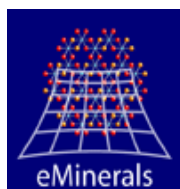# DL_SOFTWARE TUTORIAL
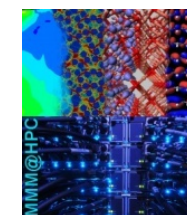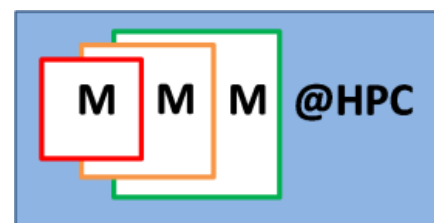
ILIAN TODOROV, BILL SMITH,
IAN BUSH, HENRY BOATENG, CHIN YONG
MICHAEL SEATON, JOHN PURTON
DAVID GUNN, ANDREY BRUKHNO

SCD, STFC DARESBURY LABORATORY, DARESBURY
WARRINGTON WA4 4AD, CHESHIRE, ENGLAND, UK

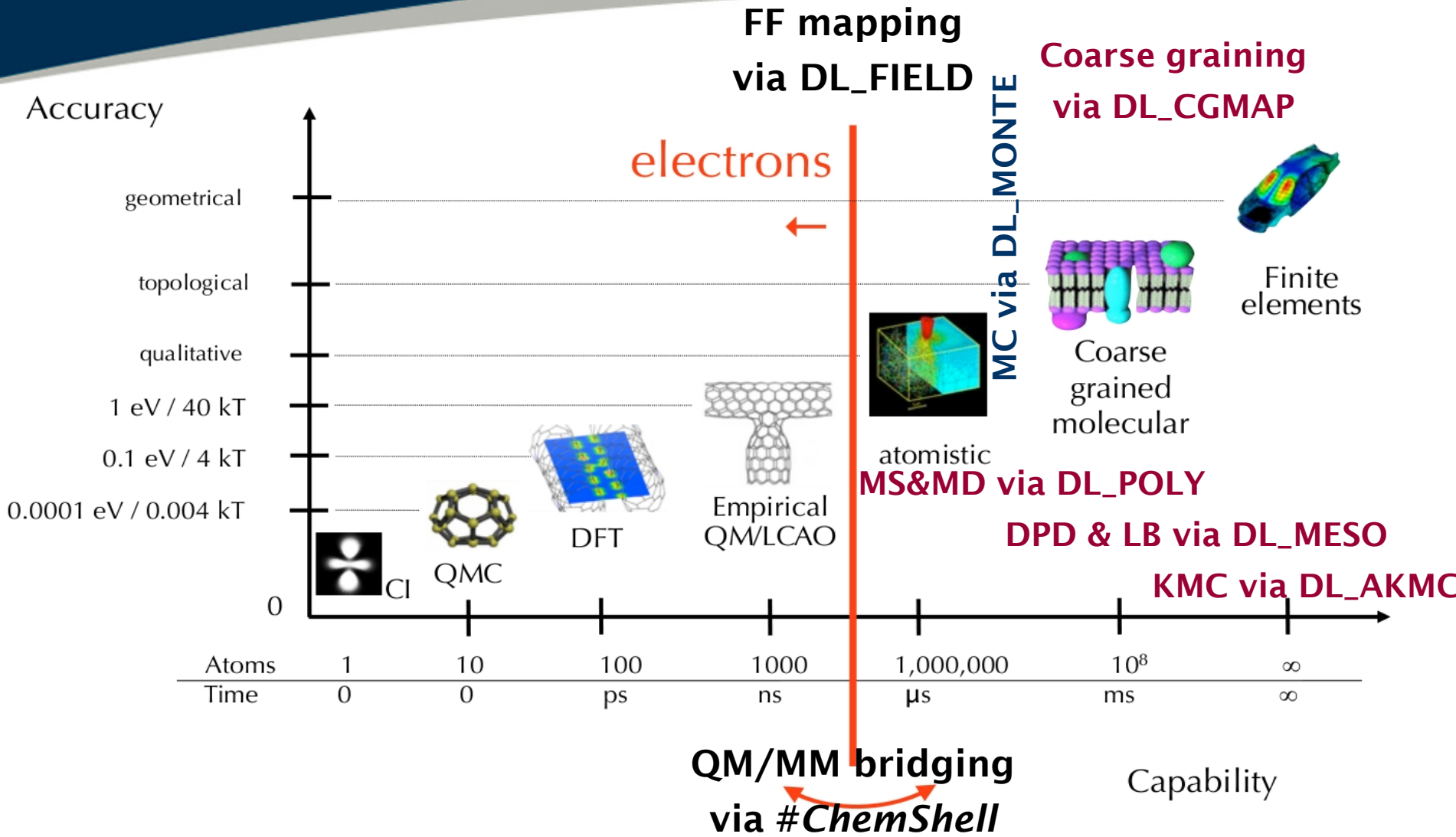Science & Technology Facilities Council

Alice's Wonderland (1865)
Lewis Carroll (Charles Lutwidge Dodgson)

Part 1

DL_POLY Project Background

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- <u>General purpose parallel (classical)</u> 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*).
- ~ 18,000 licences taken out since 1994 (~1,500 pa since 2007)
- ~ 3,250 *e*-mail list and ~100 (2015)/1,350(2005) PORTAL/FORUM

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

- **DL_POLY_4** (version 7)
  - **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 1.9)
  - **Replicated Data** parallelisation, limits up to $\approx 30,000$ 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)

WWW:

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

FTP:

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

DEV:

http://ccpforge.cse.rl.ac.uk/gf/project/dl-poly/
http://ccpforge.cse.rl.ac.uk/gf/project/dl_poly_classic/

PORTAL:

