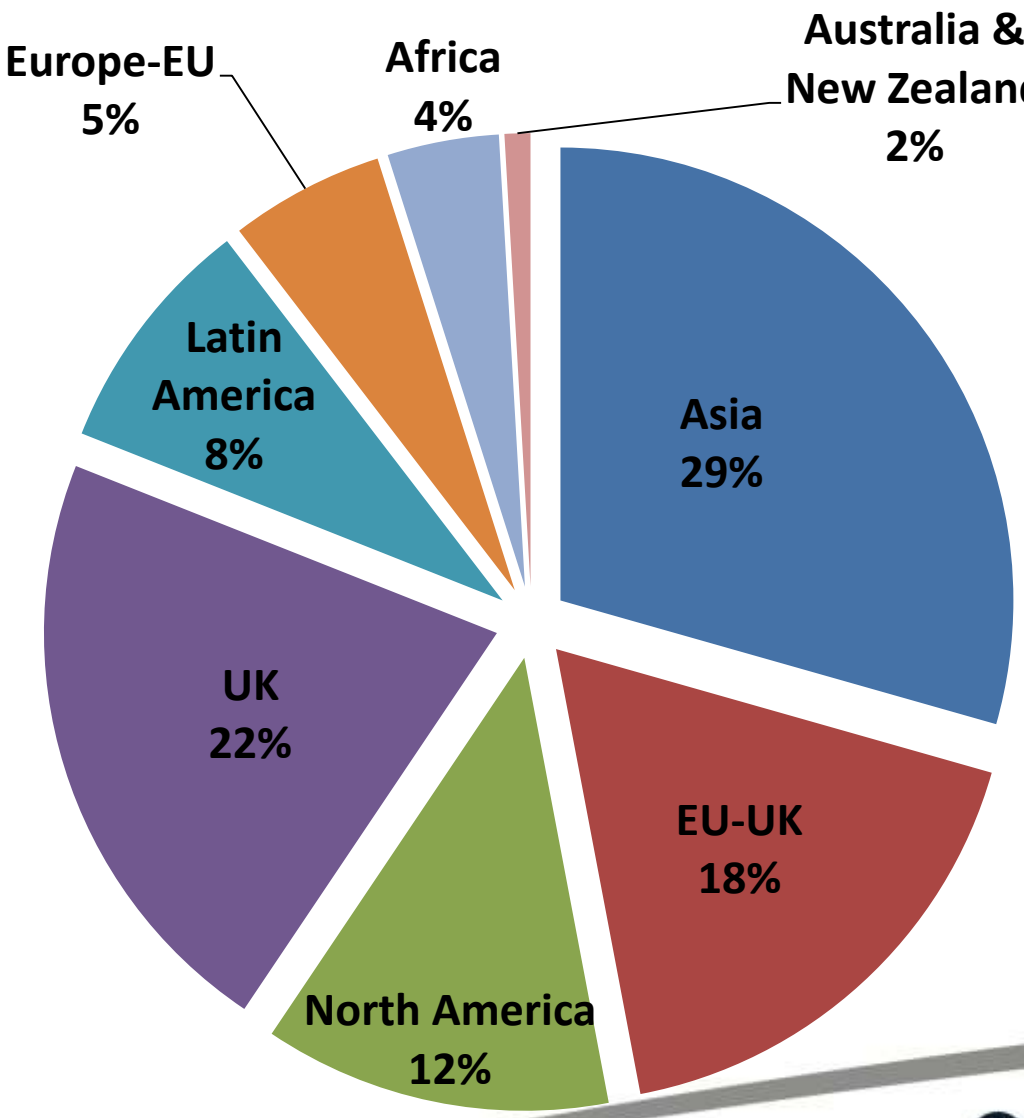


Project Impact by Google

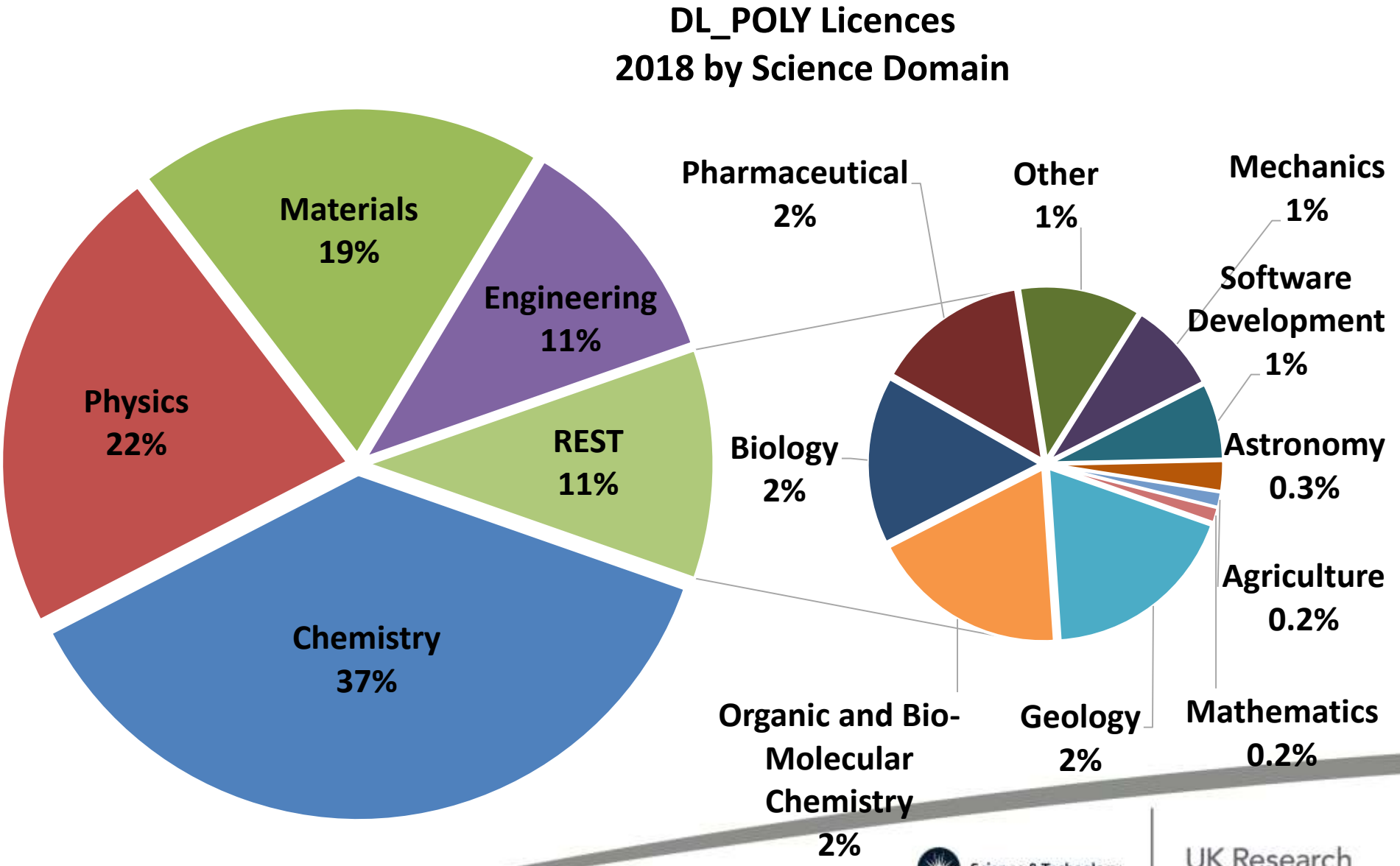


Project Reach



DL_POLY Licences 2018 by Sub-Areas

Project Reach



Project Team

Vlad Sokhan – Shaped Particles

- Anisotropic coarse-grained fields
- Gay-Berne's potentials

Alin Elena – Forward Flux Sampling

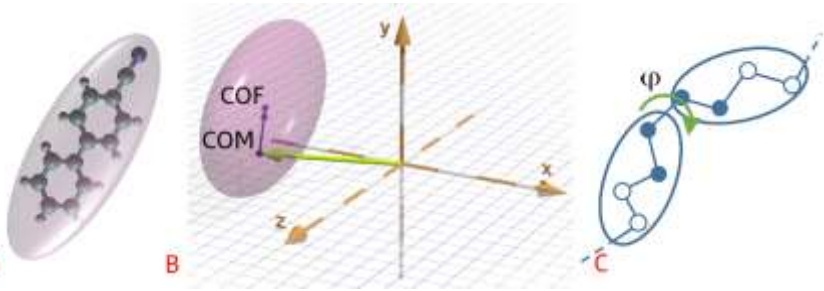
- Rare events technique originally developed for non-equilibrium systems, with stochastic element to the integration, with ability to extract reaction rates

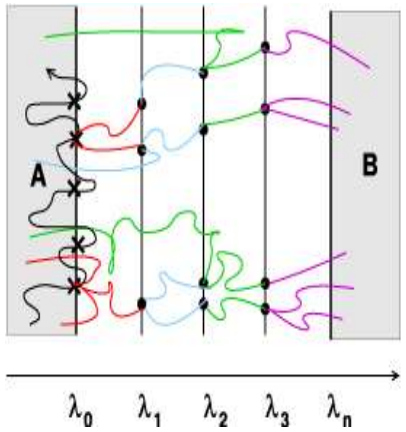
Ivan Scivetti – Empirical Valence Bond

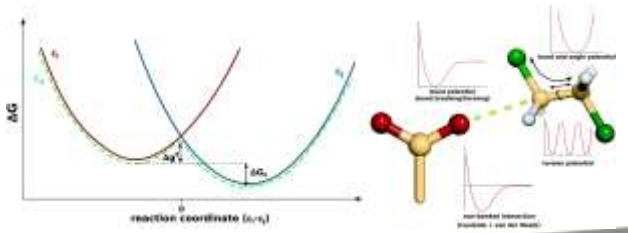
- Reactive dynamics for bond breaking and (re)making via product and reactant mixing terms

Alin Elena – DL_POLY Modernisation

- Natural Interfaces & Integration
- Best software practices & Sustainability







Project Contributors

Bill Smith – project originator

Ian Bush – 3DFFT DaFT

Andrey Brukhno – PDF for intramolecular interactions (CG)

Henry Boateng – Multipolar Electrostatics

Michael Seaton – TTM, DPD, …

Chin Yong – FF expert, DL_FIELD

Peicho Petkov – Direct Poisson Solver efforts

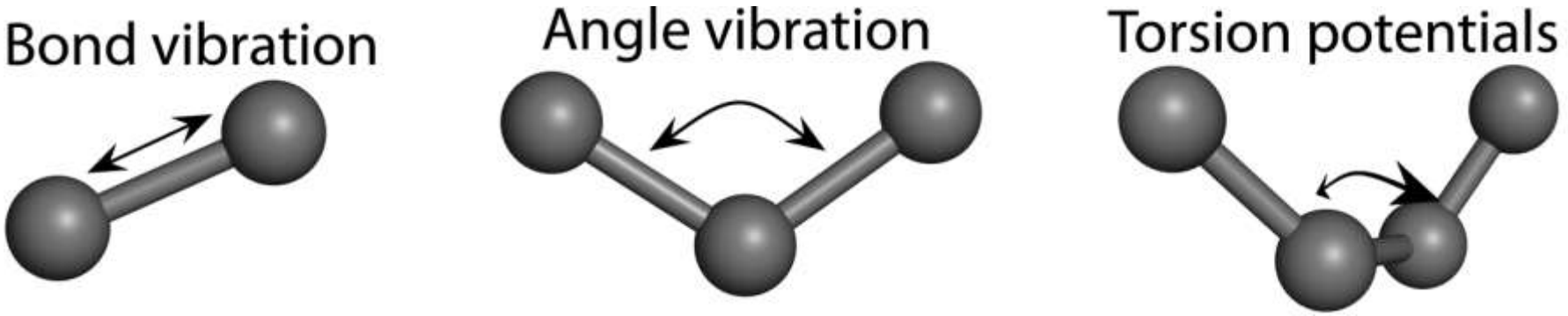
Others – ICHEC collaborators

Part 3

DL_POLY Basics & Algorithms

Simplified View of Force Field Elements

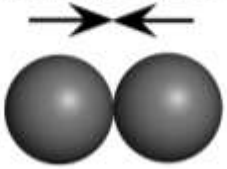
- **Bonded interactions – also referred as *intra*-molecular**



- **Non-bonded interactions – also referred as *inter*-molecular**

van der Waals interactions

$$U \propto \frac{1}{r^{12}} - \frac{1}{r^{6}}$$



short-ranged

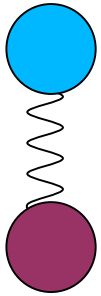
Electrostatics

$$U \propto \frac{q_1 q_2}{r}$$

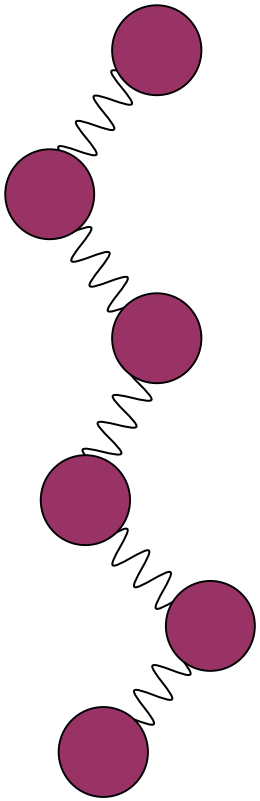
long-ranged

Supported Molecular Entities

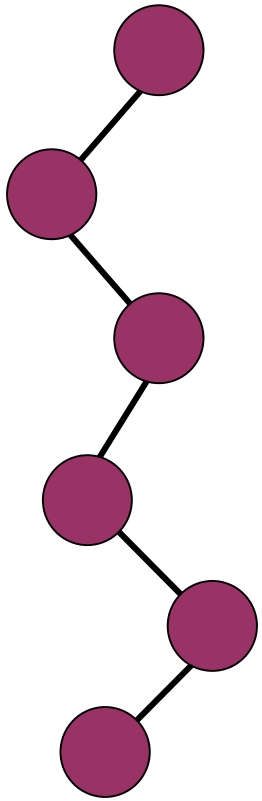
Point ions and atoms



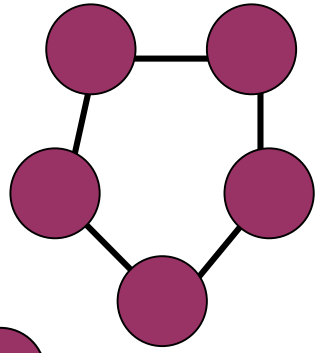
Polarisable ions (core+shell)



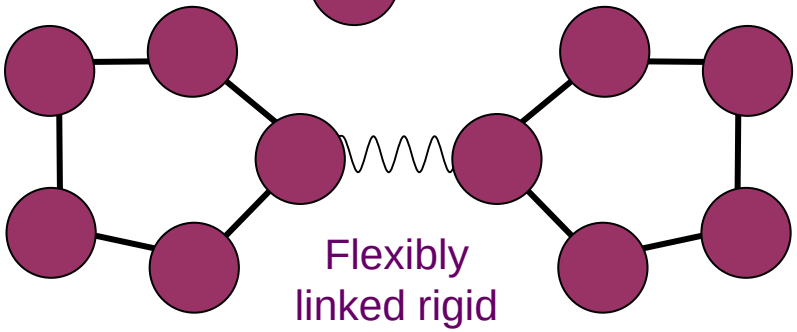
Flexible molecules



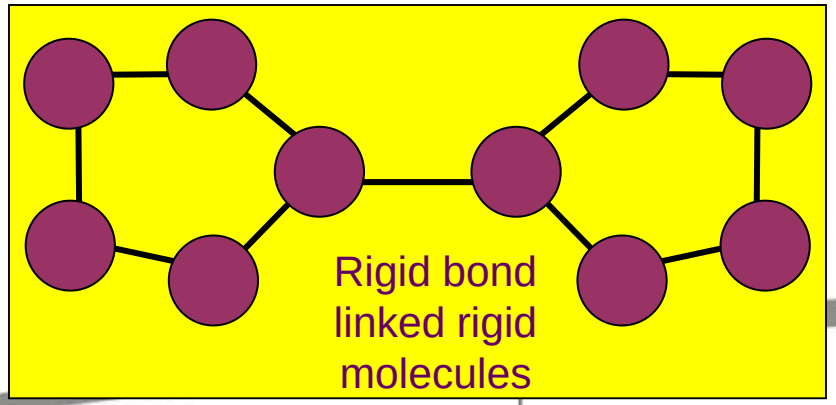
Constraint bonds



Rigid molecules



Flexibly linked rigid molecules



Rigid bond linked rigid molecules

Force Field Definitions – I

- ***particle:*** a rigid ion or an atom (charged or not), a core or a shell of a polarisable ion (with or without associated degrees of freedom), a massless charged site. A particle is a countable object and has a global ID index.
- ***site:*** a particle prototype that serves to define the chemical & physical nature (topology/connectivity/stoichiometry) of a particle (mass, charge, frozen-ness). Sites are not atoms they are prototypes!
- ***Intra-molecular interactions:*** chemical bonds, bond angles, dihedral angles, improper dihedral angles, inversions. Usually, the members in a unit do not interact via an inter-molecular term. However, this can be overridden for some interactions. These are defined by *site*.
- ***Inter-molecular interactions:*** van der Waals, metal (2B/E/EAM, Gupta, Finnis-Sinclair, Sutton-Chen), Tersoff, three-body, four-body. Defined by *species*.

Force Field Definitions – II

- ***Electrostatics:*** Standard Ewald*, Hautman-Klein (2D) Ewald*, **SPM Ewald (3D FFTs)**, Force-Shifted Coulomb, Reaction Field, Fennell damped FSC+RF, Distance dependent dielectric constant, Fuchs correction for non charge neutral MD cells.
- ***Ion polarisation*** via Dynamic (Adiabatic) or Relaxed shell model.
- ***External fields:*** Electric, Magnetic, Gravitational, Oscillating & Continuous Shear, Containing Sphere, Repulsive Wall.
- ***Intra-molecular like interactions:*** tethers, core shells units, constraint and PMF units, rigid body units. These are also defined by *site*.
- ***Potentials:*** parameterised analytical forms defining the interactions. These are always spherically symmetric!
- ***THE CHEMICAL NATURE OF PARTICLES DOES NOT CHANGE IN SPACE AND TIME!!!*** *

Force Field by Sums

$$V(\vec{r}_1,\vec{r}_2,.....,\vec{r}_N) = \sum_{i,j}^{N'} U_{pair}(|\vec{r}_i - \vec{r}_j|) + \frac{1}{4\pi\varepsilon\varepsilon_0}\sum_{i,j}^{N'}\frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} +$$

$$\sum_{i,j,k}^{N'} U_{Tersoff}\left(\vec{r}_i,\vec{r}_j,\vec{r}_k\right) + \sum_{i,j,k}^{N'} U_{3-body}\left(\vec{r}_i,\vec{r}_j,\vec{r}_k\right) + \sum_{i,j,k,n}^{N'} U_{4-body}\left(\vec{r}_i,\vec{r}_j,\vec{r}_k,\vec{r}_n\right) +$$

$$\varepsilon_{metal}\left(\sum_{i,j}^{N'} V_{pair}(|\vec{r}_i - \vec{r}_j|) + \sum_{i}^{N} F\left(\sum_{i,j}^{N'}\rho_{ij}(|\vec{r}_i - \vec{r}_j|)\right)\right) +$$

$$\sum_{i_{bond}}^{N_{bond}} U_{bond}\left(i_{bond},\vec{r}_a,\vec{r}_b\right) + \sum_{i_{angle}}^{N_{angle}} U_{angle}\left(i_{angle},\vec{r}_a,\vec{r}_b,\vec{r}_c\right) +$$

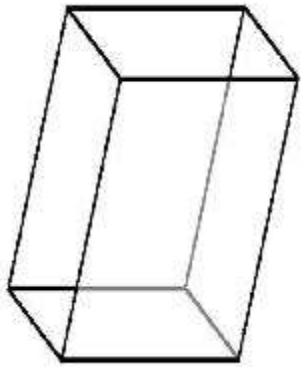
$$\sum_{i_{dihed}}^{N_{dihed}} U_{dihed}\left(i_{dihed},\vec{r}_a,\vec{r}_b,\vec{r}_c,\vec{r}_d\right) + \sum_{i_{invers}}^{N_{invers}} U_{invers}\left(i_{invers},\vec{r}_a,\vec{r}_b,\vec{r}_c,\vec{r}_d\right) +$$

$$\sum_{i_{tether}}^{N_{tether}} U_{tether}\left(i_{tether},\vec{r}_t,\vec{r}_{t=0}\right) + \sum_{i_{core\text{-}shell}}^{N_{core\text{-}shell}} U_{core\text{-}shell}\left(i_{core\text{-}shell},|\vec{r}_i - \vec{r}_j|\right) + \sum_{i=1}^{N}\Phi_{external}\left(\vec{r}_i\right)$$