http://community.hartree.stfc.ac.uk/portal/site/
DL_SOFTWARE/

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

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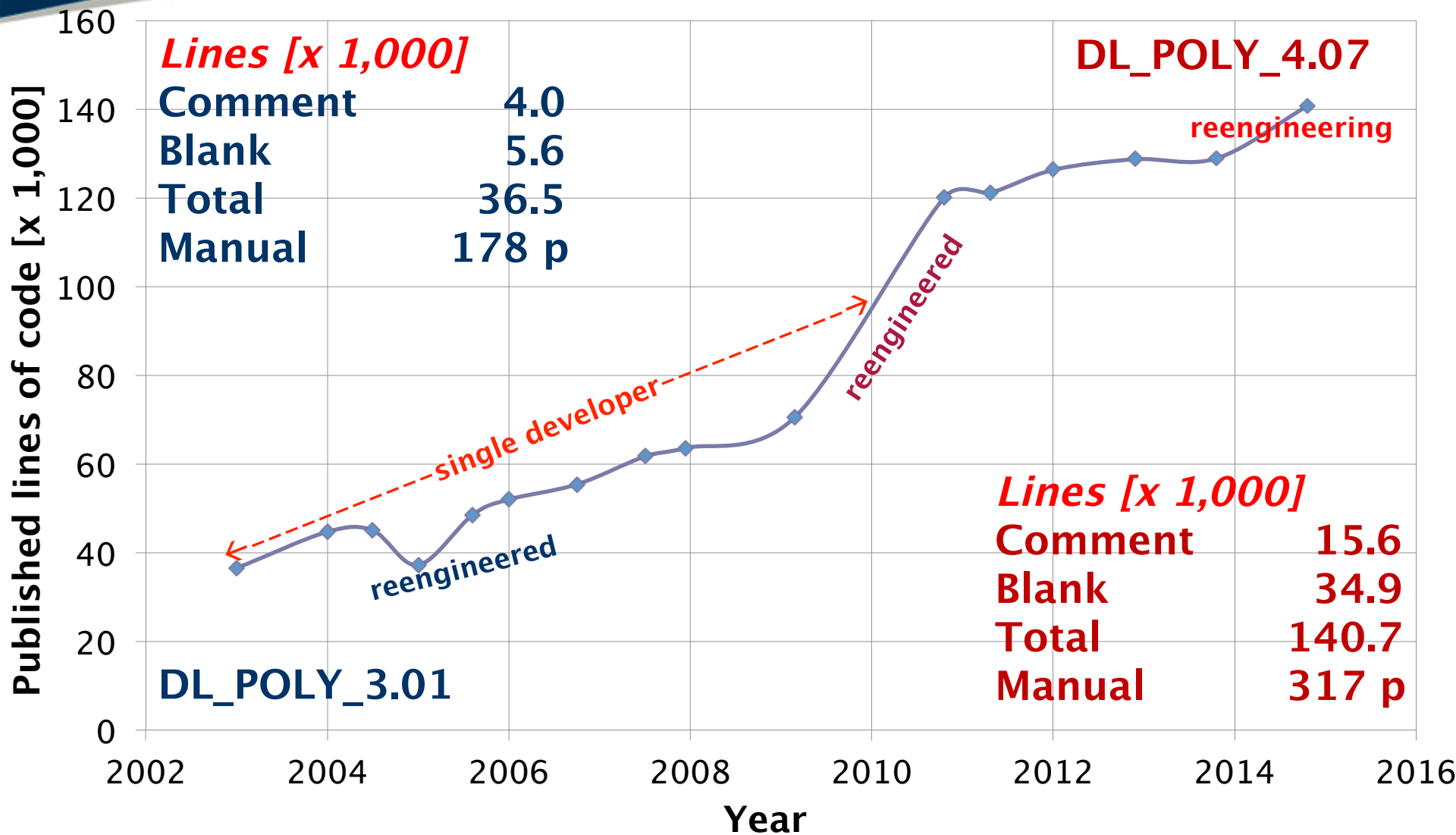 *Molecular Simulation* (2002), **28**, 385

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

DL_POLY Licence Statistics

Annual Downloads & Valid *e*Mail List Size

2010 :: DL_POLY (2+3+MULTI) – 1,000 (list end)
2013 :: DL_POLY_4   – 3,250 (list start 2011)

2014 Downloads

- EU–UK – 20.1%
- UK   – 18.5%
- USA   – 11.9%
- China – 11.6%
- India – 7.0%
- France – 4.4%

2014 Usage Statistics

- 540 Google Scholar citations
- 1,120 downloads
- 3,050 *e*Mail list

DL_POLY_2

DL_POLY_3

web–registration
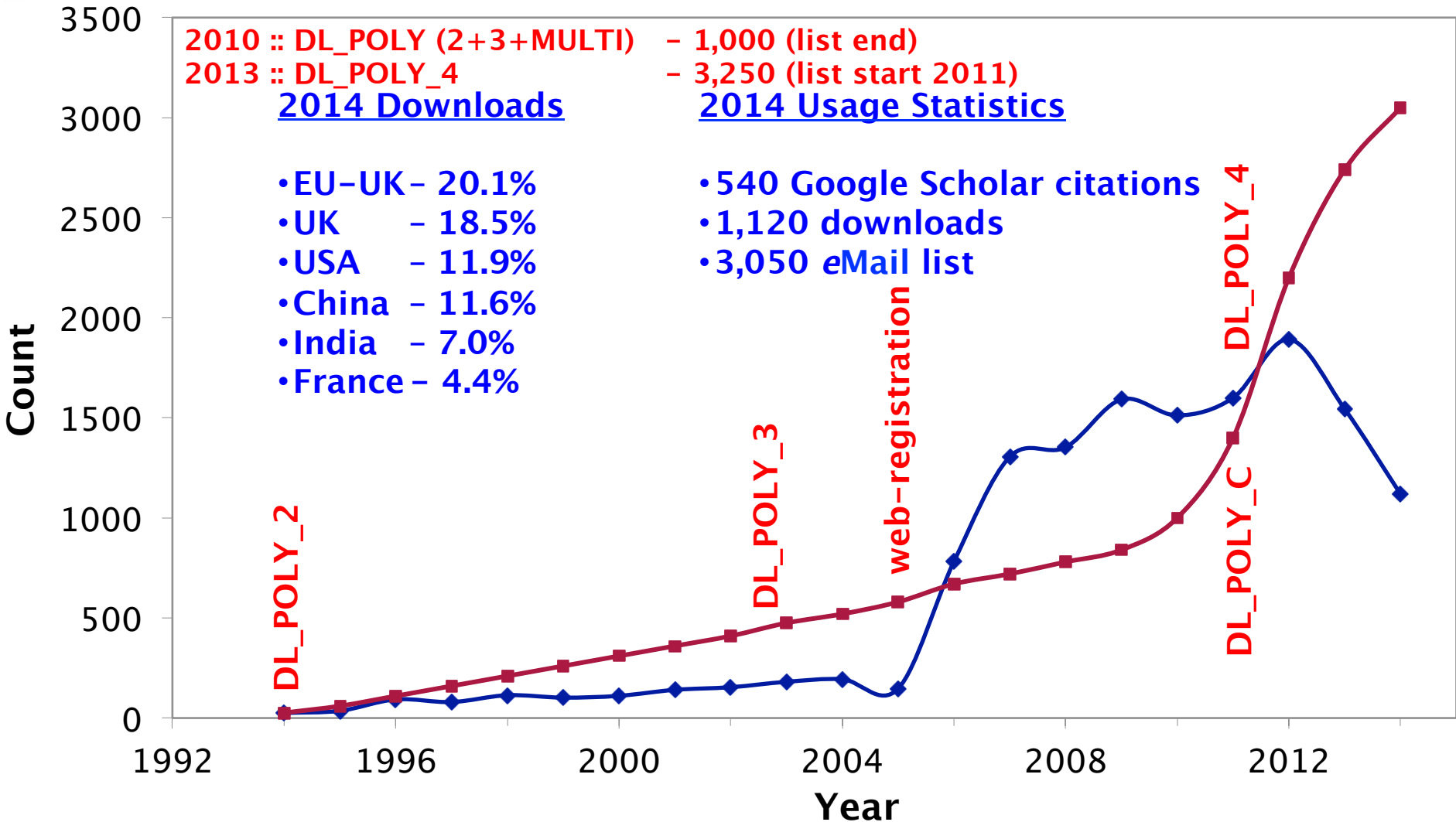
DL_POLY_4

DL_POLY_C

DL_POLY Usage Statistics
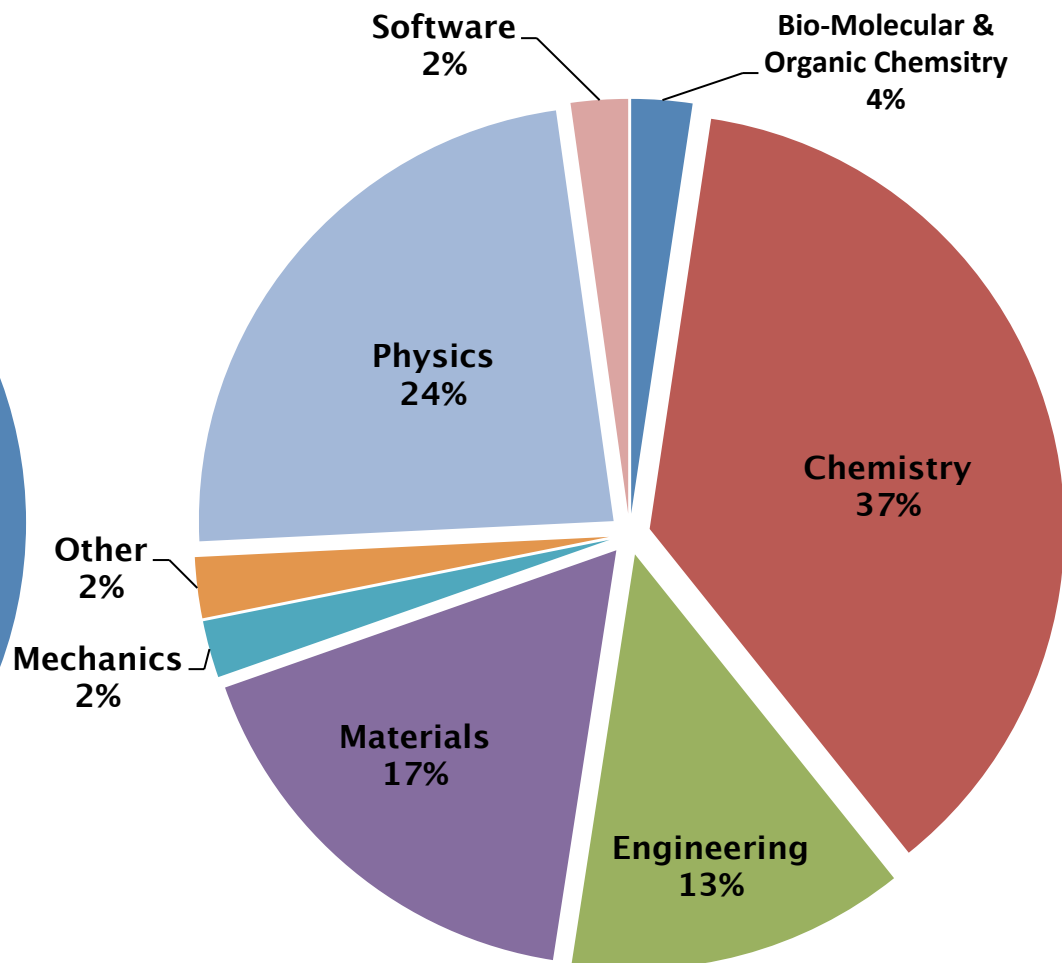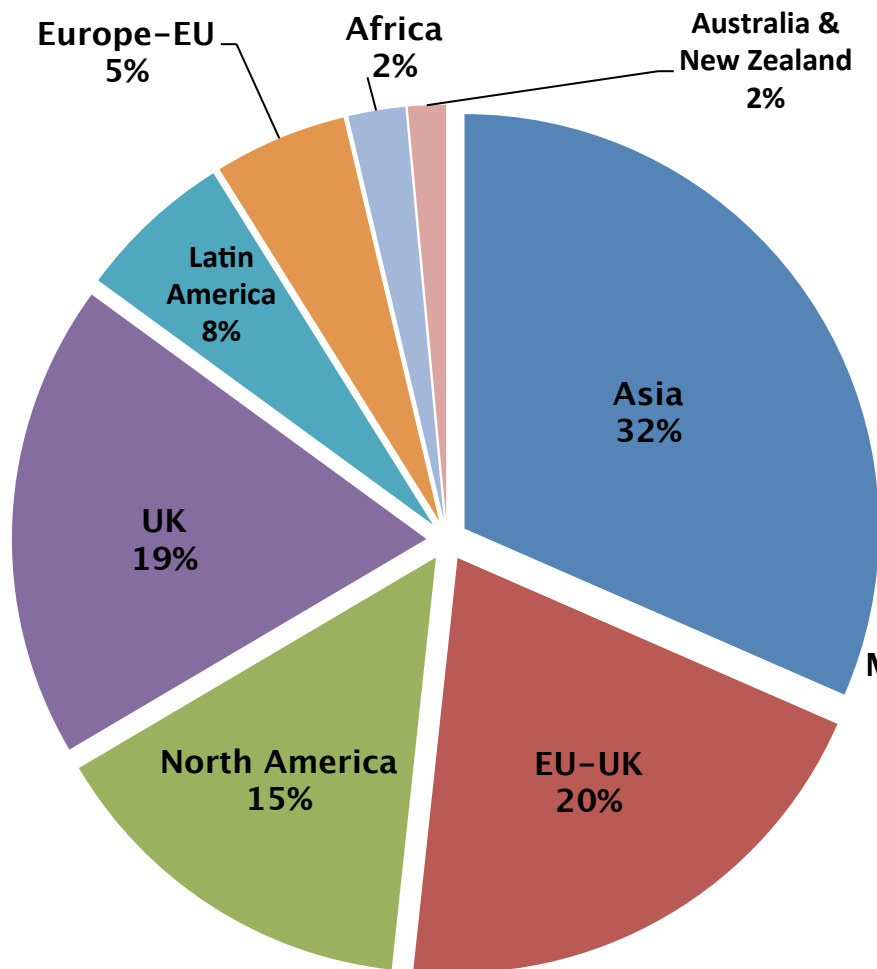
Examples of Model Systems

Proteins
solvation & binding

DNA strands
dynamics

Membranes' processes

Drug polymorphs
& discovery

Crystalline & Amorphous
Solids – damage and recovery
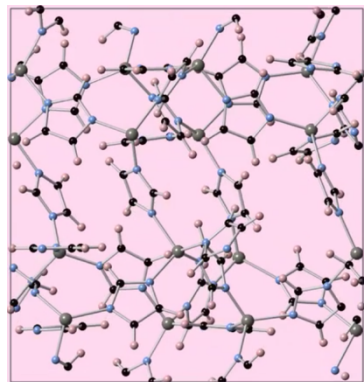
Dynamic processes in
Metal–Organic & Organic Frameworks
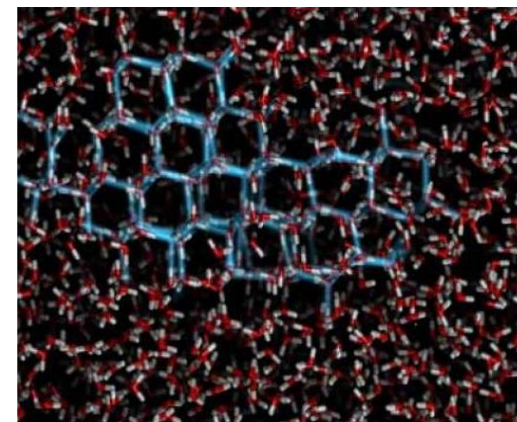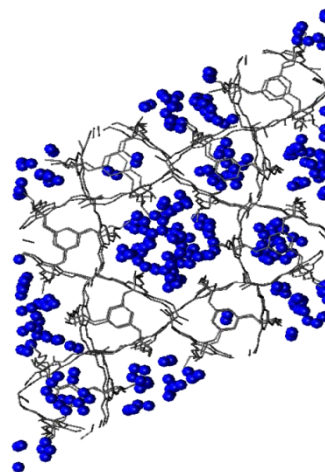
Dynamics at Interfaces &
of Phase Transformations