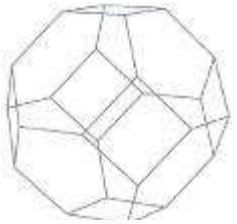
Boundary Conditions

0. None (e.g. isolated macromolecules)

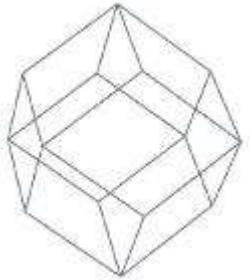
1. Cubic periodic boundaries
2. Orthorhombic periodic boundaries
3. Parallelepiped (triclinic) periodic boundaries



4. Truncated octahedral periodic boundaries*



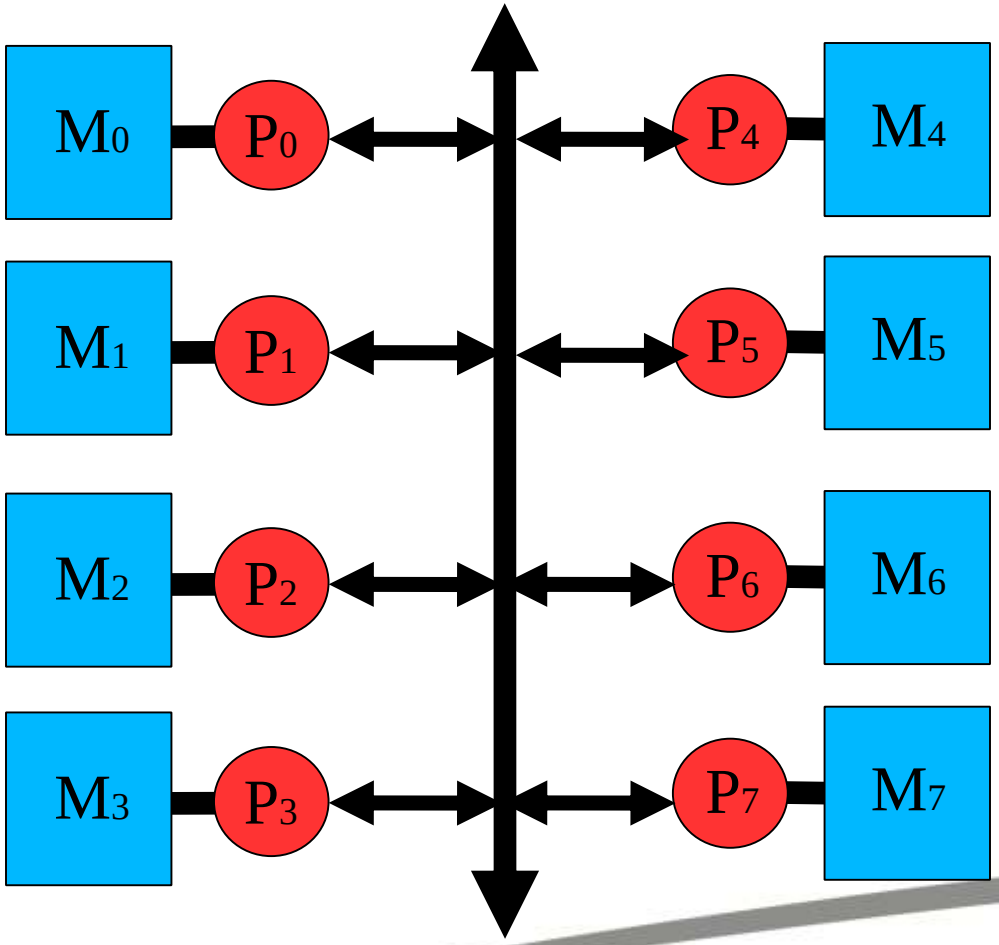
5. Rhombic dodecahedral periodic boundaries*



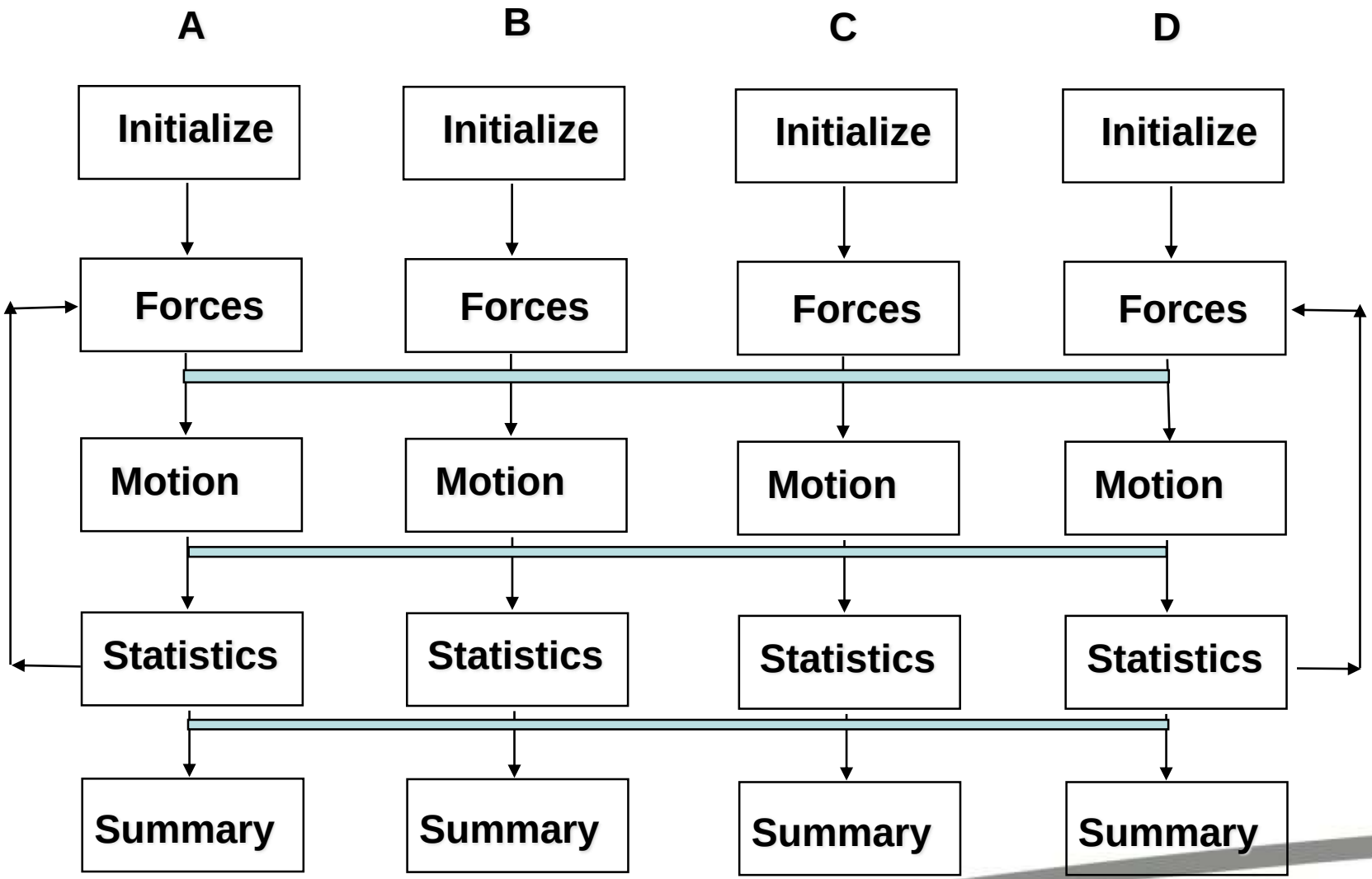
6. Slabs (i.e. x,y periodic, z non-periodic)

Assumed Parallel Architecture

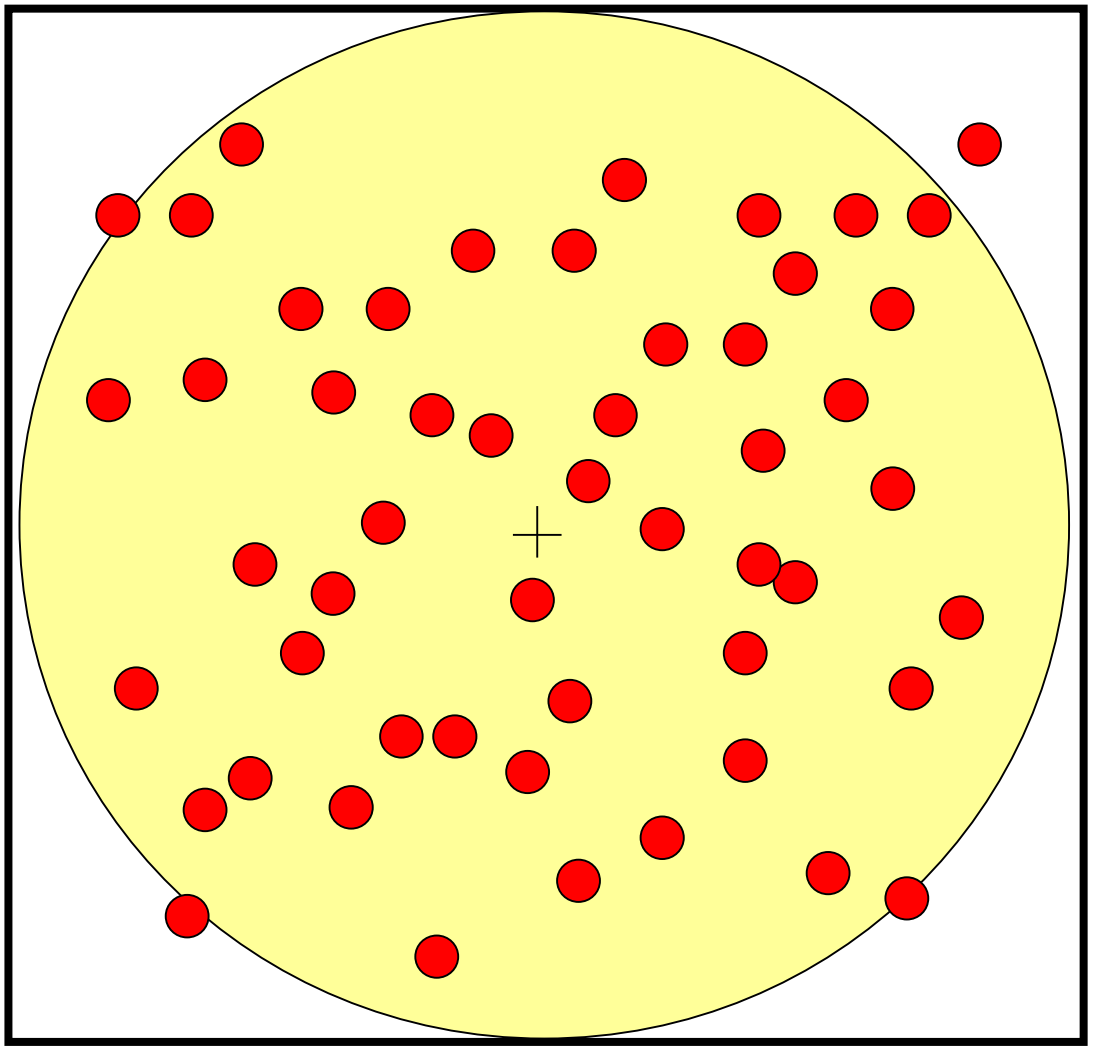
DL_POLY is designed for homogenious distributed parallel machines



Replicated Data Strategy – I



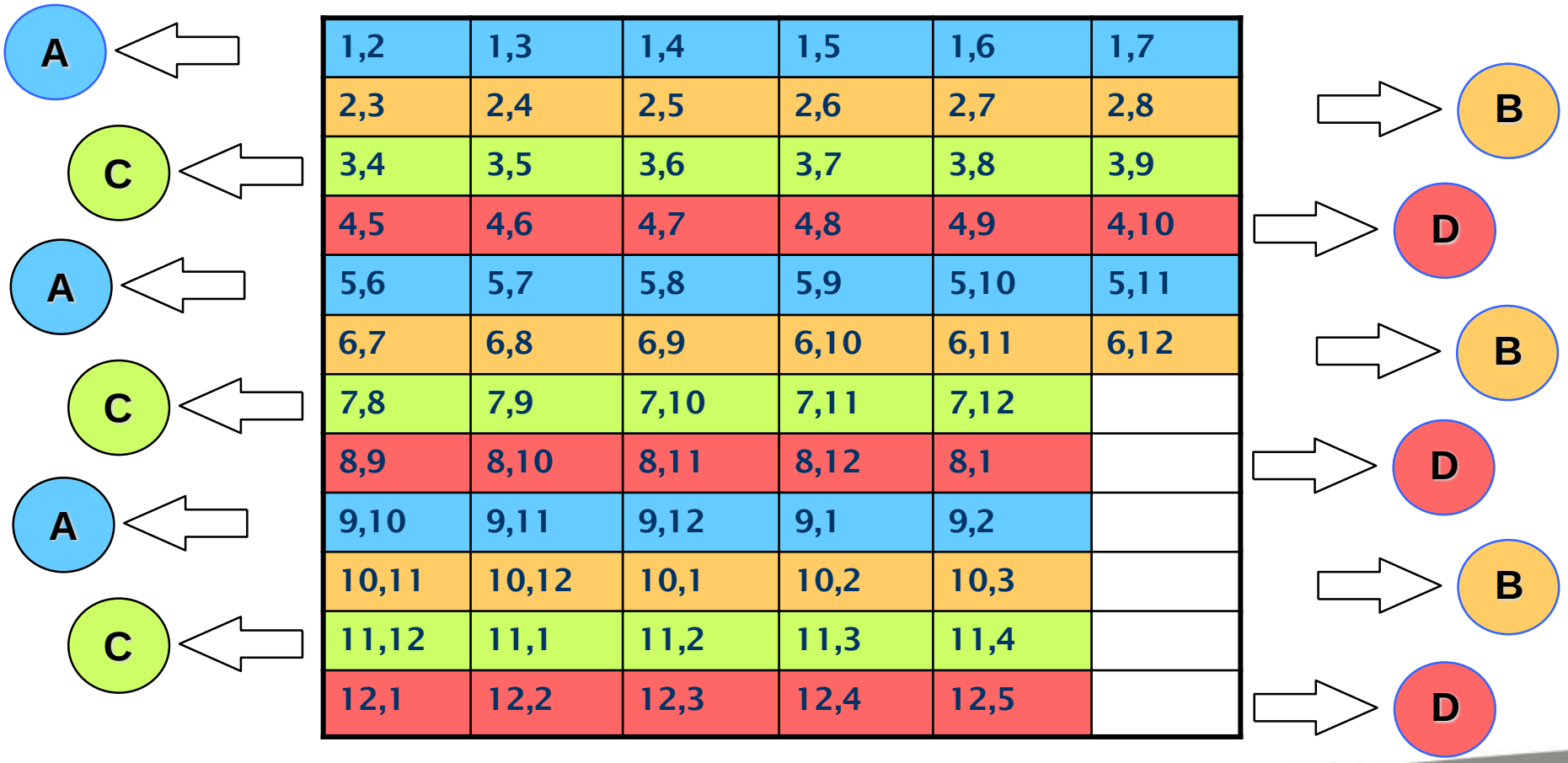
Replicated Data Strategy – II



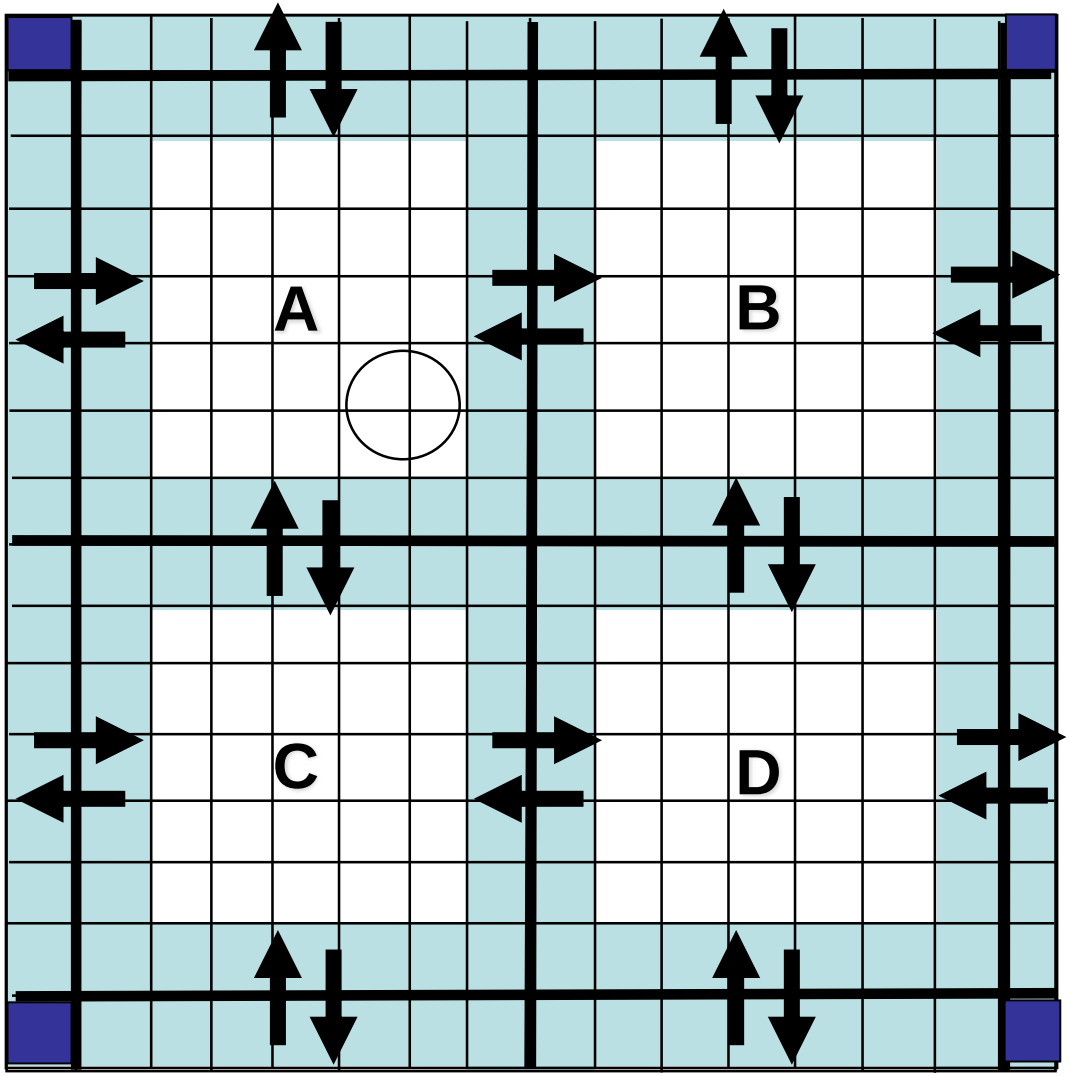
- Every processor sees the full system
- No memory distribution (performance overheads and limitations increase with increasing system size)
- Functional/algorithmic decomposition of the workload
- Cutoff ≤ 0.5 min system width
- Extensive global communications (extensive overheads increase with increasing system size)

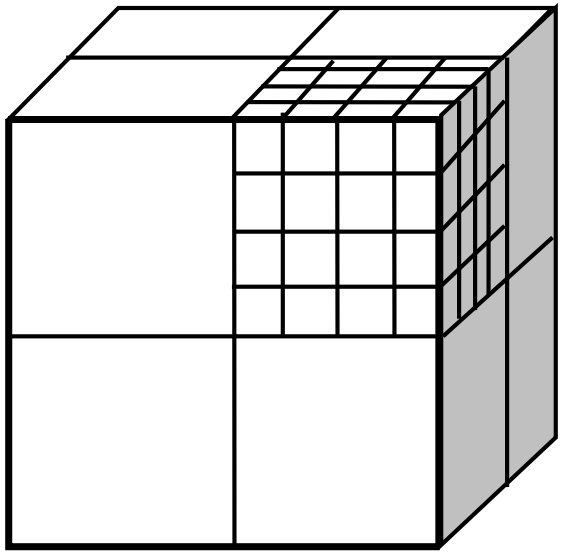
Parallel RD Verlet Neighbour List

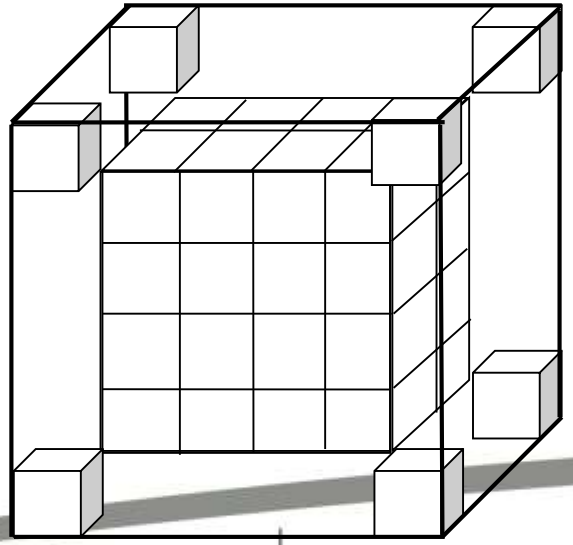
Brode-Ahlrichs distributed list!