Part 2

The Molecular Dynamics Method

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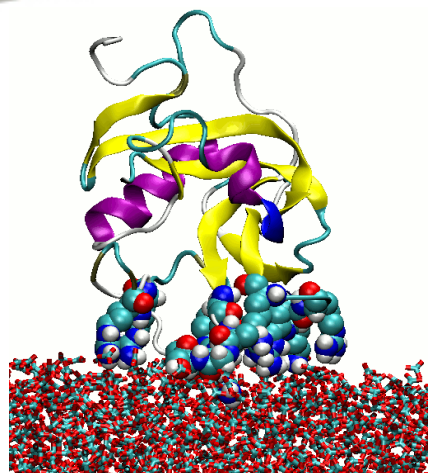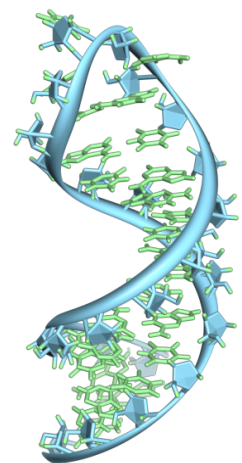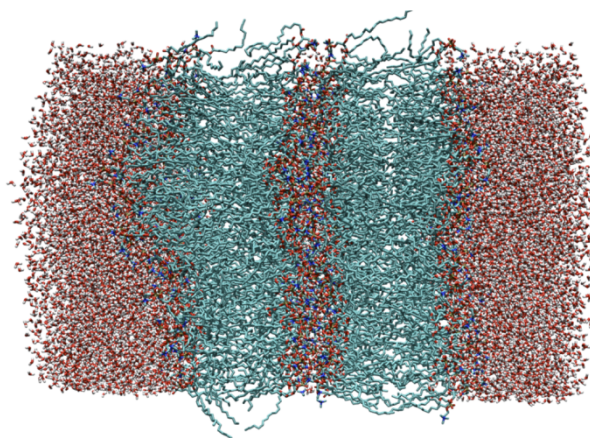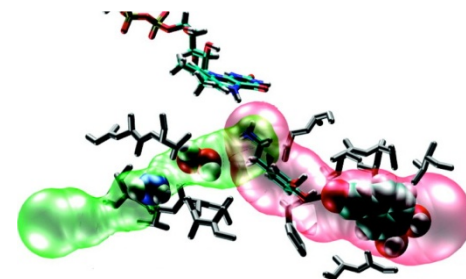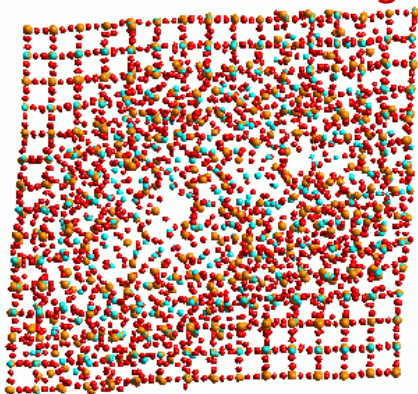- **Theoretical tool for modelling the detailed microscopic behaviour of many different types of systems, including; gases, liquids, solids, polymers, surfaces and clusters.**

- **In an MD simulation, the <u>classical equations of motion</u> governing the <u>microscopic time evolution</u> of a many body system are <u>solved numerically</u>, 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.**

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)

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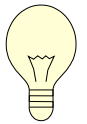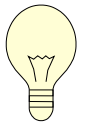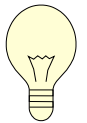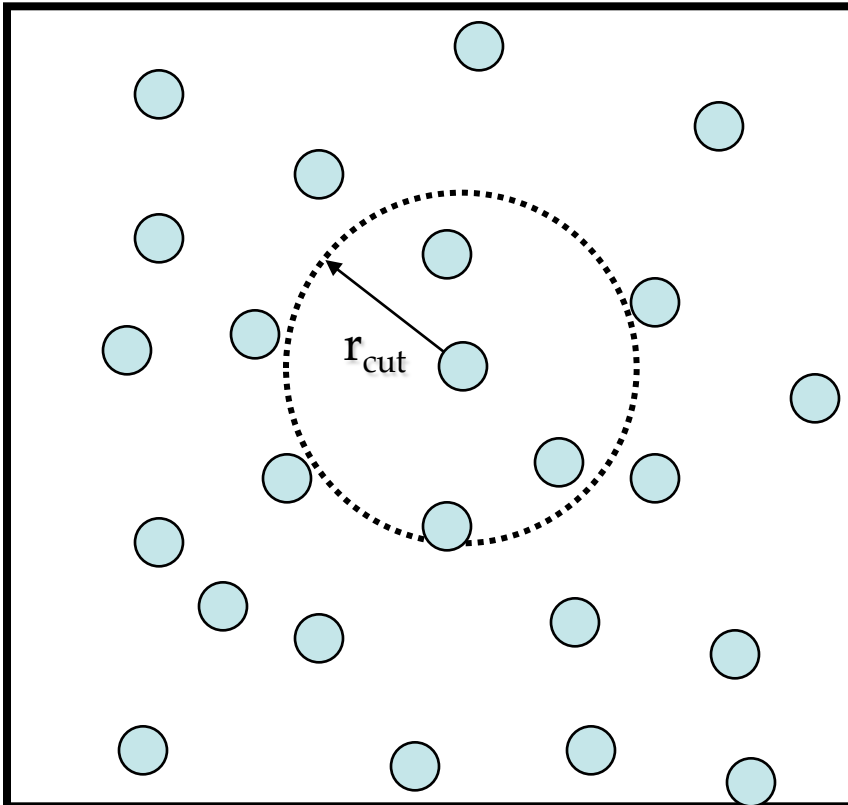
Pair Potential:

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

Lagrangian:

$$L(\vec{r}_i, \vec{v}_i) = \frac{1}{2} \sum_i^N m_i v_i^2 - \sum_i^{N-1} \sum_{j>i} V(r_{ij})$$

r_{cut}

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Facilities Council

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

$V(r)$

σ

ε

r_{cut}

r
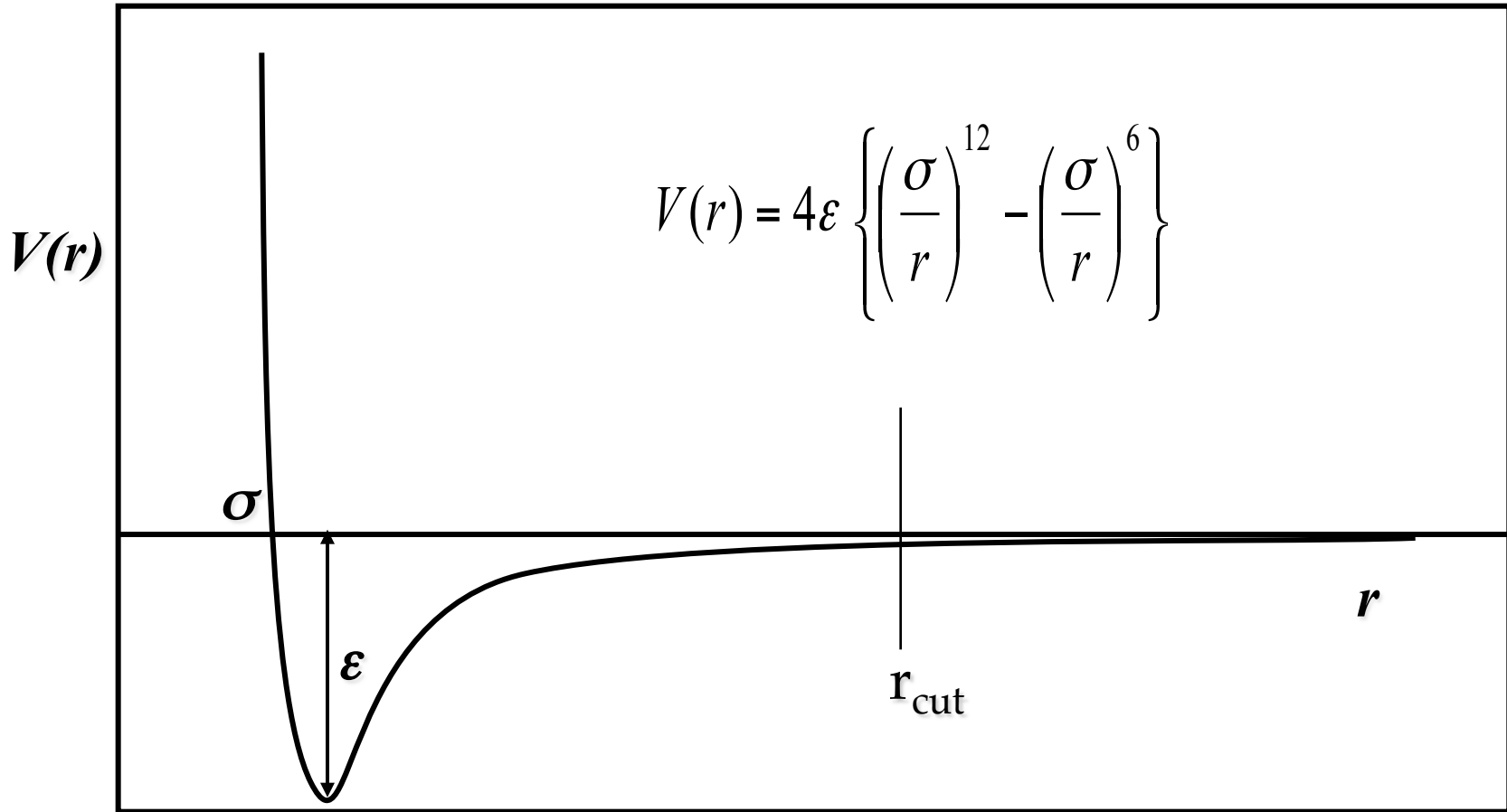
Pair-wise radial distance

$$\frac{d}{dt}\left(\frac{\partial L}{\partial v_i{}^\alpha}\right) = \frac{\partial L}{\partial r_i{}^\alpha}$$

Lagrange Equation – time evolution

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

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

Force Evaluation – particle interactions

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

2D cubic periodic

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

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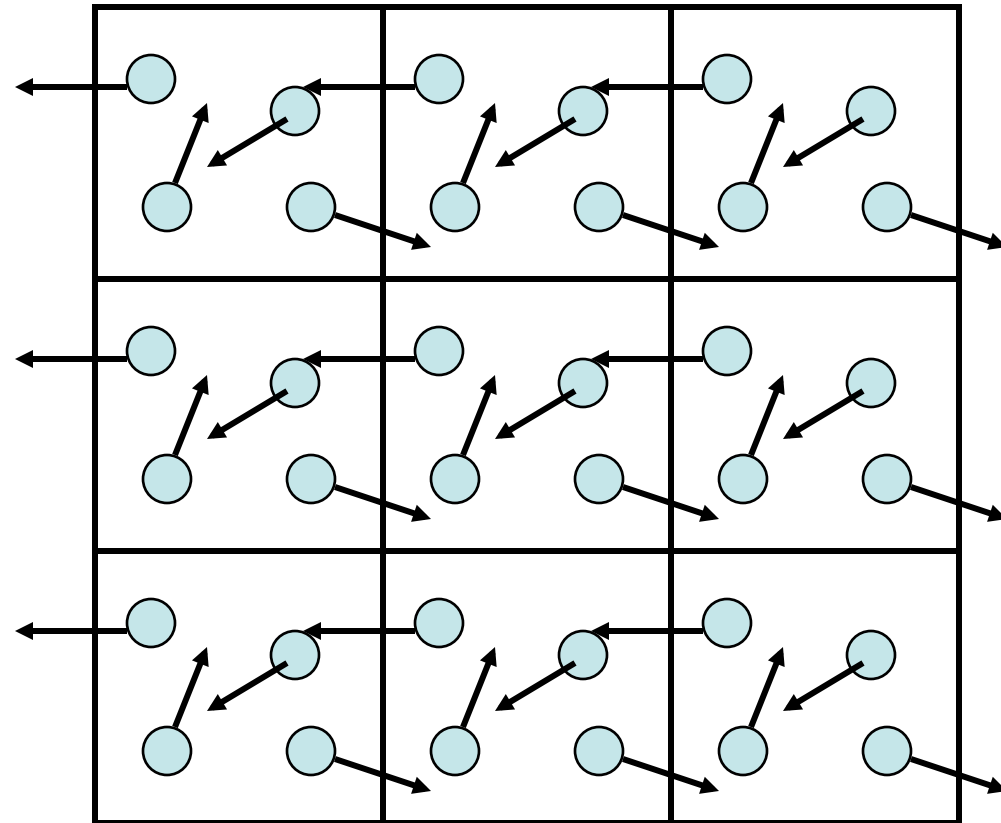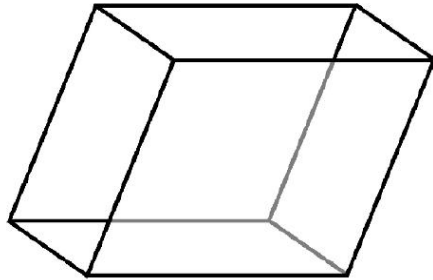
Triclinic
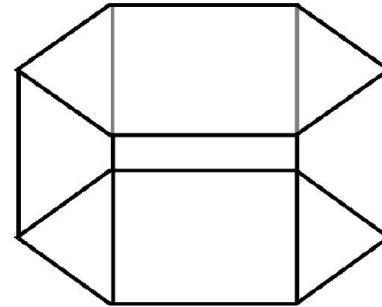
Hexagonal prism
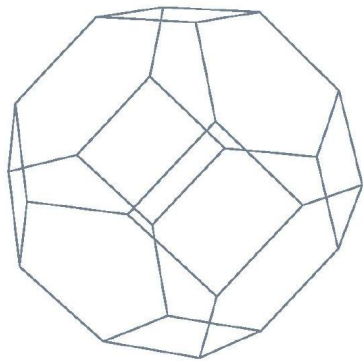
Truncated octahedron
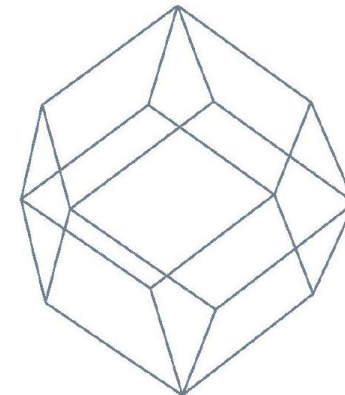
Rhombic dodecahedron