Domain Decomposition MD



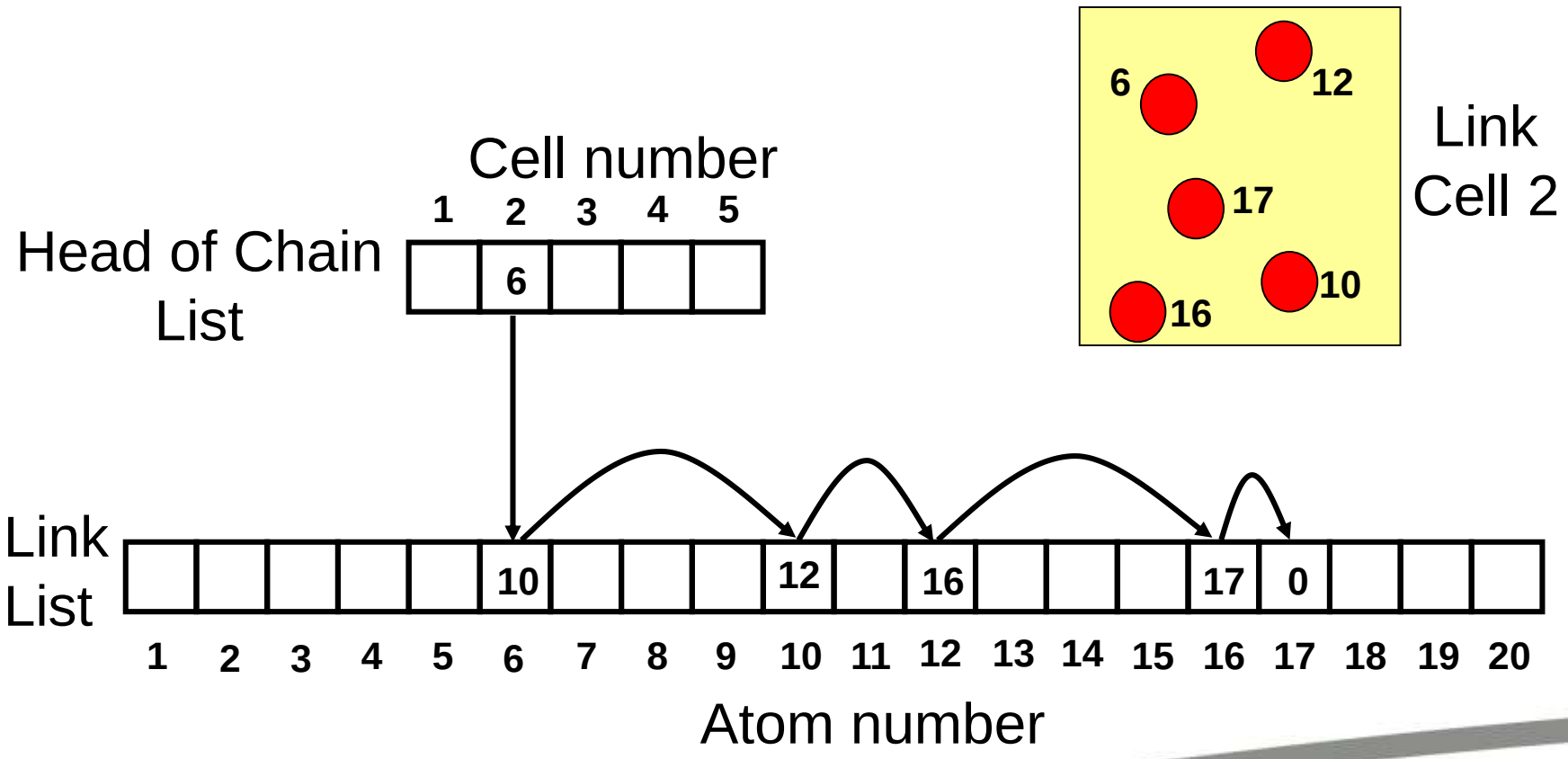




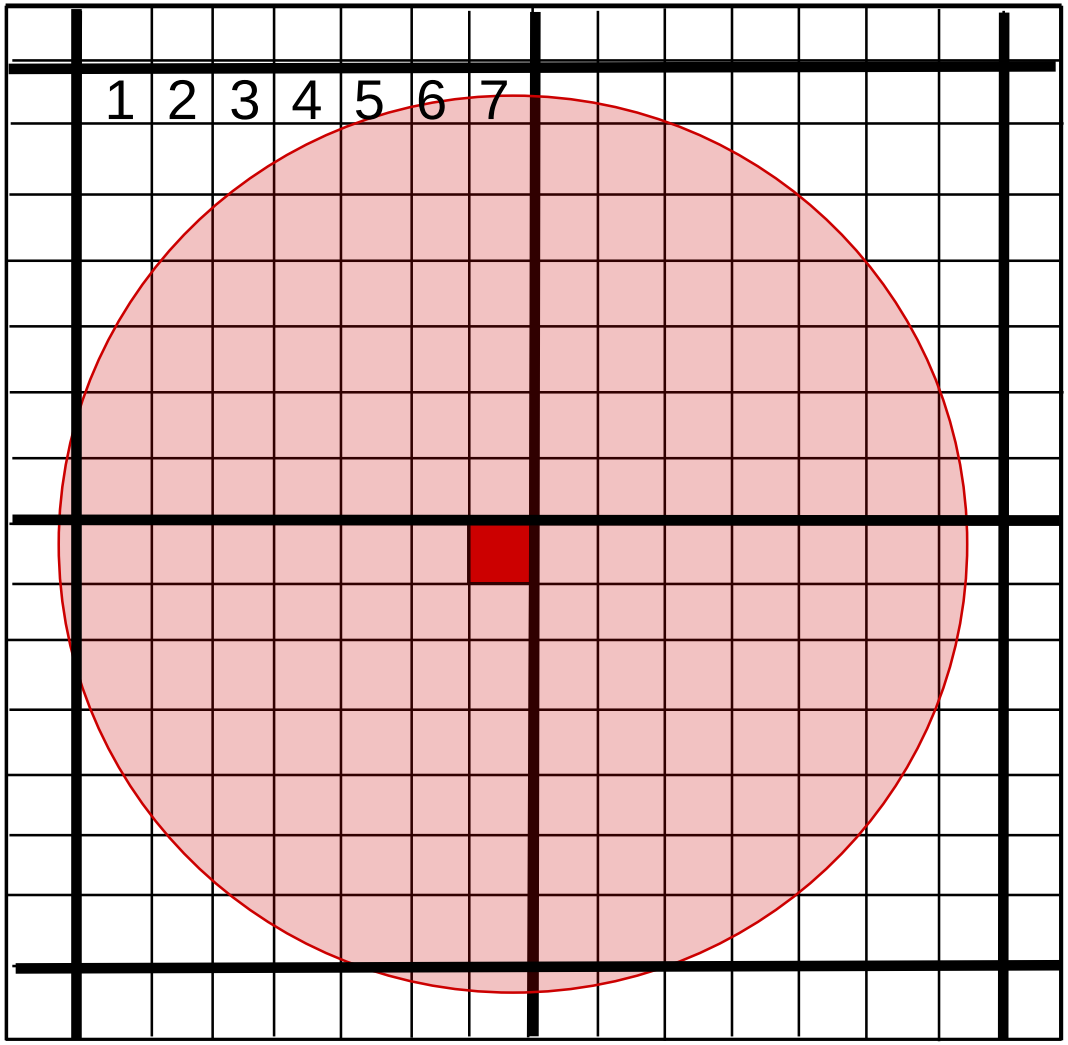
Linked Cell Lists

- Linked lists provide an elegant way to scale short-ranged two body interactions from $O(N^2/2)$ to $\approx O(N)$. The efficiency increases with increasing link cell partitioning – as a rule of thumb best efficacy is achieved for cubic-like partitioning with number of link-cells per domain ≥ 4 for any dimension.
- Linked lists can be used with the same efficiency for 3-body (bond-angles) and 4-body (dihedral & improper dihedral & inversion angles) interactions. For these, the linked cell halo is double-layered and as $cutoff^{3/4\text{-}body} \leq 0.5 * cutoff^{2\text{-}body}$ this makes the partitioning more effective than that for the 2-body interactions.
- The larger the particle density and/or the smaller the cutoff with respect to the domain width, (the larger the sub-selling and the better the spherical approximation of the search area), the shorter the Verlet neighbour-list search.

Liked Cell List Idea



Sub-celling of the LC



- Provides dynamically adjustable workload for variable local density and VNL speed up of ≈ 30% (45% theoretically).
- Provides excellent serial performance, extremely close to that of Brode-Ahlrichs method for construction of the Verlet neighbour-list when system sizes are smaller < 5000 particles.

Conditional Update of the VLN

- Replicated Data Shell Stripping – the VNL build up is extended for $r_{cut}+\delta r$ (shell width). The extended two body list is rebuild only and only when a pair of neighbouring particles has travelled more than δr apart since the last VNL build point. Rule of thumb $\delta r/r_{cut} \approx 5\text{-}15\%$.
- Domian Decomposition Particle Blurring – the VNL build up is extended for $r_{cut}+\delta r$ (domain padding). The extended two body list is rebuild only and only when a particle has travelled apart more than $\delta r/2$ apart since the last VNL build point. Rule of thumb $\delta r/r_{cut} \approx 1\text{-}5\%$.
- Consequences:
  - All short-ranged force evaluations have an additional check on pairs distance!
  - Memory and Communication over Computation and Communication balance. Force field (FF) dependent.
  - Short ranged FF 60-100% gains, FF with Ewald 10-35%.

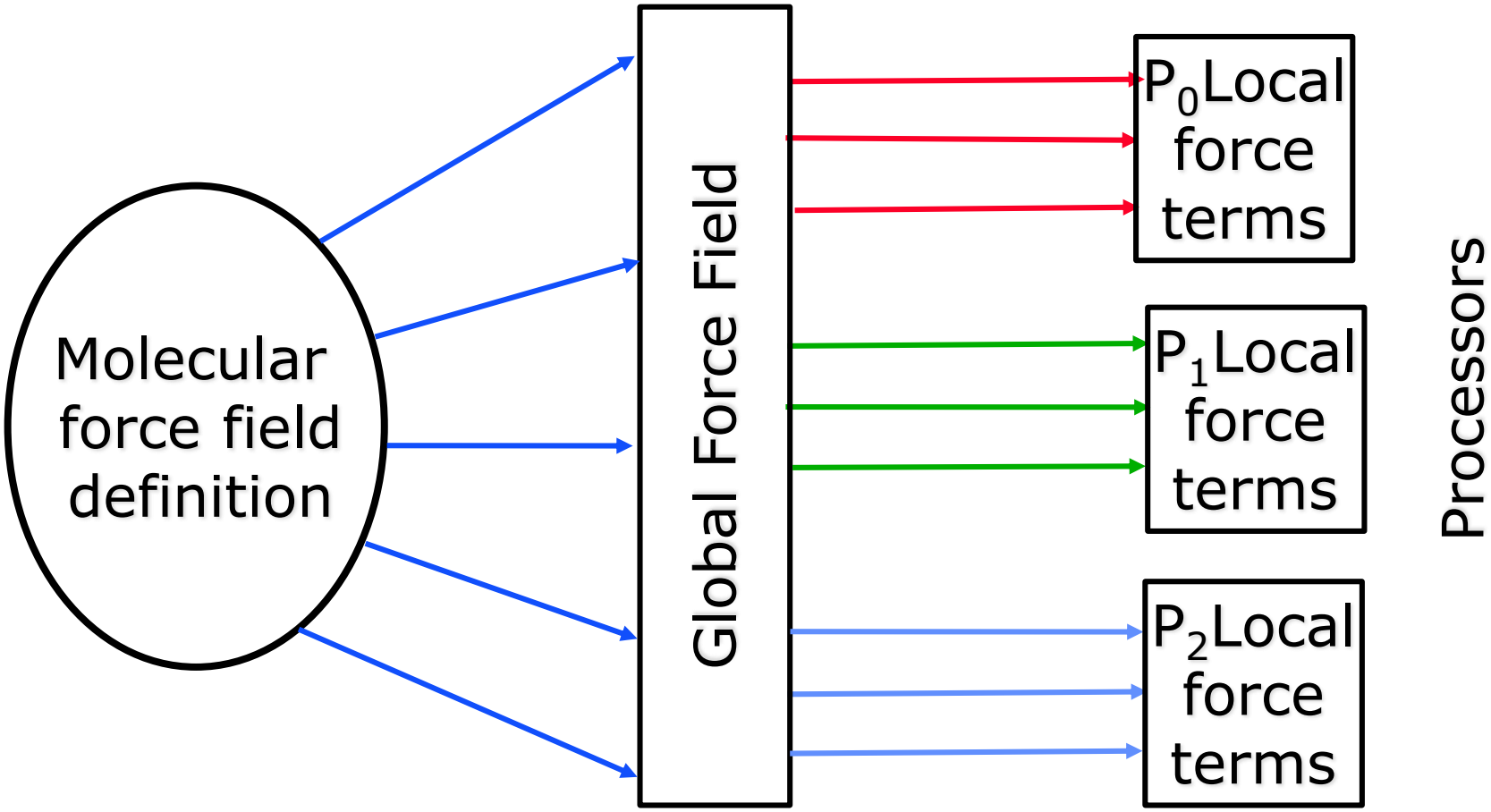
Parallel Forces Calculations

- Bonded forces:
  - Algorithmic decomposition for DL_POLY_C
  - Interactions managed by bookkeeping arrays, i.e. explicit bond definition!!!
  - Shared bookkeeping arrays

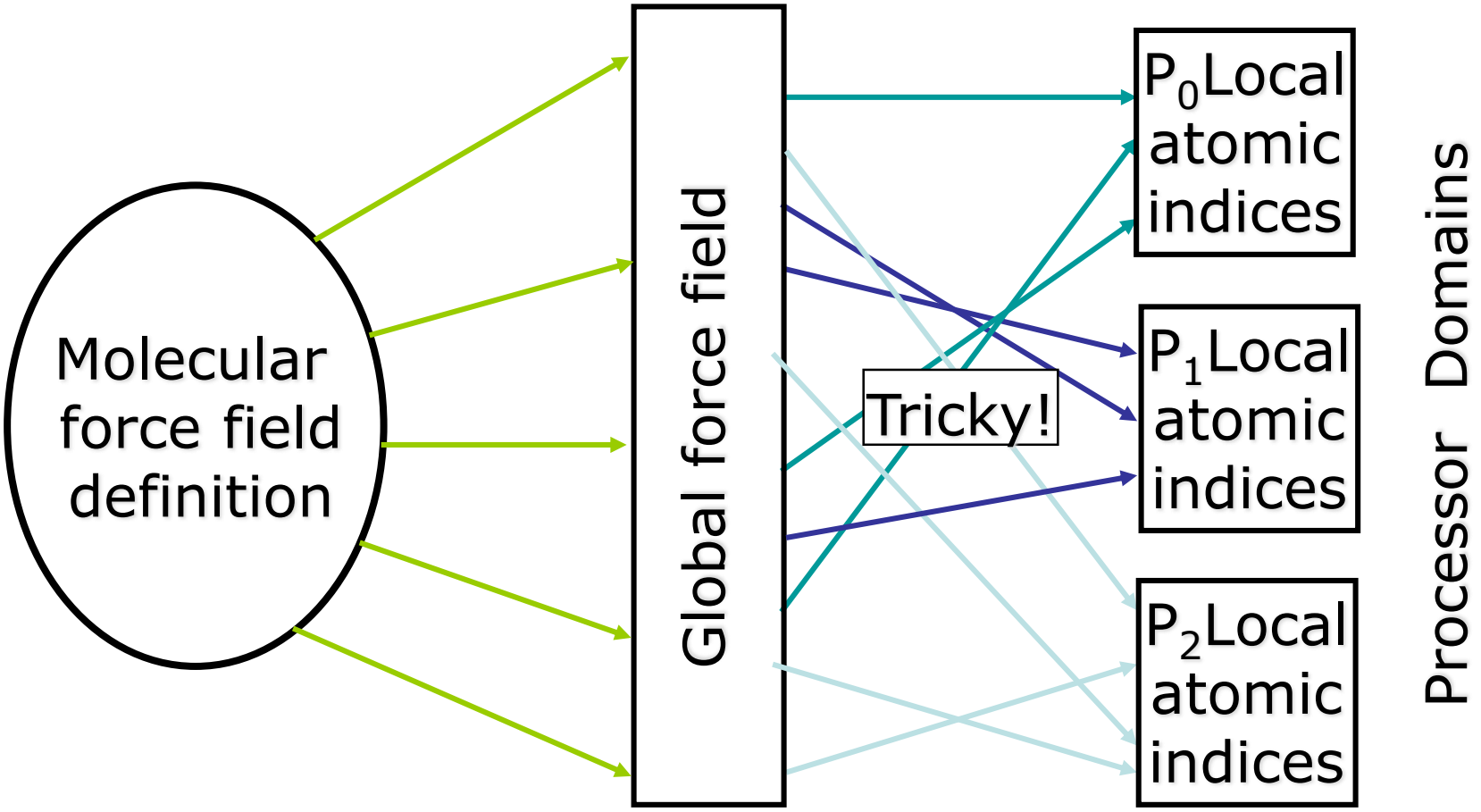
- Non-bonded forces:
  - Distributed Verlet neighbour list (pair forces)
  - Link cells (3,4-body forces)

- Implementations differ between DL_POLY_4 & C!