- **Kinetic Energy:**

$$\langle K.E. \rangle = \left\langle \frac{1}{2} \sum_{i}^{N} m_i v_i^2 \right\rangle$$

- **Temperature:**

$$T = \frac{2}{3Nk_B} \langle K.E. \rangle$$

- **Configuration Energy:**

$$U_c = \left\langle \sum_{i} \sum_{j>i}^{N} V(r_{ij}) \right\rangle$$

- **Pressure:**

$$PV = Nk_B T - \frac{1}{3} \left\langle \sum_{i}^{N} \vec{r}_i \cdot \vec{f}_i \right\rangle$$

- **Specific heat:**

$$\left\langle \delta(U_c)^2 \right\rangle_{NVE} = \frac{3}{2} Nk_B^2 T^2 \left(1 - \frac{3Nk_B}{2C_v}\right)$$

Structural Properties

– Pair correlation (Radial Distribution Function):

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

– Structure factor:

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

– Note: *S(k)* available from X-ray diffraction
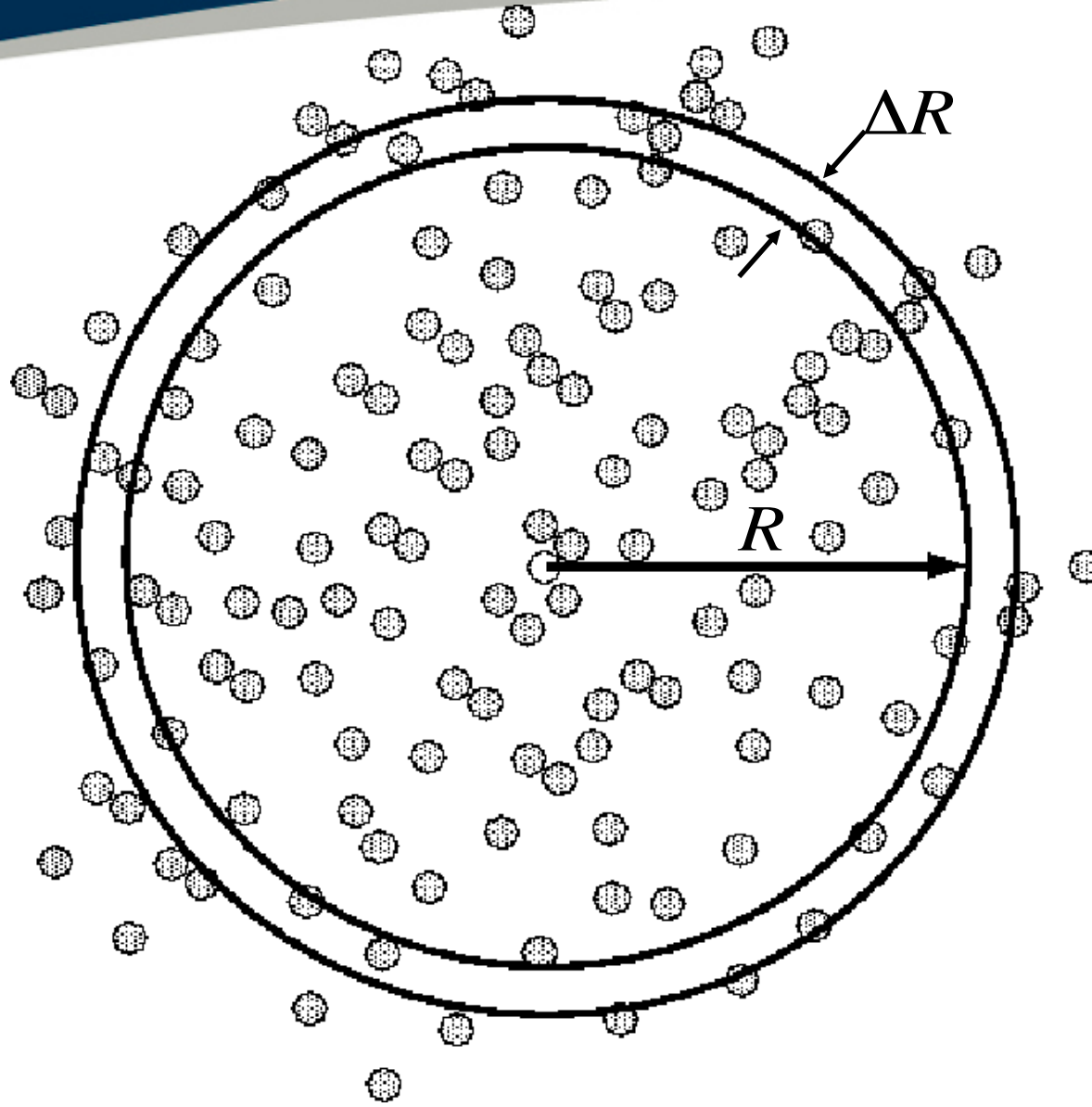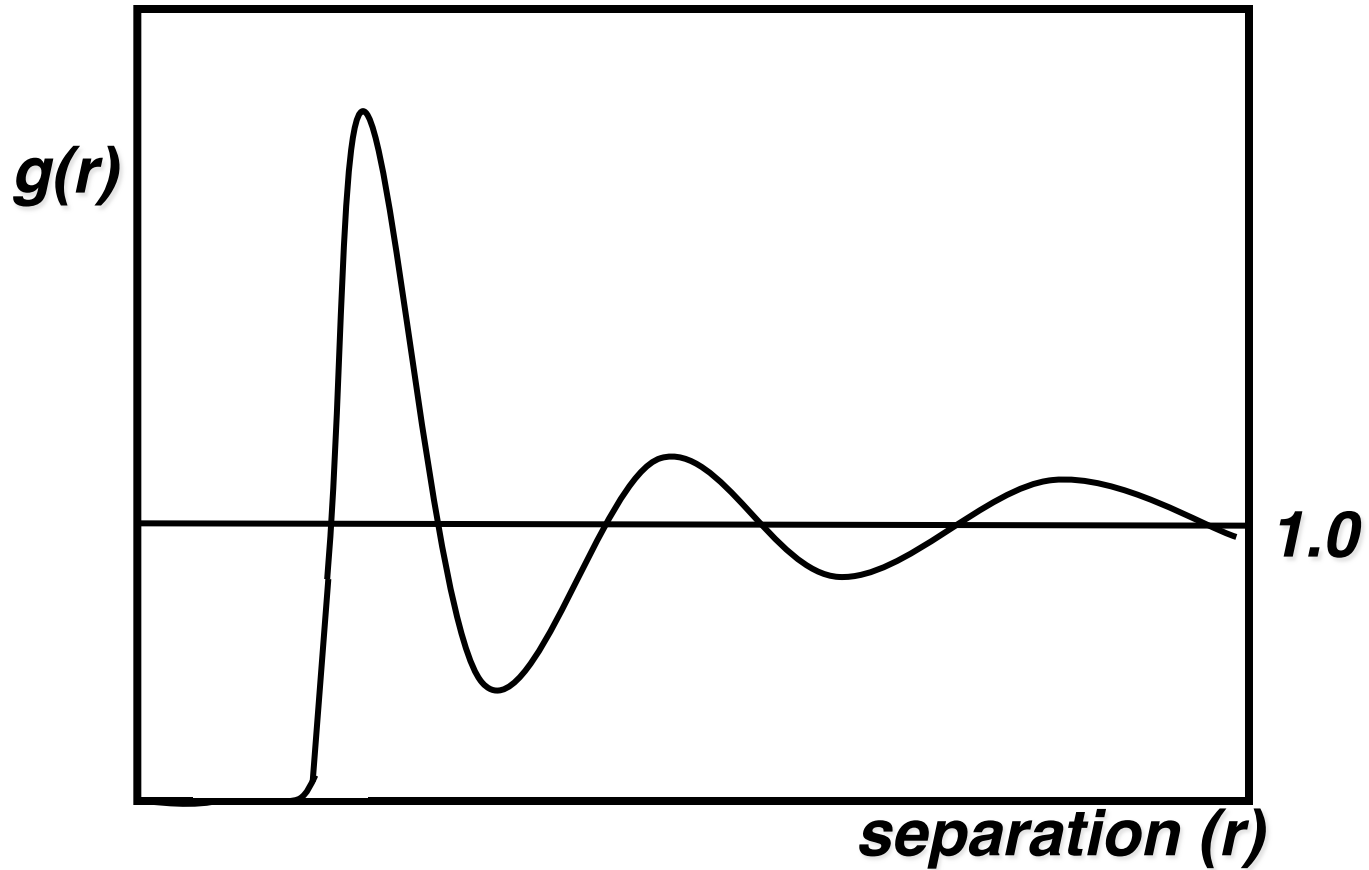
Single correlation functions:

- **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)**

$$D = \frac{1}{3}\int \left\langle v_i(t) \cdot v_i(0) \right\rangle dt$$

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**

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

- Complete description of bulk dynamical properties

- Space-time Fourier Transform of van Hove function

- Elastic properties of materials

- Energy dissipation

- Sound propagation

Obtained directly from neutron scattering

Part 3

DL_POLY Basics & Algorithms

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
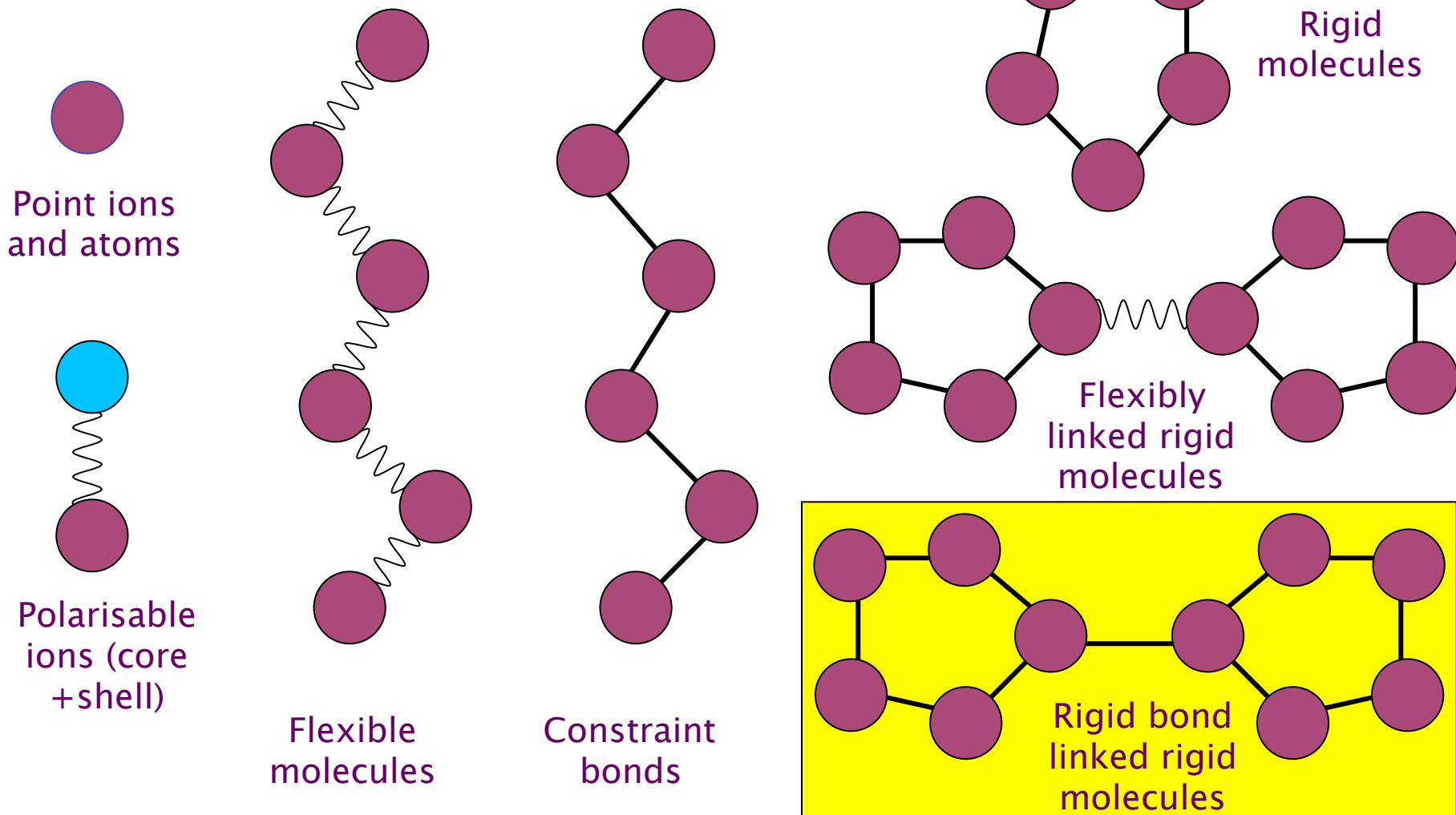
- *particle:* a rigid ion or an atom (charged or not), a core or a shell of a polarisable ion (with or without associated degrees of freedom), a massless charged site. A particle is a countable object and has a global ID index.

- *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*.

- **_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!!!_** *

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

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

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

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

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

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

- None (e.g. isolated macromolecules)

- Cubic periodic boundaries
- Orthorhombic periodic boundaries
- Parallelepiped (triclinic) periodic boundaries