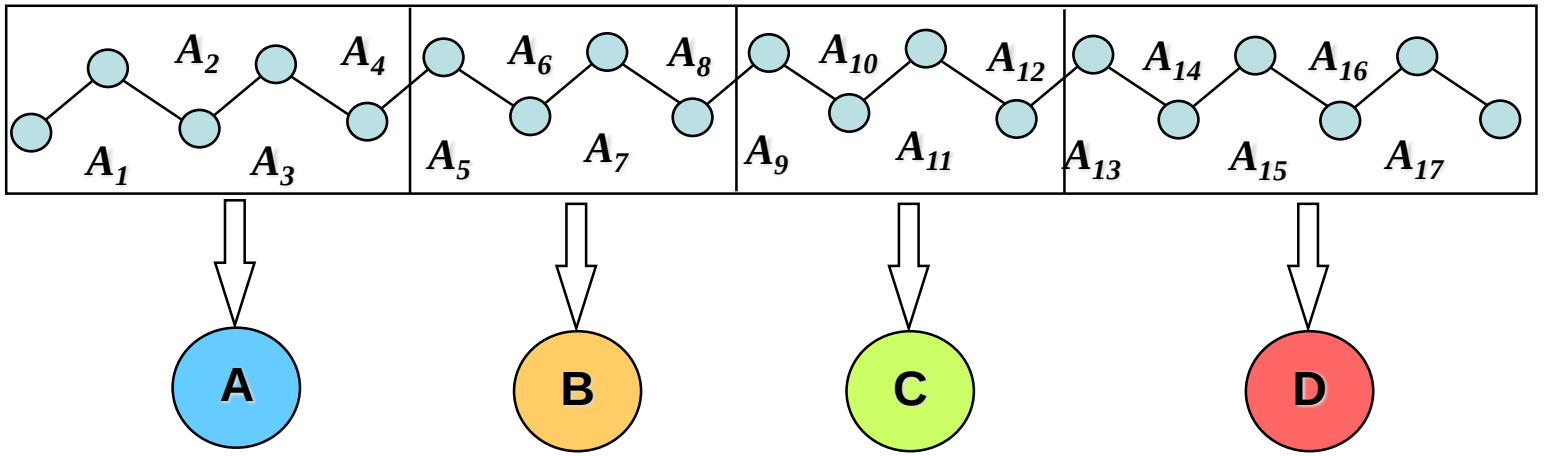
DL_POLY_C & Bonded Forces



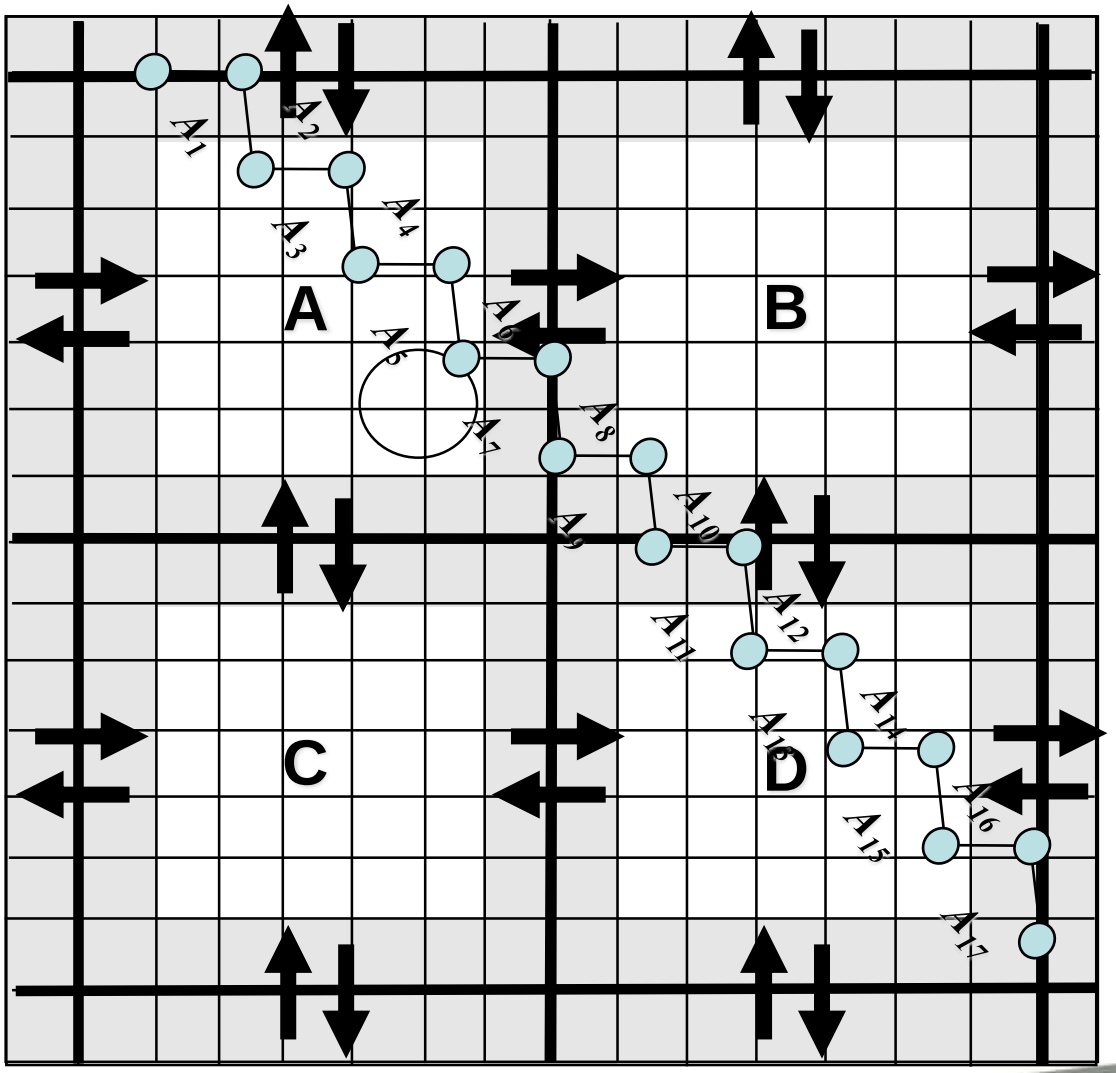
DL_POLY_4 & Bonded Forces



RD Distribution Scheme: Bonded Forces



DD Distribution Scheme: Bonded Forces



Ensembles & Algorithms

Integration:

Available as velocity Verlet (VV) or leapfrog Verlet (LFV) generating flavours of the following ensembles

- **NVE**
- **NVT (E_{kin})** Evans
- **NVT dpdS1 dpdS2** Sharlow 1st or 2nd order splitting (VV only)
- **NVT** Andersen^, Langevin^, Berendsen, Nosé-Hoover, GST
- **NPT** Langevin^, Berendsen, Nosé-Hoover, Martyna-Tuckerman-Klein^
- **NσT/NPnAT/NPnγT** Langevin^, Berendsen, Nosé-Hoover, Martyna-Tuckerman-Klein^

Note: *CoM motion is removed from non-conserving integrators!*

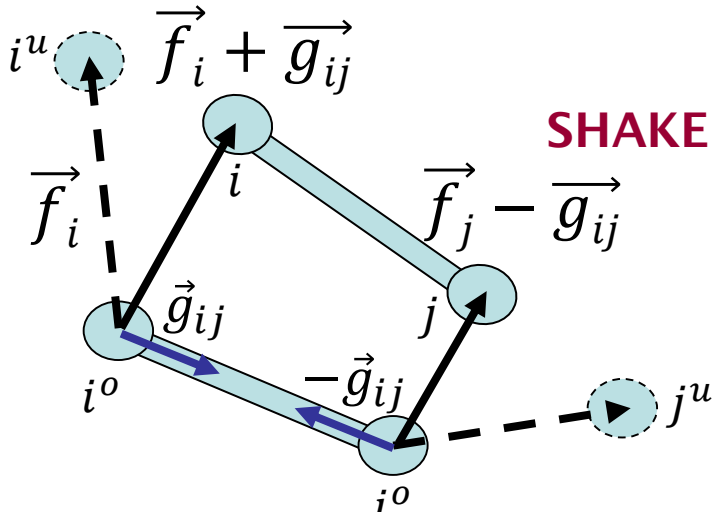
Constraints & Rigid Body Solvers:

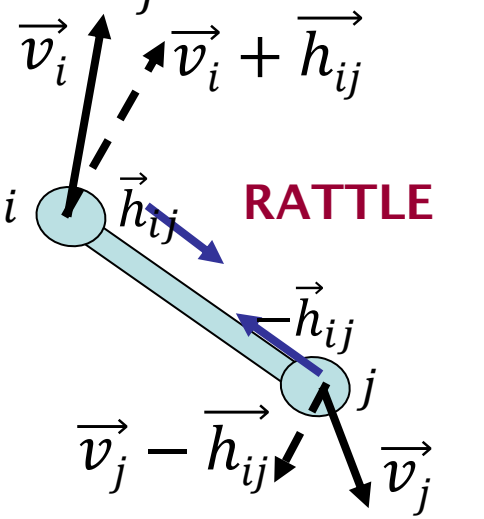
- **VV dependent – RATTLE, No_Squish, QSHAKE***
- **LFV dependent – SHAKE, Euler-Quaternion, QSHAKE***

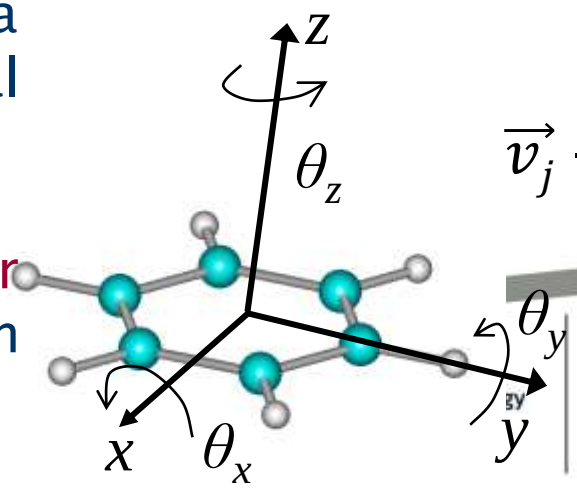
Constraint Bonds & Rigid Bodies

Constraint bonds can be used to increase the timestep size removing vibration of chemical bonds by an iterative procedure. SHAKE introduces retrospective force to get to CB's length to the desired equilibrium distance within a tolerance (*retrospective pressure effect*). RATTLE removes iteratively CBs' particles velocities components along the CBs direction (*retrospective kinetic effect*). A CB removes a half degree of freedom from each particle!

Rigid bodies provide a smarter way to move whole molecular fragments as a whole, keeping all fragments' internal distances invariant in time. A RB has up to 6 degrees freedom – 3 for CoM motion and 3 for rotation (2 for linear molecules as CO_2)! Rotational motion requires solving numerically the Eulerian equations of rotation.







Extended Ensembles in VV casting

Velocity Verlet integration algorithms can be naturally derived from the non-commutable Liouville evolution operator by using a second order Suzuki-Trotter expansion. Thus they are symplectic/true ensembles (with conserved quantities) warranting conservation of the phase-space volume, time-reversibility and long term numerical stability…

Exemplary VV Expansion of NVE to NVT, NPT & NσT

VV-Stage-1:

$r_i(t), v_i(t), f_i(t)$

$Thermostat\left(t \to t + \frac{1}{4}\Delta t\right)$: $\frac{1}{4}\Delta t$

$Barostat\left(t \to t + \frac{1}{2}\Delta t\right)$: $\frac{1}{2}\Delta t$

$Thermostat\left(t + \frac{1}{4}\Delta t \to t + \frac{1}{2}\Delta t\right)$: $\frac{1}{4}\Delta t$

$v_i\left(t + \frac{1}{2}\Delta t\right) = v_i(t) + \frac{\Delta t}{2}\frac{f_i(t)}{m_i}$: $\frac{1}{2}\Delta t$

$r_i(t + \Delta t) = r_i(t) + \Delta t\, v_i\left(t + \frac{1}{2}\Delta t\right)$: Δt

$RATTLE\_R(t \to t + \Delta t)(r_i, v_i, f_i)$: Δt

SYMMETRIC

VV-Stage-2:

$r_i(t + \Delta t), v_i\left(t + \frac{1}{2}\Delta t\right), f_i(t + \Delta t)$ – *afresh*

$v_i(t + \Delta t) = v_i\left(t + \frac{1}{2}\Delta t\right) + \frac{\Delta t}{2}\frac{f_i(t+\Delta t)}{m_i}$: $\frac{1}{2}\Delta t$

$RATTLE\_V\left(t + \frac{1}{2}\Delta t \to t + \Delta t\right)(v_i)$: Δt

$Thermostat\left(t + \frac{1}{2}\Delta t \to t + \frac{3}{4}\Delta t\right)$: $\frac{1}{4}\Delta t$

$Barostat\left(t + \frac{1}{2}\Delta t \to t + \Delta t\right)$: $\frac{1}{2}\Delta t$

$Thermostat\left(t + \frac{3}{2}\Delta t \to t + \Delta t\right)$: $\frac{1}{4}\Delta t$

$r_i(t + \Delta t), v_i(t + \Delta t), f_i(t + \Delta t)$

Choosing the coupling time constants

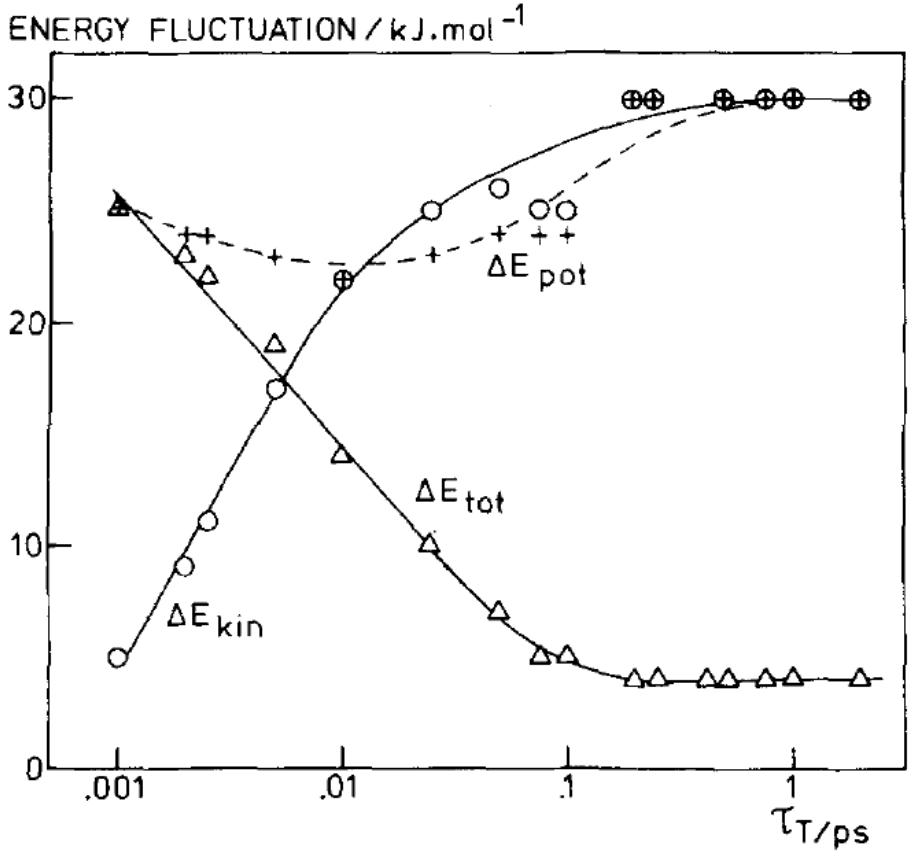


FIG. 2. Root means square fluctuations in kinetic, total, and potential energies, measured over several 0.1 ps simulations of liquid water.

Berendsen *et al.*, *J. Chem. Phys.*, **81**, 3684, (1984).

The time constants to do with thermostats/barostats control the exchange of energy between the system and the reference baths.

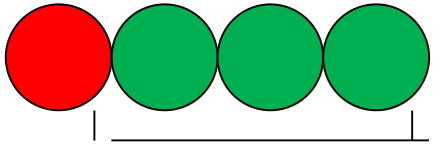
Long time constants will result in slow equilibration.

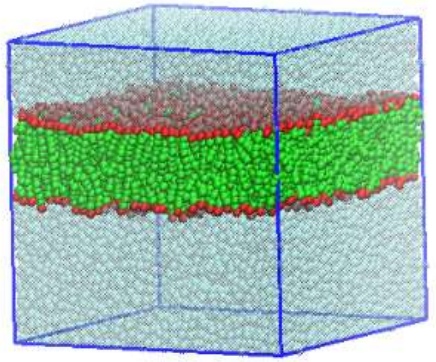
Short time constants will interfere with the simulation results, particularly those dependant on fluctuations.

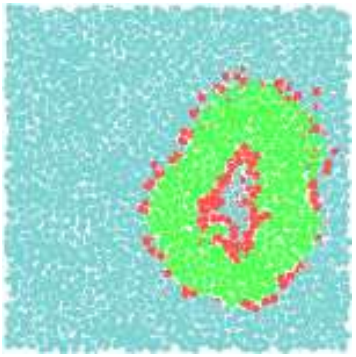
The compromise is system dependant and requires experiment!

CG & Dissipative Particle Dynamics

- Similar methodology to classical MD:
  - Condensed phase system modelled by particles (‘beads’) using pairwise potentials
  - Particle motion determined by force integration (e.g. Velocity Verlet)
  - System properties at equilibrium calculated as ensemble averages

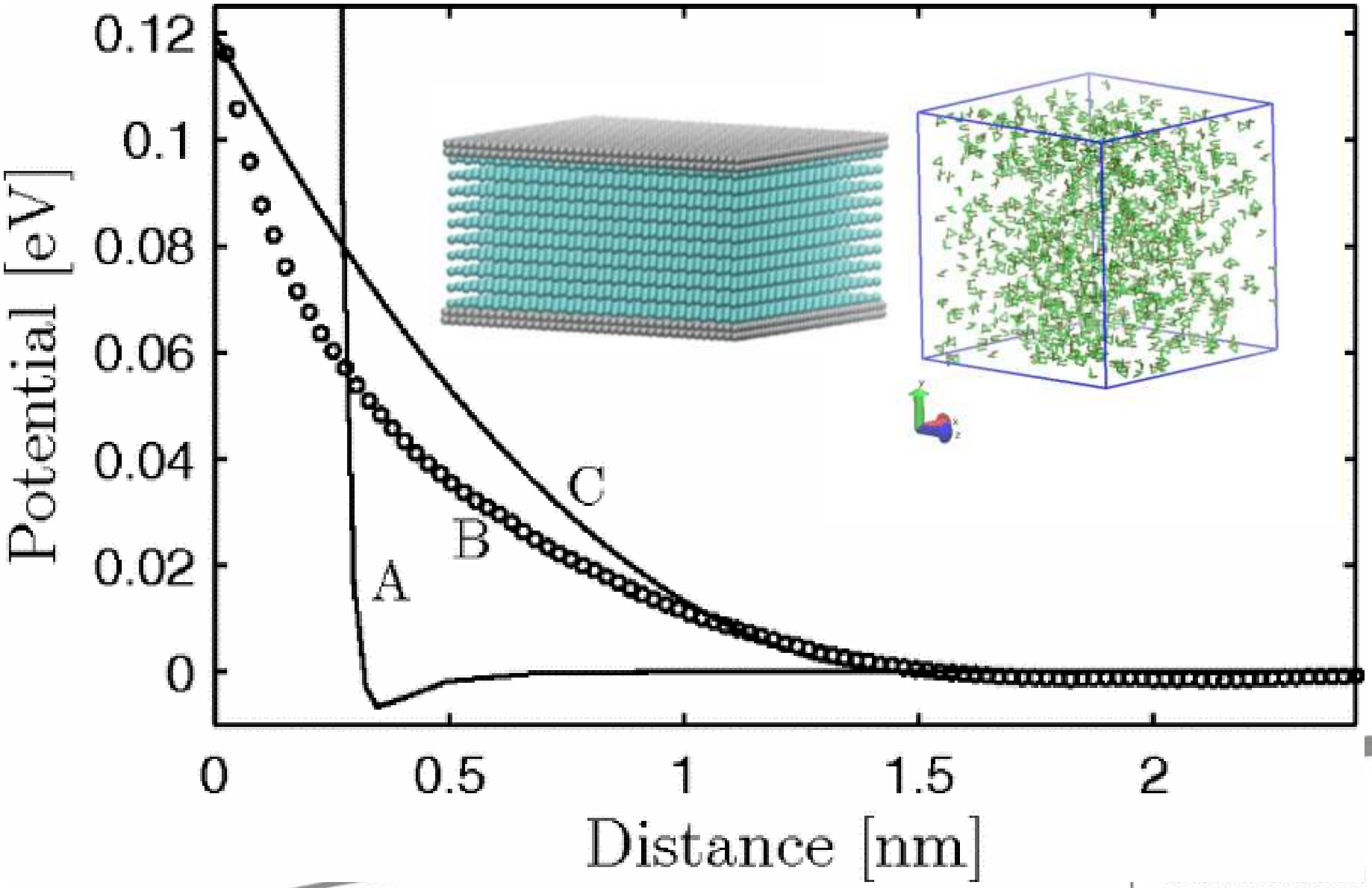




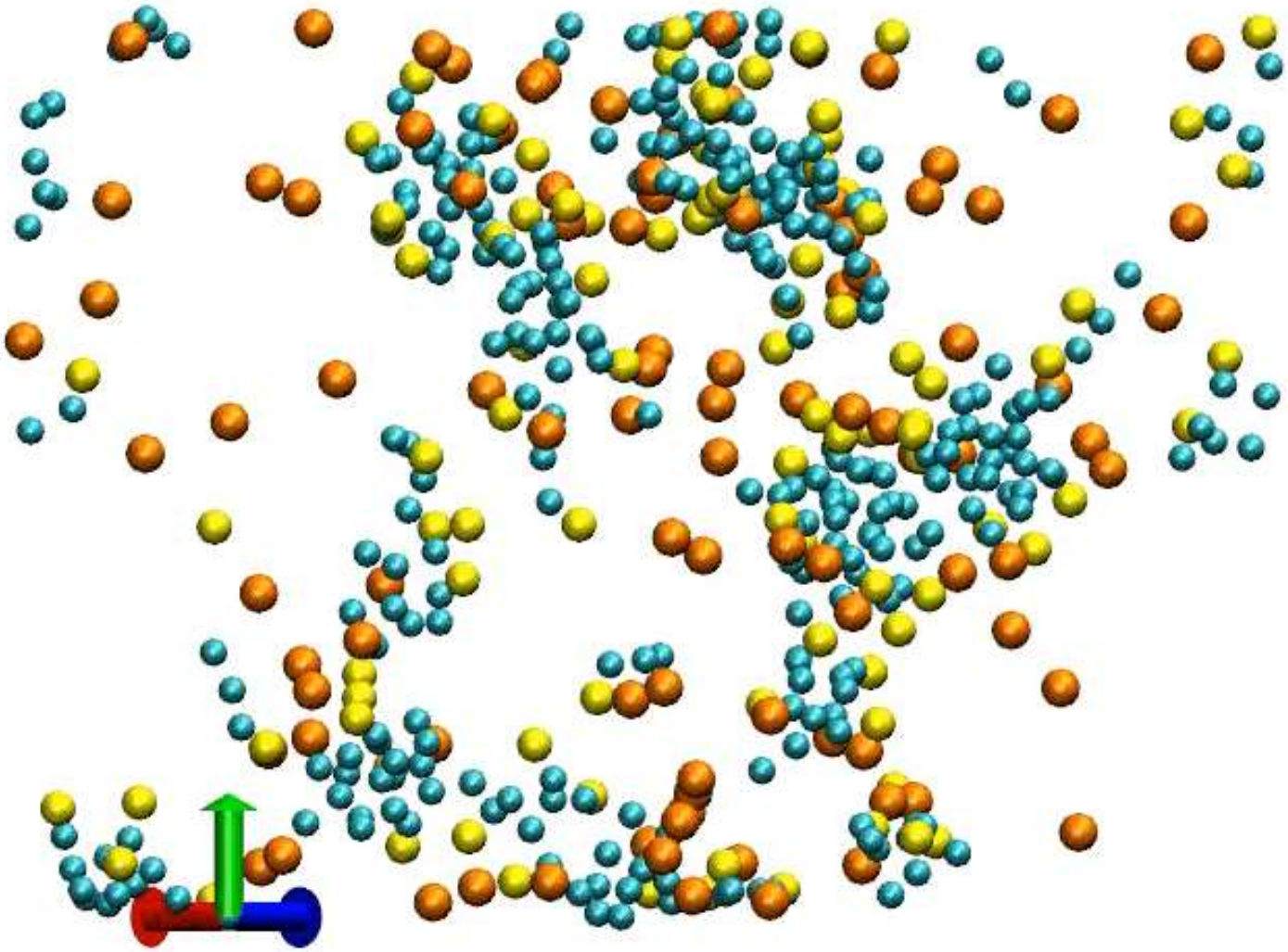


- System coupled to heat bath using pairwise dissipative and random forces
  - Pairwise thermostatting conserves system momentum and produces correct hydrodynamics

Dissipative Particle Dynamics



Coarse Grained MD



DPD Algorithm – I

- Dissipative force:

Relative velocity between particles

$$\mathbf{F}_{ij}^{D} = -\gamma w^{D}\left(r_{ij}\right)\left(\hat{\mathbf{r}}_{ij}\cdot\mathbf{v}_{ij}\right)\hat{\mathbf{r}}_{ij}$$

Distance-based screening function

- Random force:

Gaussian random number (zero mean, unity variance)

$$\mathbf{F}_{ij}^{R} = \sigma w^{R}\left(r_{ij}\right)\frac{\xi_{ij}}{\sqrt{\Delta t}}\hat{\mathbf{r}}_{ij}$$

- Fluctuation-dissipation theory demonstrates these forces act as thermostat if:

$$w^{D}\left(r_{ij}\right) = \left[w^{R}\left(r_{ij}\right)\right]^{2} \text{ and } \sigma^{2} = 2k_{B}T\gamma$$

  - Dissipative force parameter related to fluid viscosity

DPD Algorithm – II

- Conservative force often selected as

$$\mathbf{F}_{ij}^{C} = A_{ij}\left(1 - \frac{r_{ij}}{r_c}\right)\hat{\mathbf{r}}_{ij}$$

Interaction length (cutoff radius)

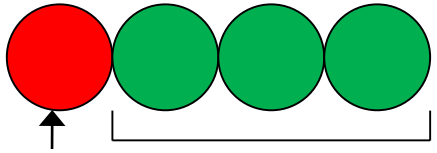
although this is not necessary for a coarse-grained (CG) MD

  - Quadratic potential: soft and repulsive
  - Gives quadratic equation of state for fluid:

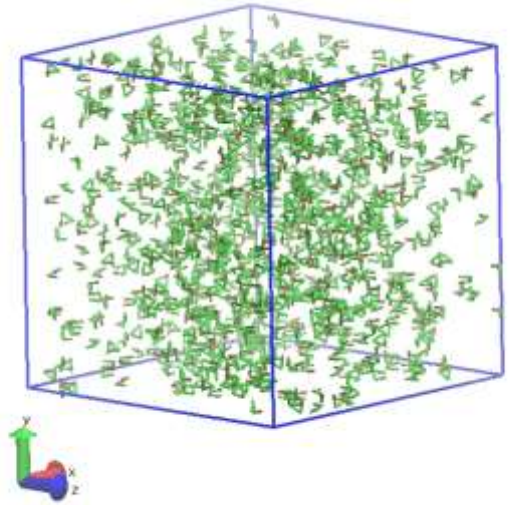
$$p \approx \rho k_B T + 0.101 A_{ij} \rho^2 r_c^4$$

  - Soft potential allows for larger time steps than classical MD: beads can 'pass through' each other and reach equilibrium in fewer time steps
  - Flexible definition of beads: either coarse-grains or 'momentum carriers'

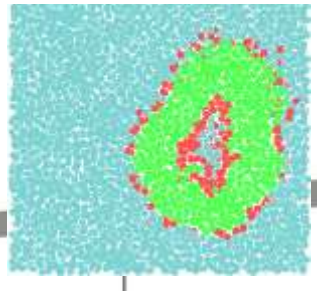
DPD Capabilities



- Flexible interactions between species pairs
  - Can specify e.g. hydrophobicity
  - Interaction parameters can be connected to Flory-Huggins solution theory



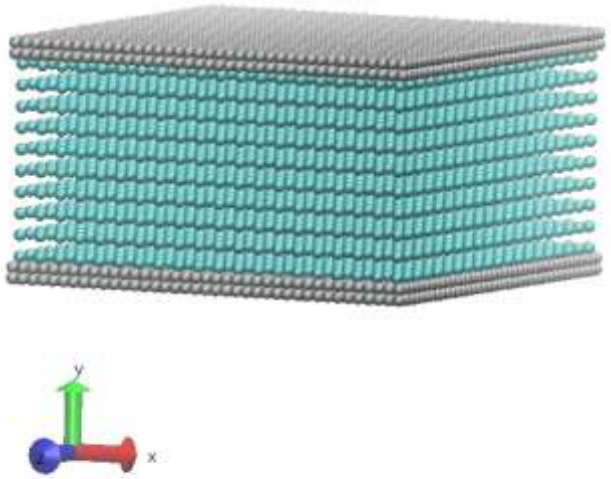
- Bond interactions
  - Allow for construction of ‘molecules’ from differently interacting beads
  - Example: spontaneous vesicle formation of amphiphilic molecules in solution



Source: Yamamoto *et al.*, *J Chem Phys*, **116**, 5842–5849 (2002)

DPD via DL_MESO

– Example: formation of water drops on hydrophobic surface under influence of gravity



Source: Johansson, *Simulating fluid flow and heat transfer using dissipative particle Dynamics*, Dept. Energy Sci., Lund University (2012)

Other Integration Algorithms

- Gear Predictor-Corrector – generally easily extendable to any high order of accuracy. It is used in satellite trajectory calculations/corrections. However, lacking long term stability.

- Trotter derived evolution algorithms – generally easily extendable to any high order of accuracy. Symplectic.

Base Functionality

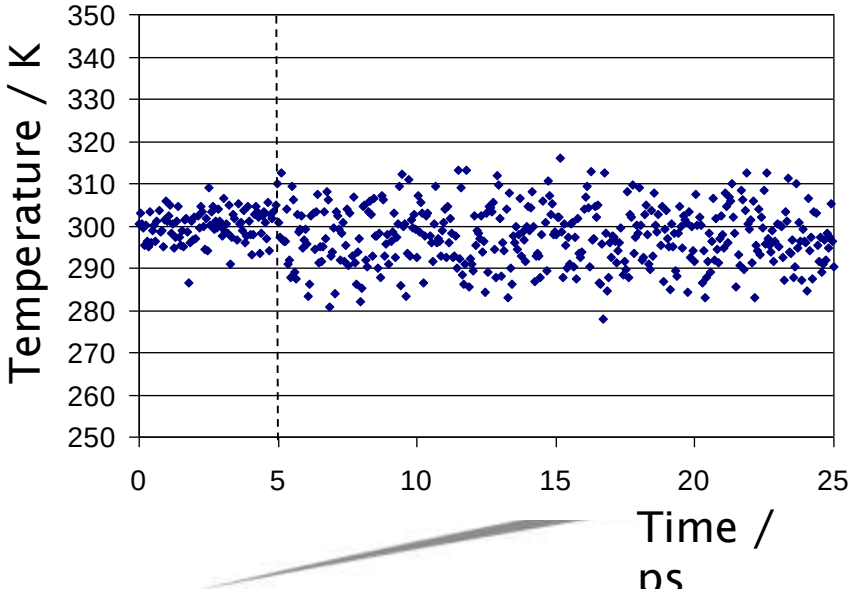
- Molecular dynamics of polyatomic systems with options to save the micro evolution trajectory at regular intervals
- Optimisation by conjugate gradients method or zero Kelvin annealing
- Statistics of common thermodynamic properties (temperature, pressure, energy, enthalpy, volume) with options to specify collection intervals and stack size for production of rolling and final averages
- Calculation of RDFs and Z-density profiles
- Temperature scaling, velocity re-Gaussing
- Force capping in equilibration

Velocity re-Scaling

To get around the problem of temperature drift we can simply remove or inject kinetic energy by scaling the velocities in the initial stages of the calculation:

$$T = \frac{2}{3Nk_B}\langle K.E.\rangle \qquad KE(t) = \tfrac{1}{2}\sum_i m_i \left|s.\underline{v}_i(t)\right|^2 \qquad s = \left(\frac{T(set)}{T(t)}\right)^{1/2}$$

Where *T(set)* is the target temperature for the simulation. This technique is referred to as velocity scaling and is used during the equilibration period of the simulation.



Example MD run with T set at 300K, velocity scaling used up to 5ps.

Thereafter fluctuations in T increase but no drift away from average.

Specialised Functionality

- Radiation damage driven features:
  - defects analysis
  - boundary/stochastic thermostats
  - volumetric expansion (integer) – *nfold Nx Ny Nz*
  - replay history
  - variable time step algorithm
- Extra ensembles:
  - DPD, Langevin, Andersen, MTK, GST
  - extensions of NsT to NP_nAT and $NP_n\gamma T$
- Infrequent k-space Ewald evaluation
- Direct VdW/Metal
- Force shifted VdW
- I/O driven features Parallel I/O & netCDF
- Extra Reporting (& opting out of nagging)
- Extensions: PLUMED, OpenKIM
- VdW potentials mixing schemes

CONTROL for Equilibration

```
DL_POLY_4 GENERIC EQUILIBRATION SET OF CONTROL DIRECTIVES

temperature       300        Kelvin
pressure          0.001      k-atmospheres

#ensemble nst ber 0.75 1.7      # uncomment only for non-liquid or non-bio/organo-chemical systems!!!
#ensemble nst ber 0.75 1.7 orth # uncomment for non-liquid or non-bio/organo-chemical systems!!!

variable timestep   0.0015     pico-seconds
maxdis              0.11       Angstroms
mindis              0.04       Angstroms
mxstep              0.005      pico-seconds

steps           3000
equilibration   1500

scale every       7
#regauss every    70
cap             1000        k-T/Angstrom

#zero fire 12 # uncomment for really bad starting configurations!!!

#minimise force 115 10.0  # uncomment only for non-liquid or non-bio/organo-chemical systems!!!
#minimise dist  115  0.06 # uncomment for liquid or bio/organo-chemical systems (solvent/H motion)!

#rlxtol 75 # uncomment for models with difficult relaxed shell convergence
#shake              1.0e-7     force units # uncomment for making constrained units good for rigid body
shake              1.0e-5     force units

cutoff            10.0       Angstrom # remember 3 (2-5) times the largest sigma from LJ interactions
ewald precision   1.0e-5     # 1.0e-6 for non-metallic solids & Ionic Liquids!

finish
```

Part 4

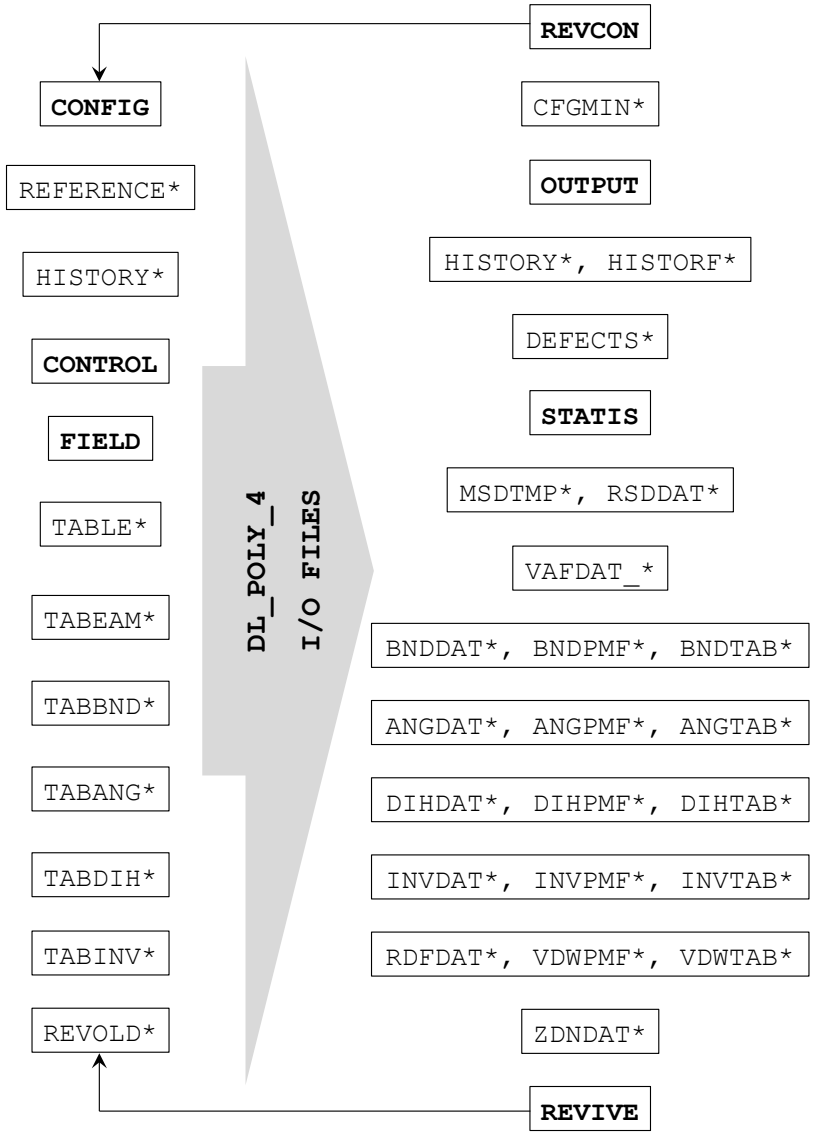
DL_POLY I/O Files

I/O Files

- Crystallographic (Dynamic) data
- Reference data for DEFECTS
- Traj. data for replay
- Simulation controls
- Molecular/Topological Data

- Tabulated interactions

- Restart data



- Final & CGM configurations
- Best CGM configuration
- Simulation summary data
- Trajectory data
- Defects data
- Statistics data

- RSD, MSD & T_{inst} data
- VAF data

- Intra PDF data

- Inter PDF/RDF data

- Z density data
- Restart data

DL_POLY Units

Internally, DL_POLY uses atomic scale units:

- **Mass – mass of H atom (D) [Daltons]**
- **Charge – charge on proton (e)**
- **Length – Angstroms (Å)**
- **Time – picoseconds (ps)**
- **Force – D Å ps^{-2}**
- **Energy – D $Å^2$ ps^{-2} [10 J mol^{-1}]**

- **Temperature is expressed in Kelvin for I/O**
- **Pressure is expressed in k-atm for I/O**
- **Angles are expressed in degrees (not radians)**

Acceptable DL_POLY Units

UNITS directive in FIELD file allows to opt for the following energy units

- **Internal DL_POLY units – 10 J mol^{-1}**
- **Electron-volts – eV**
- **kilo calories per mol – k-cal mol^{-1}**
- **kilo Joules per mol – k-J mol^{-1}**
- **Kelvin per Boltzmann – K $Boltzmann^{-1}$**

All interaction MUST have the same energy units!
Not only in FIELD but in TABLE, TABEAM, TAB*INT*!

CONTROL File

- SIMULATION CONTROL
- Free Format
- Mandatory
- Driven by *keywords:*

keyword [options] {data}

e.g.:

ensemble NPT Hoover 1.0 8.0

```
DL_POLY TEST CASE 1: K Na disilicate glass

temperature      1000.0
pressure         0.0000
ensemble nve

steps              500
equilibration      200
multiple step        5
scale               10
print               10
stack              100
stats               10
rdf                 10

timestep         0.0010
primary cutoff   9.0000
cutoff           12.030
delr width       1.0000
rvdw cutoff      7.6000
ewald precision  1.0E-5
print rdf

job time              1200.0
close time            100.00

finish
```

CONFIG [REVCON,CFGMIN] File

- Initial atomic coordinates
- Format
  - Integers (I10)
  - Reals (F20)
  - Names (A8)
- Mandatory
- Units:
  - Position – Angstroms (Å)
  - Velocity – Å ps^{-1}
  - Force – D Å ps^{-2}
- Construction: Some kind of GUI or DL_FIELD essential for complex systems

```
DL_POLY TEST CASE 1: K Na disilicate glass structure
         2         3
  24.1790000000          .0000000000          .0000000000
   .0000000000        24.1790000000          .0000000000
   .0000000000          .0000000000        24.1790000000
Na+             1
  -10.18970354         -11.14553975          2.950816701
  -10.92491513         -11.32922344         -1.683043107
   8078.967958          7831.492182          14290.88665
K_+             2
   4.203354201         -6.599949388          11.67055019
  -.4336920163         -8.629860244          .5802665381
   14372.08258          9808.543805          4104.320538
Na+             3
   11.90756913         -3.986750583          .8846158473
   7.418084829         -6.374985769          3.895762997
  -1417.528114         -3882.775455          906.1837533
K_+             4
   3.507280530         -7.793662912         -6.292661606
   10.31603370         -10.41715131         -4.280009692
   2416.375138          1825.582828          4092.039688
Na+             5
   3.461171708         -7.578232190          5.932411530
  -1.095217789         -1.174904220         -3.990554703
  -10432.37938          6228.183582         -10280.33991
K_+             6
   5.950806200         -6.205017024          6.104974282
  -.9325536022E-01      -6.757387763          2.025695932
  -2228.699102         -4655.604575          10544.62228
Na+             7
  -2.842267238          7.394332997          1.865677792
  -17.68579103          4.615099801          2.644830030
   253.4967609          3720.053118          408.3262594
```

FIELD File

- Force Field specification
- Mandatory
- Format:
  - Integers (I5)
  - Reals (F12)
  - Names (A8)
  - Keywords (A4)
- Maps on to CONFIG file structure
- Construction
  - Small systems – by hand
  - Large systems – nfold or GUI or DL_FIELD!

```
DL_POLY TEST CASE 4: Water dynamical shell model
UNITS kJ
NEUTRAL GROUPS
MOLECULAR TYPES 1
SPC WATER
NUMMOLS 256
ATOMS 4
OW        15.0000      -0.32     1    0    1
HW         1.0000       0.41     2    0    1
O_shell    1.0000      -0.50     1    0    1
SHELL 1
    1    4   100.0
RIGID UNITS 1
    3    1    2    3
FINISH
VDW 5
O_shell O_shell  lj        .36854      3.1650
O_shell OW       lj        .21059      3.1650
OW      OW       lj        .05265      3.1650
OW      HW       lj        .00000      3.1650
O_shell HW       lj        .00000      3.1650
CLOSE
```

TABLE File

- Defines non-analytic pair (vdw) potentials
- Format
  - Integers (I10)
  - Reals (F15)
  - Names (A8)
- Conditional, activated by FIELD file option
- Potential & Force
- NB force (here) is:

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

```
DL_POLY TEST CASE 1: Silica Potentials
  1.5212170E-03  7.6000000E+00       5000
Si4+    O_2-
  9.5140002E+06  9.4702042E+06  9.4266099E+06  9.3832162E+06
  9.3400223E+06  9.2970273E+06  9.2542301E+06  9.2116300E+06
  9.1692260E+06  9.1270171E+06  9.0850026E+06  9.0431815E+06
  9.0015529E+06  8.9601159E+06  8.9188696E+06  8.8778133E+06
  8.8369459E+06  8.7962667E+06  8.7557747E+06  8.7154691E+06
  8.6753490E+06  8.6354137E+06  8.5956621E+06  8.5560936E+06
  8.5167072E+06  8.4775021E+06  8.4384775E+06  8.3996325E+06
  8.3609664E+06  8.3224782E+06  8.2841672E+06  8.2460326E+06
  8.2080735E+06  8.1702892E+06  8.1326787E+06  8.0952415E+06
  8.0579765E+06  8.0208831E+06  7.9839605E+06  7.9472078E+06
  7.9106243E+06  7.8742092E+06  7.8379617E+06  7.8018811E+06
  7.7659666E+06  7.7302174E+06  7.6946328E+06  7.6592120E+06
  7.6239542E+06  7.5888587E+06  7.5539248E+06  7.5191517E+06
  7.4845387E+06  7.4500850E+06  7.4157899E+06  7.3816527E+06
  7.3476726E+06  7.3138490E+06  7.2801810E+06  7.2466681E+06
  7.2133094E+06  7.1801042E+06  7.1470520E+06  7.1141518E+06
  7.0814031E+06  7.0488052E+06  7.0163573E+06  6.9840588E+06
  6.9519090E+06  6.9199072E+06  6.8880527E+06  6.8563448E+06
  6.8247829E+06  6.7933663E+06  6.7620942E+06  6.7309662E+06
  6.6999814E+06  6.6691393E+06  6.6384392E+06  6.6078803E+06
  6.5774622E+06  6.5471841E+06  6.5170453E+06  6.4870453E+06
  6.4571834E+06  6.4274589E+06  6.3978713E+06  6.3684199E+06
  6.3391041E+06  6.3099232E+06  6.2808766E+06  6.2519637E+06
  6.2231840E+06  6.1945367E+06  6.1660213E+06  6.1376372E+06
  6.1093837E+06  6.0812603E+06  6.0532663E+06  6.0254012E+06
  5.9976644E+06  5.9700553E+06  5.9425732E+06  5.9152177E+06
  5.8879881E+06  5.8608838E+06  5.8339043E+06  5.8070490E+06
  5.7803173E+06  5.7537087E+06  5.7272226E+06  5.7008584E+06
```

TABEAM File

- Defines embedded atom potentials
- Format
  - Integers (I10)
  - Reals (F15)
  - Names (A8)
- Conditional, activated by FIELD file option
- Potentials only
- pair, embed & dens keywords for atom types followed by data records (4 real numbers per record)
- Individual interpolation arrays

REVOLD [REVIVE] File

- Provides program restart capability
- File is unformatted (not human readable)
- Contains thermodynamic accumulators, RDF data, MSD data and other checkpoint data
- REVIVE (output file) ---> REVOLD (input file)

OUTPUT File

- Provides Job Summary (mandatory!)
- Formatted to be human readable
- Contents:
  - Summary of input data
  - Instantaneous thermodynamic data at selected intervals
  - Rolling averages of thermodynamic data
  - Statistical averages
  - Final configuration
  - Radial distribution data
  - Estimated mean-square displacements and 3D diffusion coefficient
- Plus:
  - Timing data, CGM and relaxed shell model iteration data
  - Warning & Error reports

STATIS File

- System properties at intervals selected by user
- Optional
- Formatted (I10,E14)
- Intended use: statistical analysis (e.g. error) and plotting vs. time.
- Recommend use with GUI!
- Header:
  - Title
  - Units
- Data:
  - Time step, time, #entries
  - System data

```
DL_POLY TEST CASE 1: K Na disilicate glass structure

 ENERGY UNITS = DL_POLY Internal UNITS
         10  1.000000E-02         40
-3.205280E+08  1.008482E+03 -3.218852E+08  8.415979E+07 -4.070454E+08
 0.000000E+00  1.000478E+06  0.000000E+00  0.000000E+00 -3.032144E+08
 0.000000E+00 -4.922665E+07 -4.517780E+08  4.070324E+08  0.000000E+00
-4.480974E+06  0.000000E+00  0.000000E+00  1.413562E+04  0.000000E+00
 0.000000E+00  0.000000E+00  9.000000E+01  9.000000E+01  9.000000E+01
 0.000000E+00  2.006775E+02  0.000000E+00  0.000000E+00  0.000000E+00
 0.000000E+00  2.167462E+02 -2.966174E+00  9.929801E-01 -2.966174E+00
 1.954298E+02  2.026411E+00  9.929801E-01  2.026411E+00  1.898565E+02
         20  2.000000E-02         40
-3.205146E+08  9.854523E+02 -3.218408E+08  8.420167E+07 -4.070089E+08
 0.000000E+00  9.664992E+05  0.000000E+00  0.000000E+00 -3.030159E+08
 0.000000E+00 -4.984402E+07 -4.521951E+08  4.069810E+08  0.000000E+00
-4.629916E+06  0.000000E+00  0.000000E+00  1.413562E+04  0.000000E+00
 0.000000E+00  0.000000E+00  9.000000E+01  9.000000E+01  9.000000E+01
 0.000000E+00  2.028233E+02  0.000000E+00  0.000000E+00  0.000000E+00
 0.000000E+00  2.133485E+02  1.064831E-01 -6.994367E+00  1.064831E-01
 1.992877E+02 -9.291212E-01 -6.994367E+00 -9.291212E-01  1.958336E+02
         30  3.000000E-02         40
-3.205199E+08  1.016426E+03 -3.218877E+08  8.443556E+07 -4.073304E+08
 0.000000E+00  1.007151E+06  0.000000E+00  0.000000E+00 -3.029124E+08
 0.000000E+00 -5.008689E+07 -4.529860E+08  4.073139E+08  0.000000E+00
-4.414858E+06  0.000000E+00  0.000000E+00  1.413562E+04  0.000000E+00
 0.000000E+00  0.000000E+00  9.000000E+01  9.000000E+01  9.000000E+01
 0.000000E+00  2.040837E+02  0.000000E+00  0.000000E+00  0.000000E+00
 0.000000E+00  2.178241E+02  6.607459E+00 -1.175251E+01  6.607459E+00
 1.898177E+02 -4.690431E-01 -1.175251E+01 -4.690431E-01  2.046095E+02
         40  4.000000E-02         40
-3.205438E+08  1.008437E+03 -3.219008E+08  8.419891E+07 -4.070237E+08
 0.000000E+00  9.239793E+05  0.000000E+00  0.000000E+00 -3.032935E+08
 0.000000E+00 -4.903683E+07 -4.520697E+08  4.070132E+08  0.000000E+00
-3.980336E+06  0.000000E+00  0.000000E+00  1.413562E+04  0.000000E+00
 0.000000E+00  0.000000E+00  9.000000E+01  9.000000E+01  9.000000E+01
```

HISTORY [HISTORF] File

- Configuration data at user selected intervals
  - Formatted
  - Optional
- Header:
  - Title
  - Data level, cell key, number
- Configuration data:
  - Time step and data keys
  - Cell Matrix
  - Atom name, mass, charge
  - X,Y,Z coordinates (level 0)
  - X,Y,Z velocities (level 1)
  - X,Y,Z forces (level 2)

```
DL_POLY TEST CASE 10: DNA Strand in SPC Wate
         2          7       3378
timestep          1       3378          2          7    0.001000
   52.00        0.000        0.000
   0.000        30.02        0.000
   0.000        0.000        64.34
P_3               1   30.973800    1.165900
 -8.6522E+00  4.6430E+00 -3.1314E+01
  3.8840E+00  7.9765E-01 -2.1608E+00
 -9.8599E+02  1.1857E+03  1.9631E+03
O_2               2   15.999400   -0.776100
 -9.8537E+00  3.8644E+00 -3.1469E+01
  3.1055E+00  2.7294E+00 -5.9096E+00
 -1.3153E+03  2.2118E+03  1.2624E+02
O_2               3   15.999400   -0.776100
 -8.1115E+00  3.6735E+00  3.2111E+01
  4.3244E+00  1.7421E+00 -2.9006E+00
  1.5923E+03  1.6067E+03  1.2143E+03
O_3               4   15.999400   -0.495400
 -8.4095E+00  3.7741E+00 -3.0066E+01
 -3.7534E+00  1.5520E+00 -1.2485E-01
  1.6786E+03  7.2103E+02  2.4525E+02
C_3               5   12.011000   -0.006900
 -8.2889E+00  4.2697E+00 -2.8741E+01
 -3.2596E+00  1.1117E+00 -4.9447E-03
 -3.9063E+02  2.3338E+02  4.4700E+02
H_                6    1.008000    0.075400
 -7.9345E+00  3.3762E+00 -2.8227E+01
  9.5048E+00  1.0488E+01  7.7937E+00
 -2.4981E+03 -4.9711E+02  4.6945E+02
H_                7    1.008000    0.075400
 -9.2952E+00  4.5264E+00 -2.8410E+01
 -6.0025E+00  6.4848E+00 -1.2228E+01
  3.5275E+02 -1.2279E+03  1.8052E+03
```

RDFDAT [ZDNDAT] File

- Formatted (A8,I10,E14)
- Plotable
- Optional
- RDFs from pair forces
- Header:
  - Title
  - No. plots & length of plot
- RDF data:
  - Atom symbols (2)
  - Radius (A) & RDF
  - Repeated…
- ZDNDAT file has same format

```
 Silver Iodide Alpha Phase
           3         160
Ag+      Ag+
  2.375000E+00  1.932754E-03
  2.425000E+00  7.415510E-03
  2.475000E+00  7.118930E-03
  2.525000E+00  1.196964E-02
  2.575000E+00  1.315351E-02
  2.625000E+00  1.582152E-02
  2.675000E+00  3.199477E-02
  2.725000E+00  3.964044E-02
  2.775000E+00  5.662942E-02
  2.825000E+00  7.786575E-02
  2.875000E+00  1.002413E-01
  2.925000E+00  1.197803E-01
  2.975000E+00  2.020131E-01
  3.025000E+00  2.501949E-01
  3.075000E+00  2.594195E-01
  3.125000E+00  3.460766E-01
  3.175000E+00  4.152931E-01
  3.225000E+00  5.335431E-01
  3.275000E+00  5.824296E-01
  3.325000E+00  7.090180E-01
  3.375000E+00  7.570784E-01
  3.425000E+00  8.996351E-01
  3.475000E+00  9.226854E-01
  3.525000E+00  1.020409E+00
  3.575000E+00  1.103812E+00
  3.625000E+00  1.164834E+00
  3.675000E+00  1.147884E+00
  3.725000E+00  1.247703E+00
  3.775000E+00  1.328861E+00
  3.825000E+00  1.342782E+00
  3.875000E+00  1.380233E+00
  3.925000E+00  1.393415E+00
  3.975000E+00  1.416540E+00
  4.025000E+00  1.436074E+00
```

Other Extra Files

- REFERENCE file
  - Reference structure to compare against
- DEFECTS file
  - Trajectory file of vacancies and interstitials migration
- MSDTMP file
  - Trajectory like file containing particles' Sqrt(MSD_{mean}) and T_{mean}
- RSDDAT file
  - Trajectory like file containing particles' Sqrt(RSD from origin)
- TAB*INT* file
  - Table file for *INT*ra-molecular interactions
- *INT*DAT file
  - Probability Distribution Functions for *INT*ra-molecular interactions
- HISTORF file
  - Force replayed HISTORY
- …

Part 5

DL_POLY_4 Performance

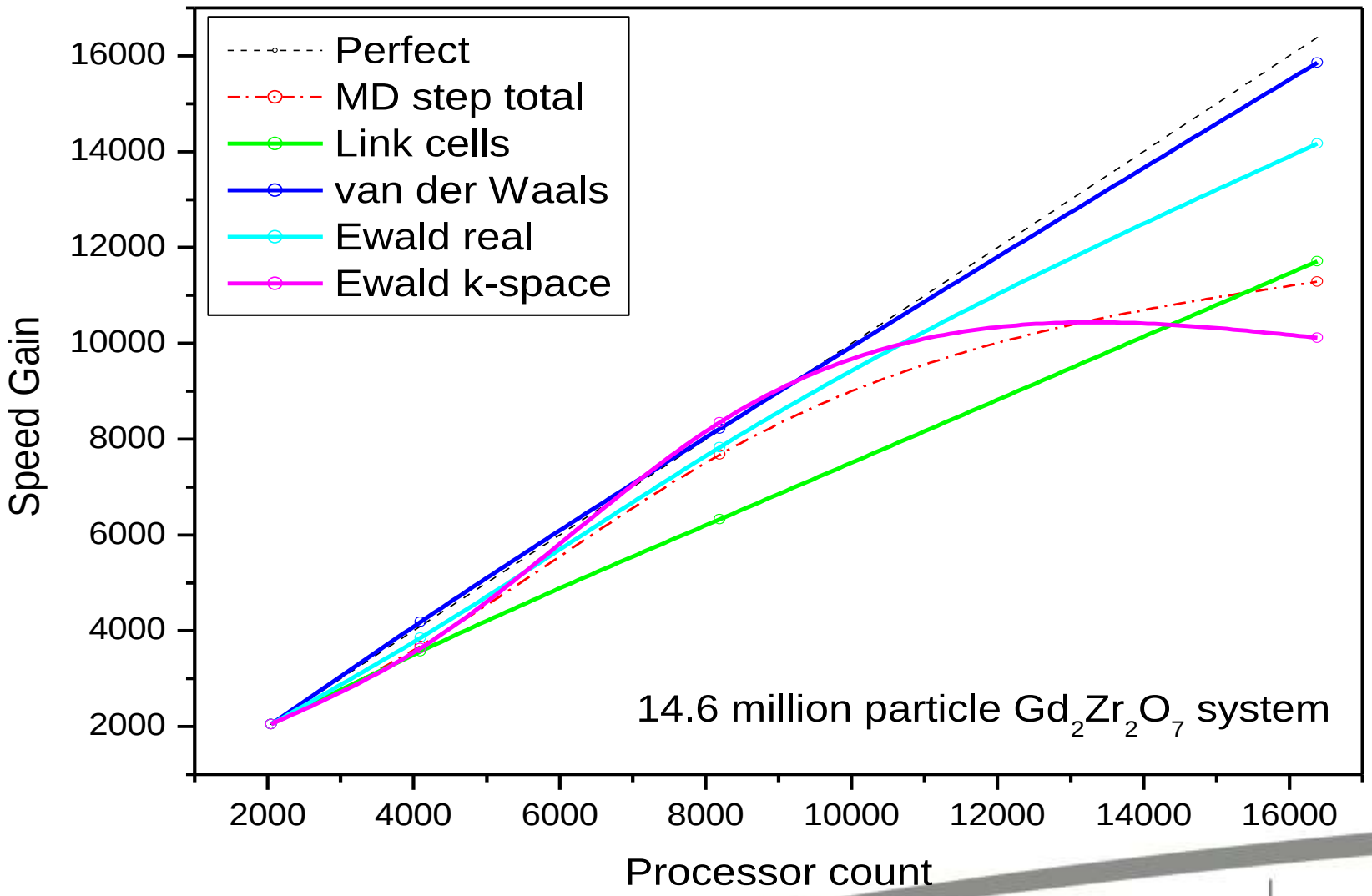
Proof of Concept

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

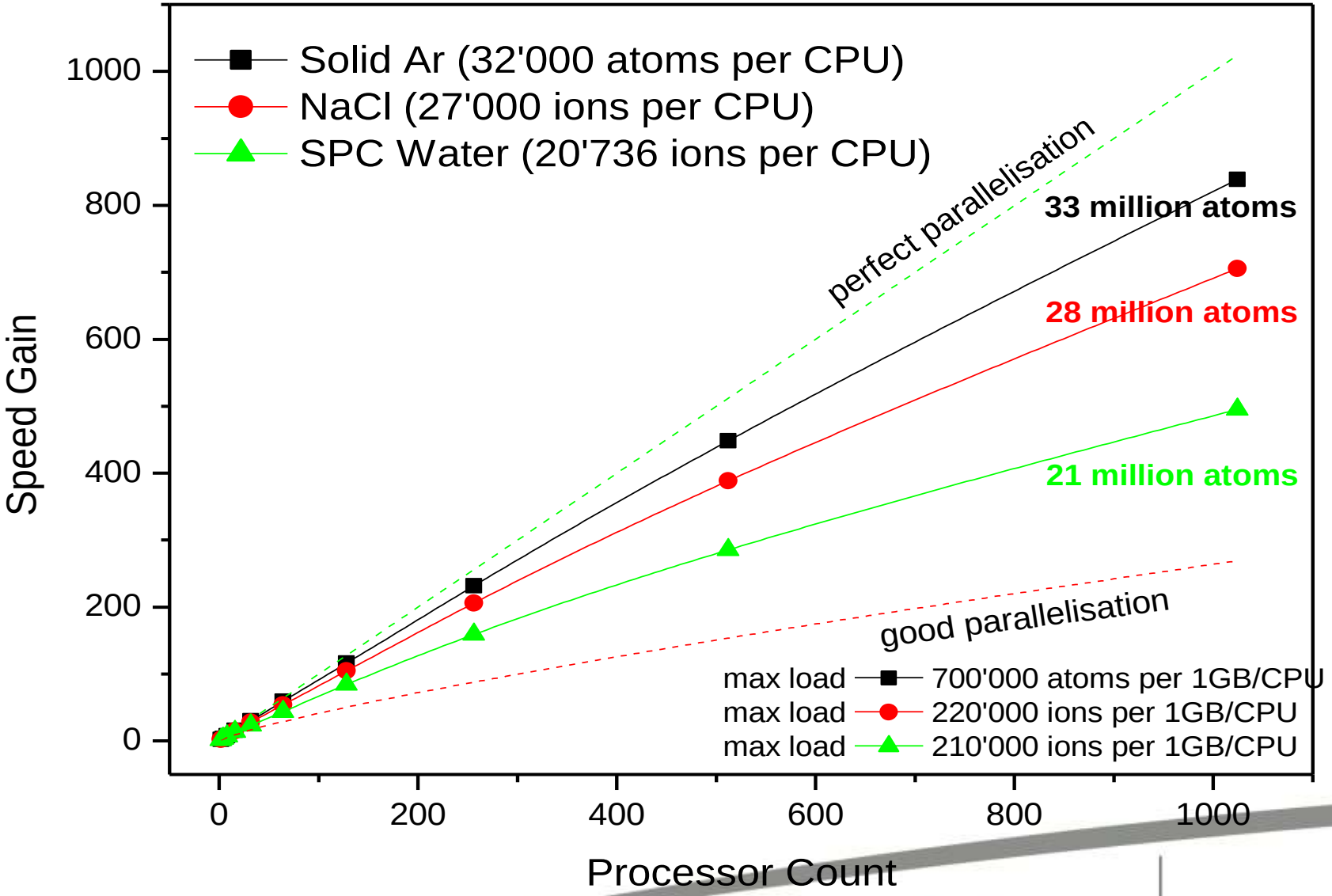
	IBM p575 2004/5	Cray XE6 2013/4
• Start-up time	≈ 60 min	≈ 15 min
• Timestep time	≈ 68 sec	≈ 23 sec
• FFT evaluation	≈ 55 sec	≈ 18 sec

In theory ,the system can be seen by the eye. Although you would need a very good microscope – the MD cell size for this system is 2μm along the side and as the wavelength of the visible light is 0.5μm so it should be theoretically possible.

Benchmarking BG/L Jülich 2007

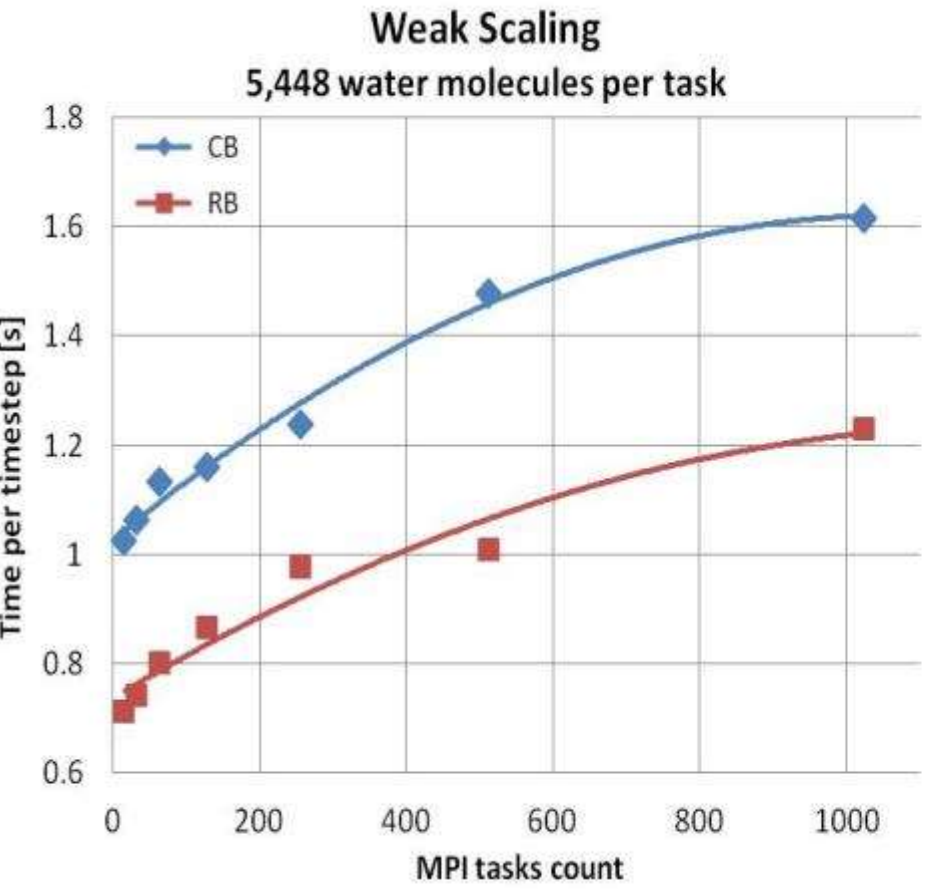


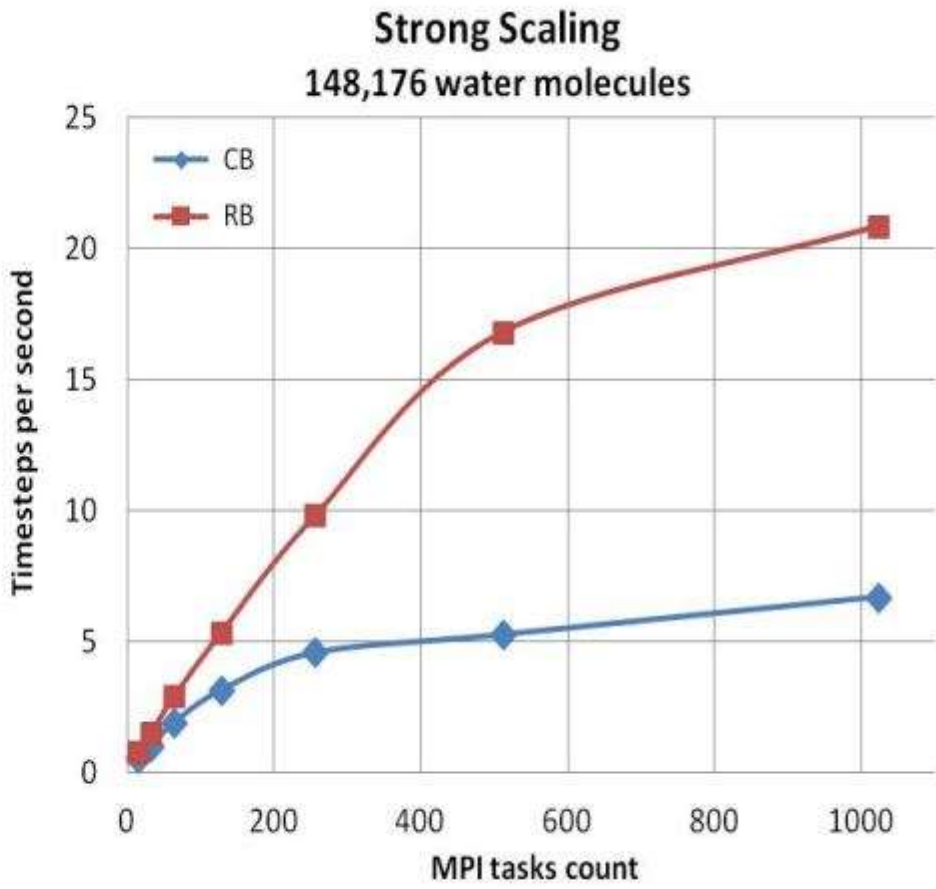
Weak Scaling



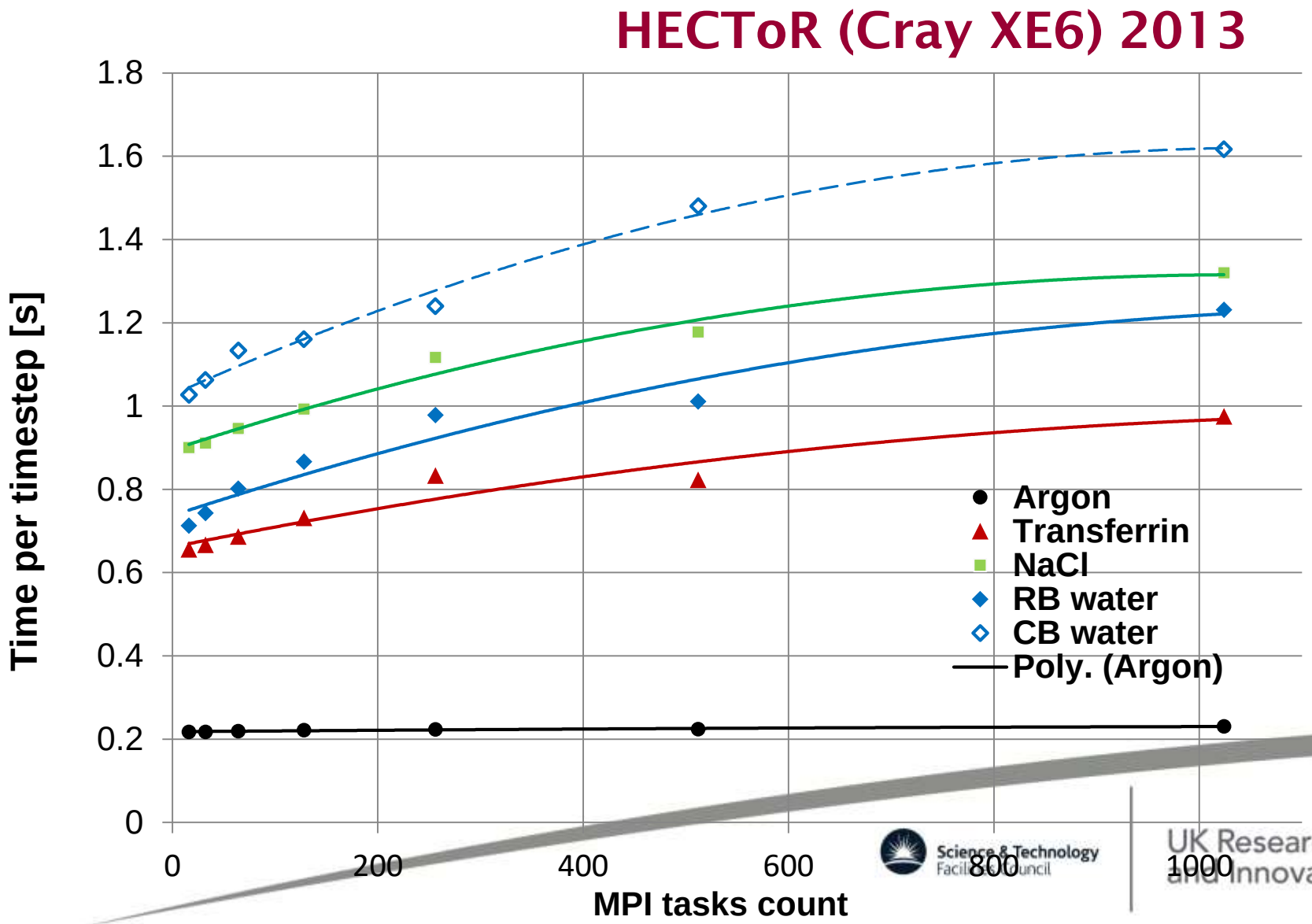
RB v/s CB Performance & Scalability

HECToR (Cray XE6) 2013





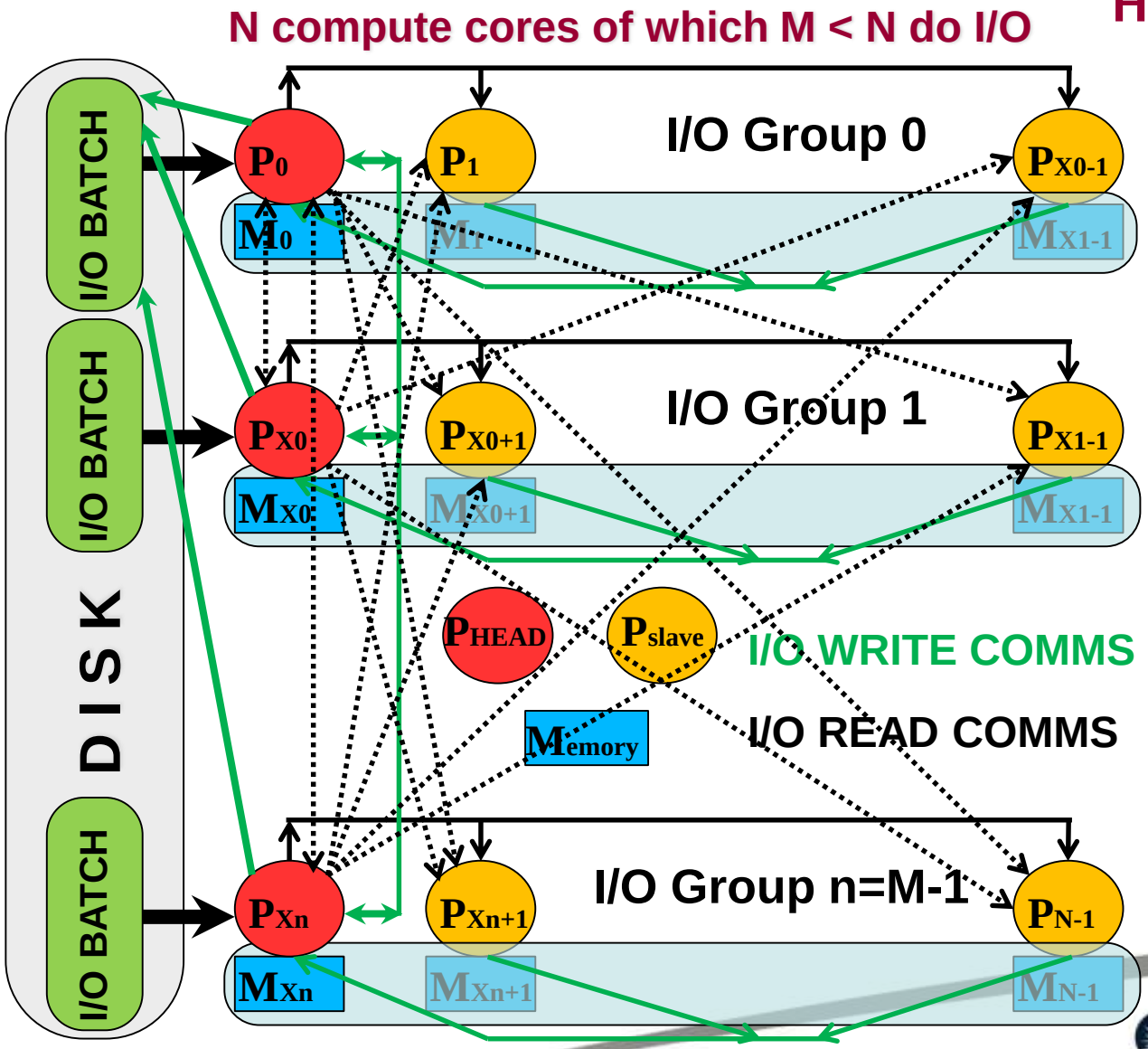
Weak Scaling and Cost Complexity



I/O Solutions

1. **Serial read and write (sorted/unsorted)** – where only a single MPI task, the master, handles it all and all the rest communicate in turn to or get broadcasted to while the master completes writing a configuration of the time evolution.
2. **Parallel write via direct access or MPI-I/O (sorted/unsorted)** – where **ALL / SOME** MPI tasks print in the same file in some orderly manner so (no overlapping occurs using Fortran direct access printing. However, it should be noted that the behaviour of this method is not defined by the Fortran standard, and in particular we have experienced problems when disk cache is not coherent with the memory).
3. **Parallel read via MPI-I/O or Fortran**
4. **Serial NetCDF read and write** using NetCDF libraries for machine-independent data formats of array-based, scientific data (widely used by various scientific communities).

The Advanced Parallel I/O Strategy



HECToR (Cray XE6) 2013

- 72 I/O NODES
- READ ~ 50-300 Mbyte/s with best performance on 16 to 128 I/O Groups
- WRITE ~ 50-150 Mbyte/s with best performance on 64 to 512 I/O Groups
- Performance depends on user defined number of I/O groups, and I/O batch (memory CPU to disk) and buffer (memory of comms transactions between CPUs)
- Reasonable defaults as a function of all MPI tasks are provided

Part 5

Obtaining & Building DL_POLY

DL_POLY_4 Licensing & Support

- Online Licence Facility at http://www.ccp5.ac.uk/DL_POLY/
- The licence is
  - To protect copyright of STFC Daresbury Laboratory
  - To reserve commercial rights
  - To provide documentary evidence justifying continued support by UK Research Councils (UKRI)
- It covers only the DL_POLY_4 package
- Registered users are entered on the DL_POLY mailshot list
  - Support is available (under CCP5 & MCC SLA via EPSRC) *only* to UK academic researchers
  - For the rest of the world there is the JISC Community List
- Last but not least there is a detailed, interactive, self-referencing PDF (LaTeX) user manual

Supply of DL_POLY_4

- Register at http://www.ccp5.ac.uk/DL_POLY/
- Registration provides a decryption key, sent by e-mail
- Source is provided as an encrypted ZIP file on the FTP
- Successful unpacking produces a unix directory structure
- TEST, BENCH and TUTORIAL data are also available on the FTP

DL_POLY_Classic Support

- **Full documentation of software supplied with source**
- **Support is available through the CCP5 user community**

WWW:

http://www.ccp5.ac.uk/DL_POLY_CLASSIC/

FTP:

ftp://ftp.dl.ac.uk/ccp5/DL_POLY/

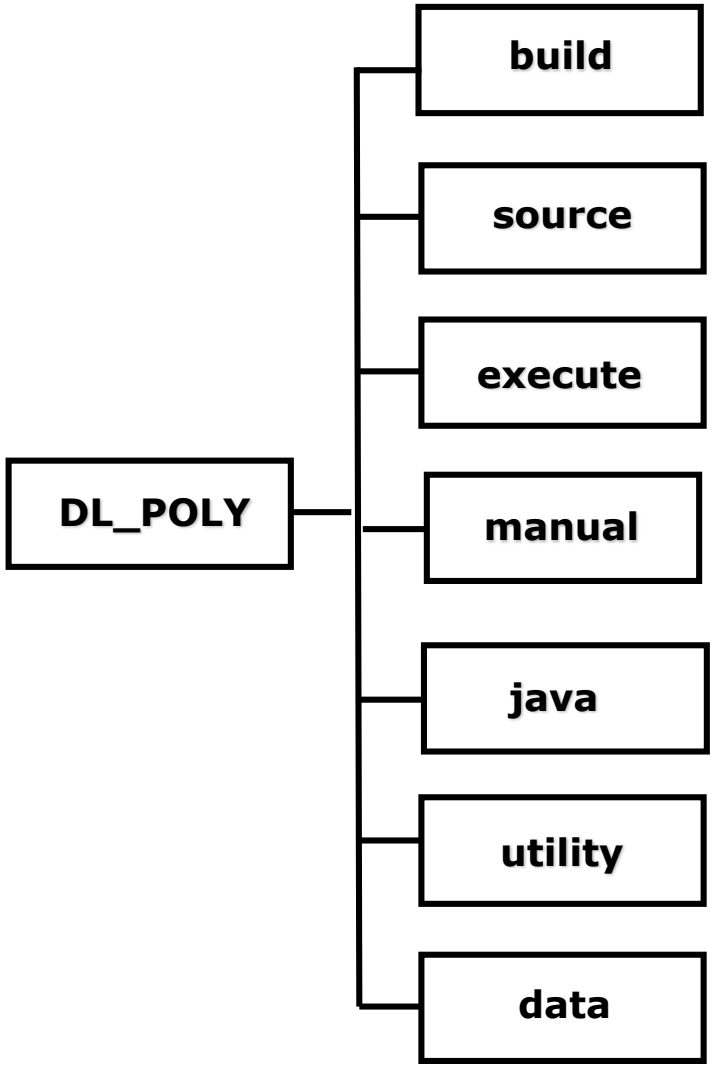
COMM:

http:/www.jiscmail.ac.uk/DLPOLY/

Supply of DL_POLY_Classic

- Downloads are available from CCP5 website
- No registration required – BSD licence
- Sources is a in tarred and gzipped form
- Successful unpacking produces a unix directory structure
- Test data are also available

DL_POLY Directory Structure



Home of makefiles

DL_POLY source code

Home of executable & Working Directory

Home of Manuals

Java GUI source code

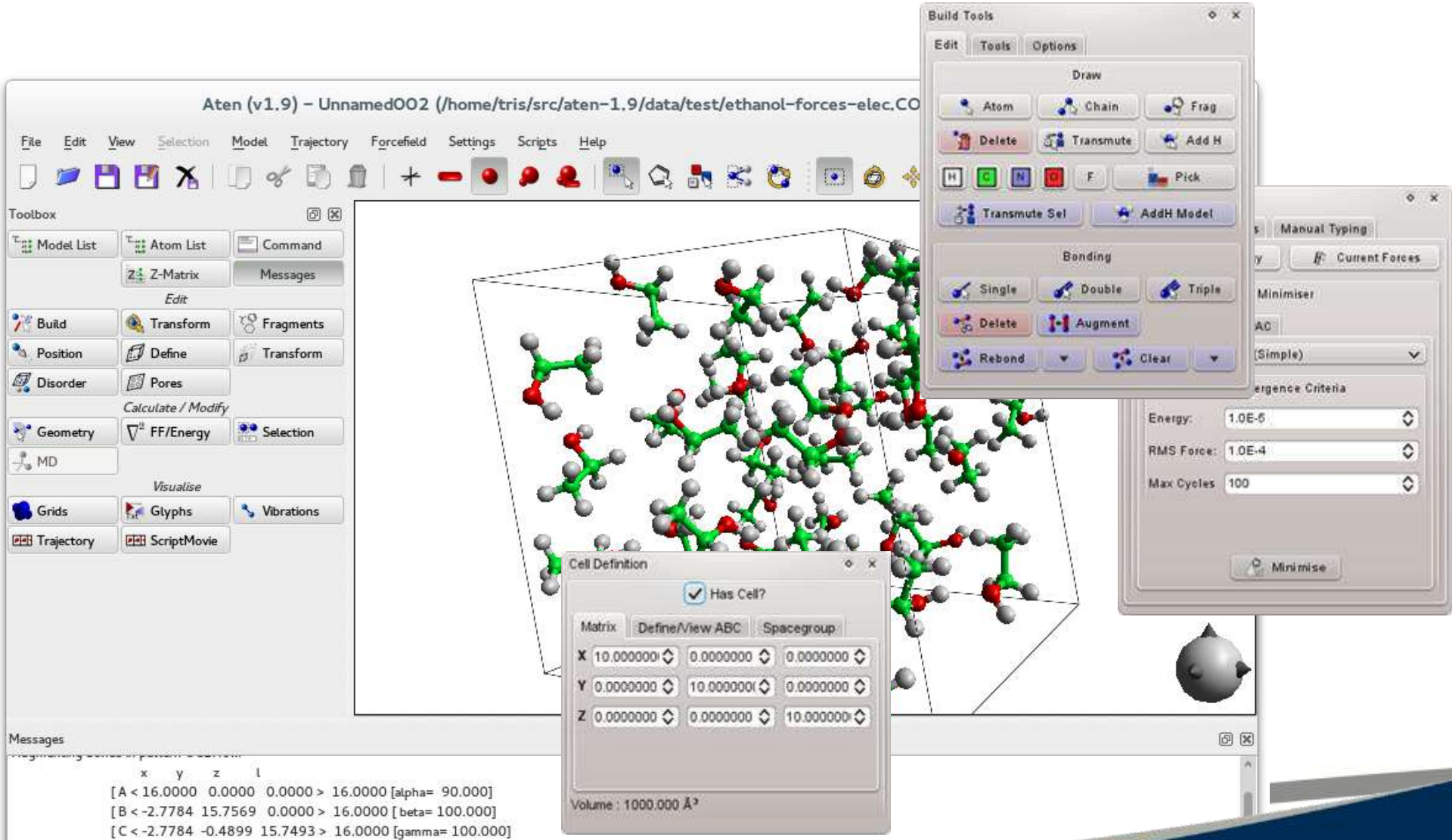
Utility codes

Test data

Part 6

Usability

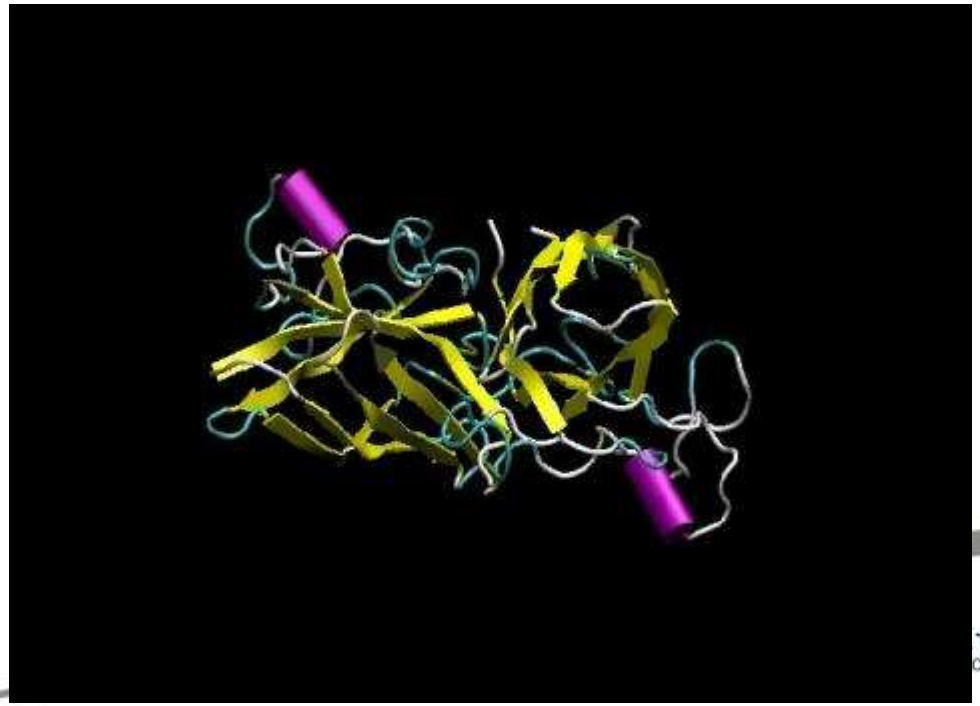
DL_POLY & Project ATEN



Science & Technology Facilities Council
ISIS

DL_POLY & VMD

- VMD is a free software package for visualising MD data.
- Website: http://www.ks.uiuc.edu/Research/vmd/
- Useful for viewing snapshots and movies.
  - A plug in is available for DL_POLY HISTORY files
  - Otherwise convert HISTORY to XYZ or PDB format

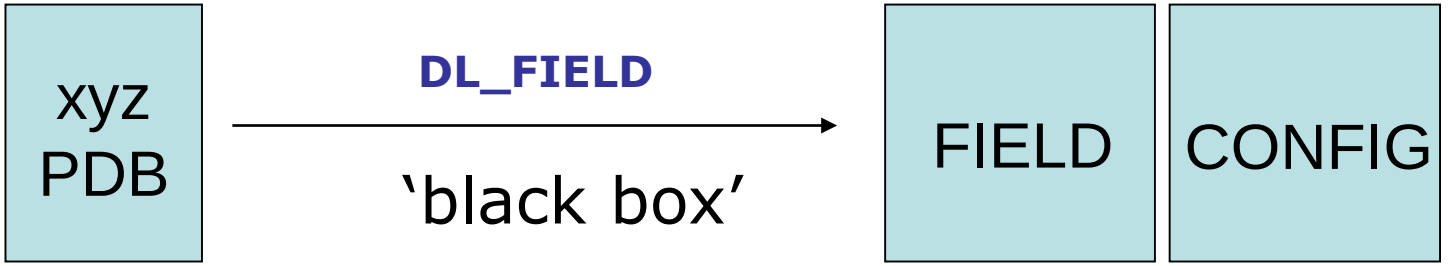


DL_FIELD/ANALYSER

Developed by Chin Yong

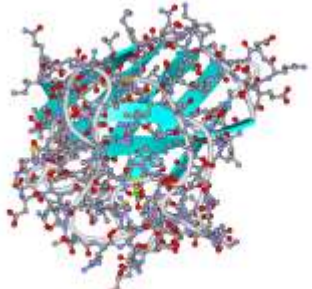
http://www.ccp5.ac.uk/DL_FIELD/

- **Orgainic Fields** – AMBER+Glycam, CHARM, OPLS-AA, PCFF, Drieding, CHARM19 (united atom)
- **Inorganic Fields** including a core-shell polarisation option
- Solvation Features, Auto-CONNECT feature for mapping complex random structures such as gels and random polymers
- input units freedom and molecular rigidification



Protonated

SOD



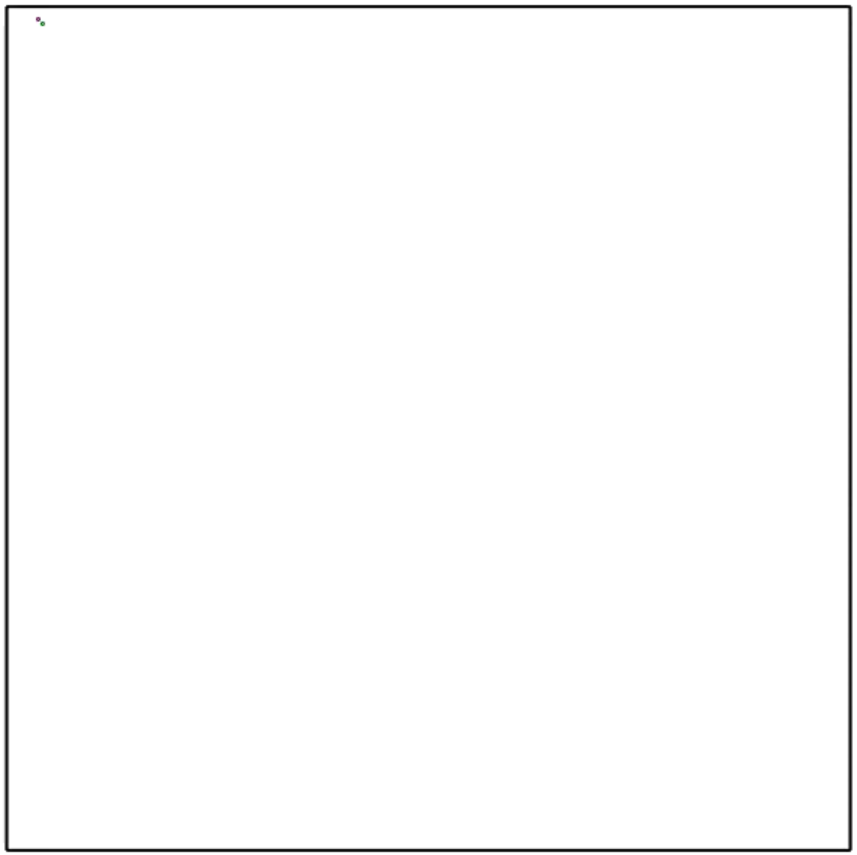
4382 atoms (excluding water)
19400 bond interactions
7993 angles interactions
13000 dihedral interactions
730 VDW interactions

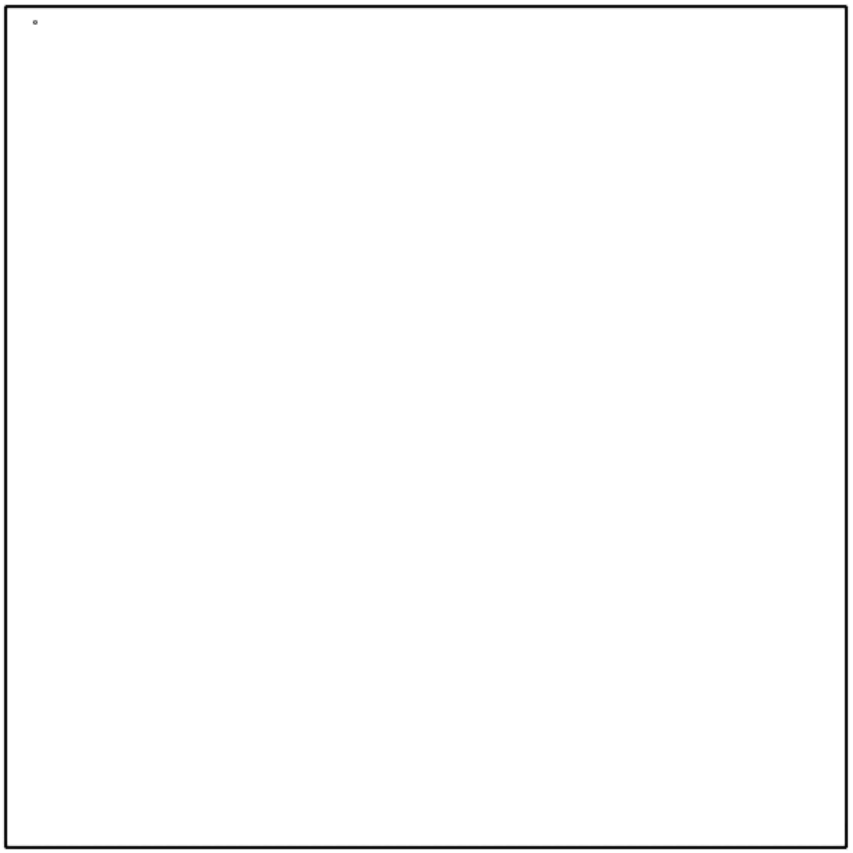
ftp://ftp.dl.ac.uk/ccp5/DL_POLY/DL_POLY_4.0/TUTORIAL/

DL_POLY Hands-On

Thank You

500 keV cascade in 200 million Fe system using TTM





Electronic effects in high-energy radiation damage in iron, E. Zarkadoula, S.L. Daraszewicz, D.M. Duffy, M.A. Seaton, I.T. Todorov, K. Nordlund, M.T. Dove and K. Trachenko, *J. Phys.: Condens. Matter* **26** (2014) 085401 (8pp), doi:10.1088/0953-8984/26/8/085401

Part 7

The DL_POLY Java GUI
W. Smith

GUI Overview

- Java is Free!
- Facilitate use of code
- Selection of options (control of capability)
- Construct (model) input files
- Control of job submission
- Analysis of output
- Portable and easily extended by user

Compiling/Editing the GUI

- Edit source in *java* directory
- Edit using vi, emacs, nano, gedit, *whatever*
- Compile in *java* directory:

```
javac *.java
jar -cfm GUI.jar manifesto *.class
```

- Executable is *GUI.jar*
- *But.....*

*****Don't Panic!*****

The GUI.jar file is provided in the download or may be not

Invoking the GUI

- Invoke the GUI from within the *execute* directory (or equivalent):

  java -jar ../java/GUI.jar

- Colour scheme options:

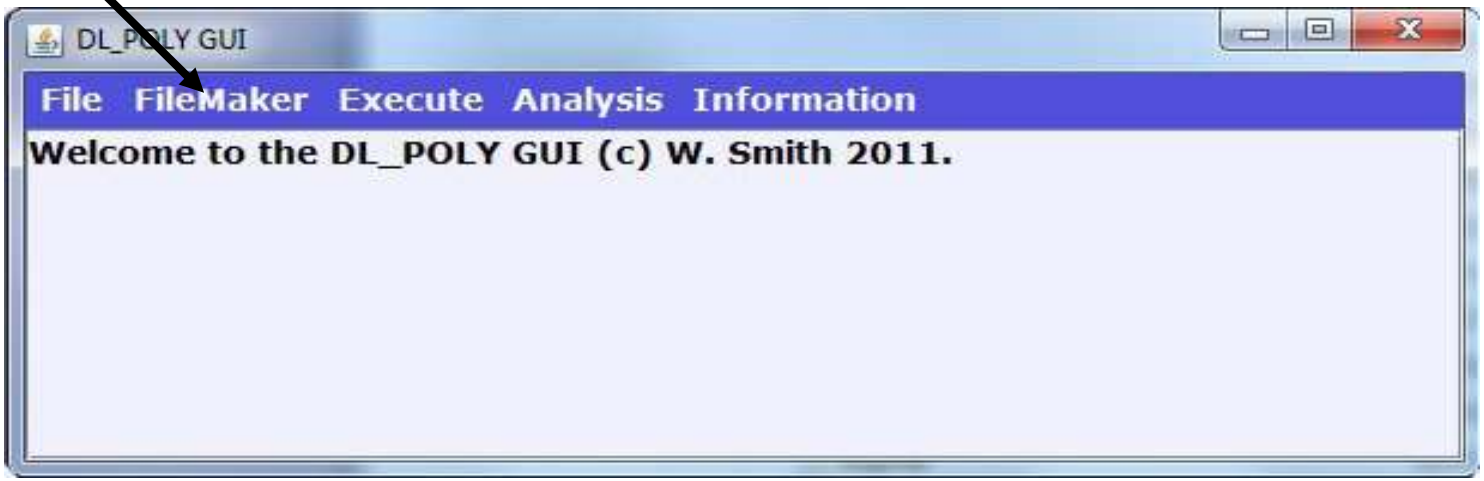
  java -jar ../java/GUI.jar –*colourscheme*

with *colourscheme* one of:

monet, vangoch, picasso, cezanne, mondrian (default picasso).

The Monitor Window

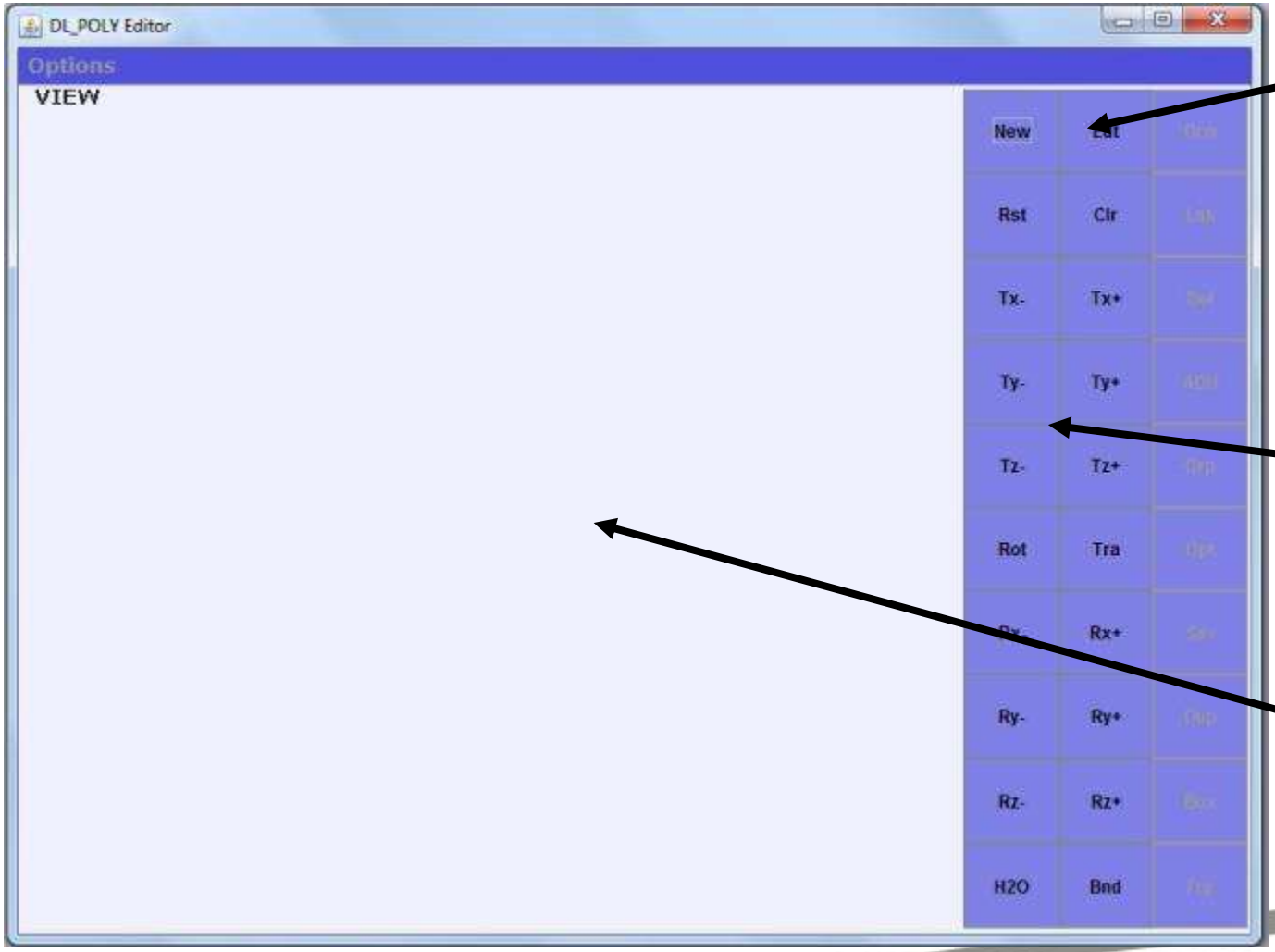
Menus



Using Menus

Show Editor Option

The Molecular Viewer

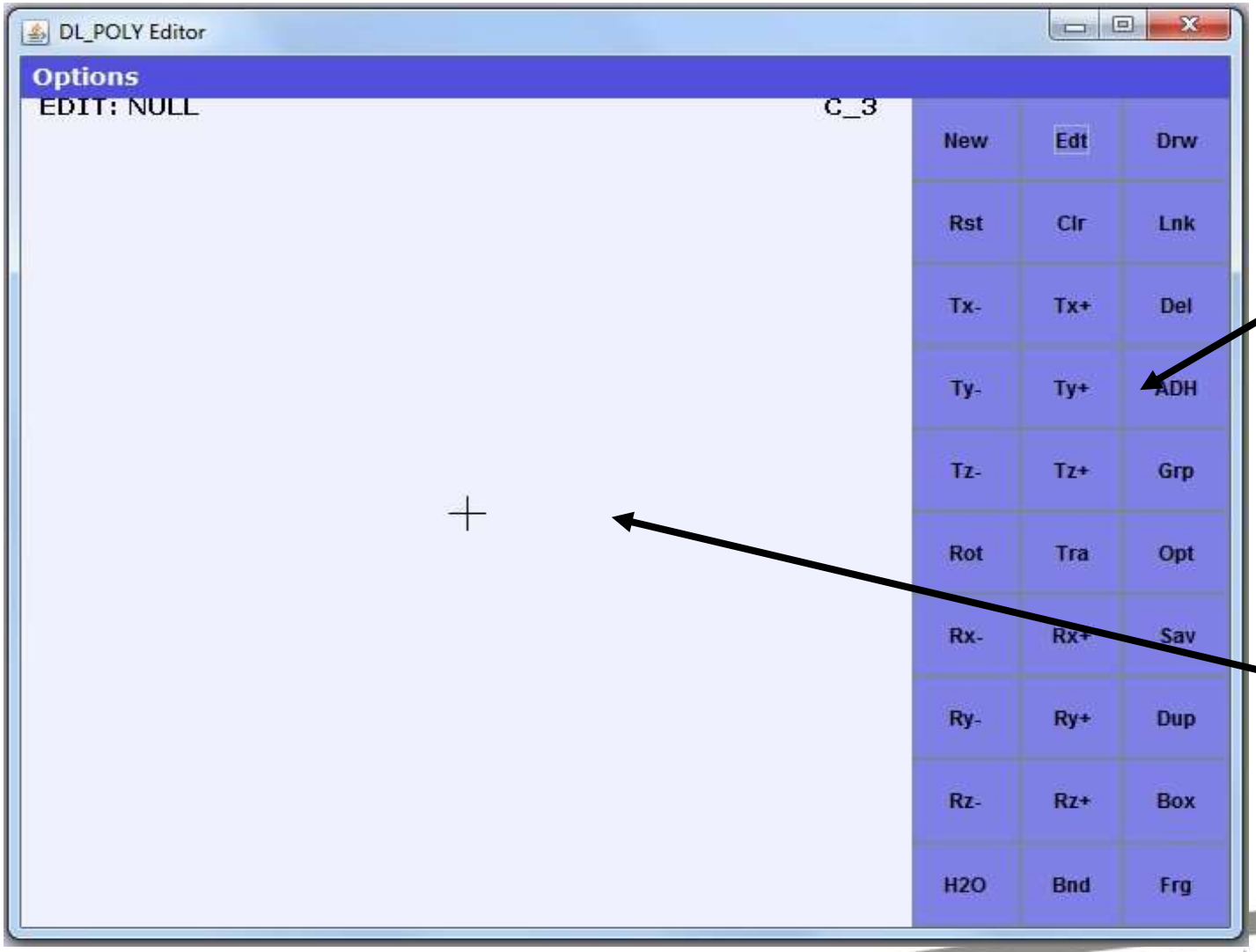


Editor Button

Graphics Buttons

Graphics Window

The Molecular Editor



Editor Buttons

Editor Window

Available Menus

- File - Simple file manipulation, exit etc.
- FileMaker - make input files:
  - CONTROL, FIELD, CONFIG, TABLE
- Execute
  - Select/store input files, run job
- Analysis
  - Static, dynamic,statistics,viewing,plotting
- Information
  - Licence, Force Field files, disclaimers etc.

A Typical GUI Panel