- Truncated octahedral periodic boundaries*

- Rhombic dodecahedral periodic boundaries*

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

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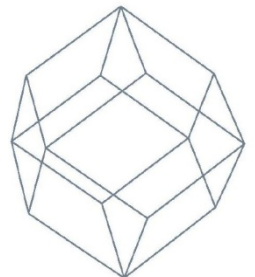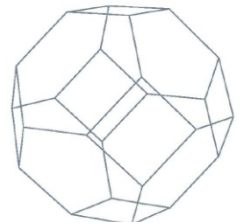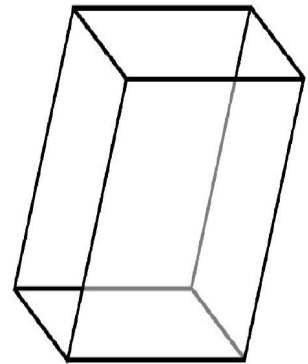
DL_POLY is designed for homogenious distributed parallel machines
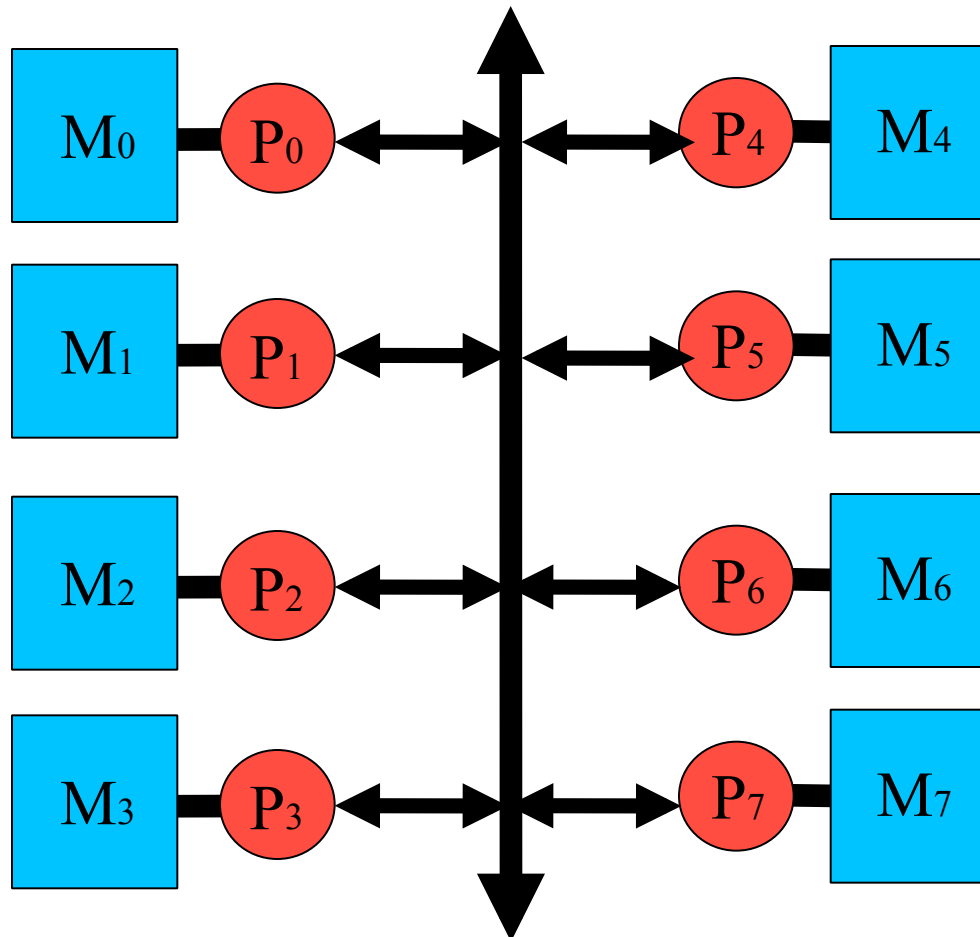
Replicated Data Strategy – II
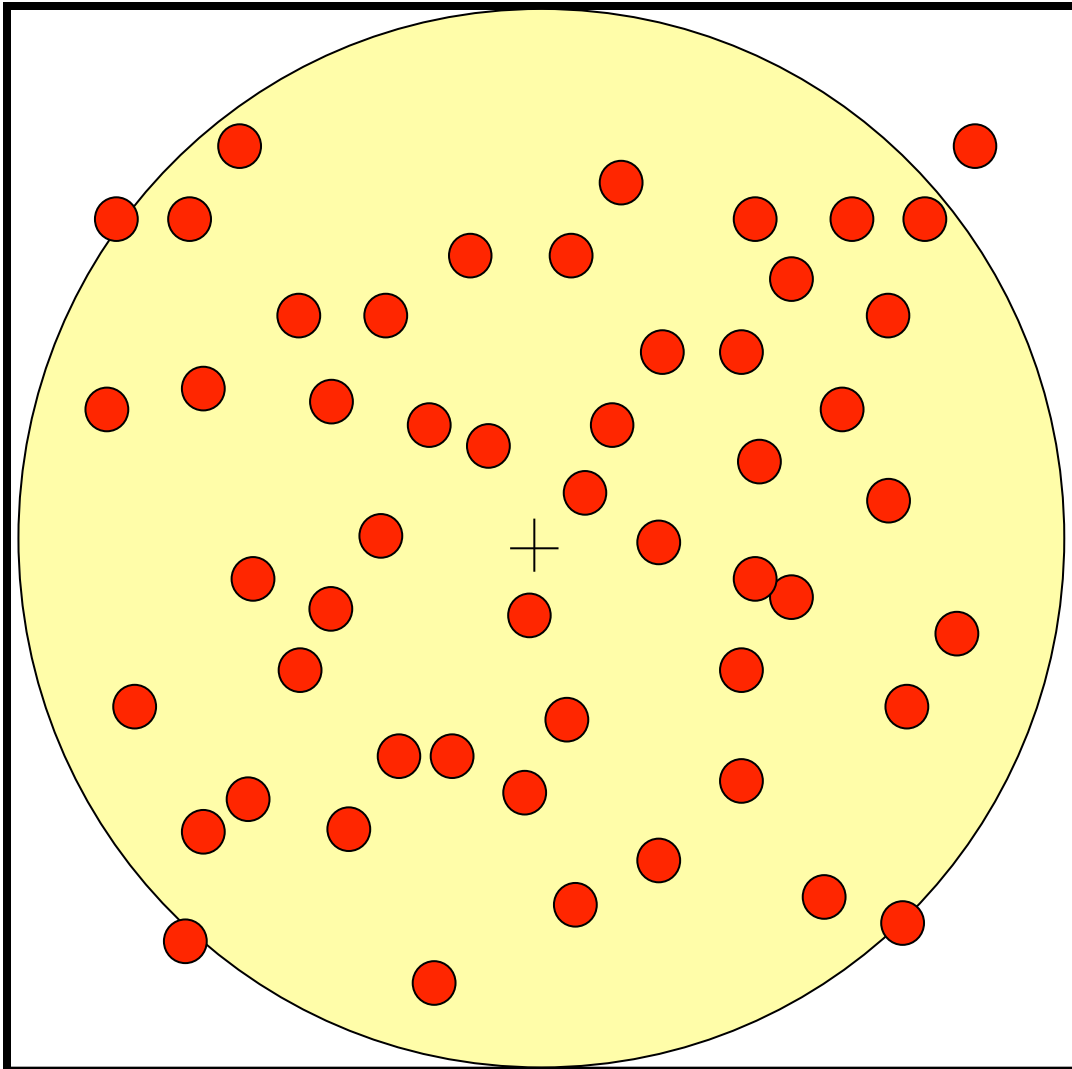
- Every processor sees the full system
- No memory distribution (performance overheads and limitations increase with increasing system size)
- Functional/algorithmic decomposition of the workload
- Cutoff ≤ 0.5 min system width
- Extensive global communications (extensive overheads increase with increasing system size)

Parallel (RD) Verlet List

Brode–Ahlrichs distributed list!

1,2	1,3	1,4	1,5	1,6	1,7
2,3	2,4	2,5	2,6	2,7	2,8
3,4	3,5	3,6	3,7	3,8	3,9
4,5	4,6	4,7	4,8	4,9	4,10
5,6	5,7	5,8	5,9	5,10	5,11
6,7	6,8	6,9	6,10	6,11	6,12
7,8	7,9	7,10	7,11	7,12	
8,9	8,10	8,11	8,12	8,1	
9,10	9,11	9,12	9,1	9,2	
10,11	10,12	10,1	10,2	10,3	
11,12	11,1	11,2	11,3	11,4	
12,1	12,2	12,3	12,4	12,5	

A → C → A → C → A → C (left labels)

B ← D ← B ← D ← B ← D (right labels)
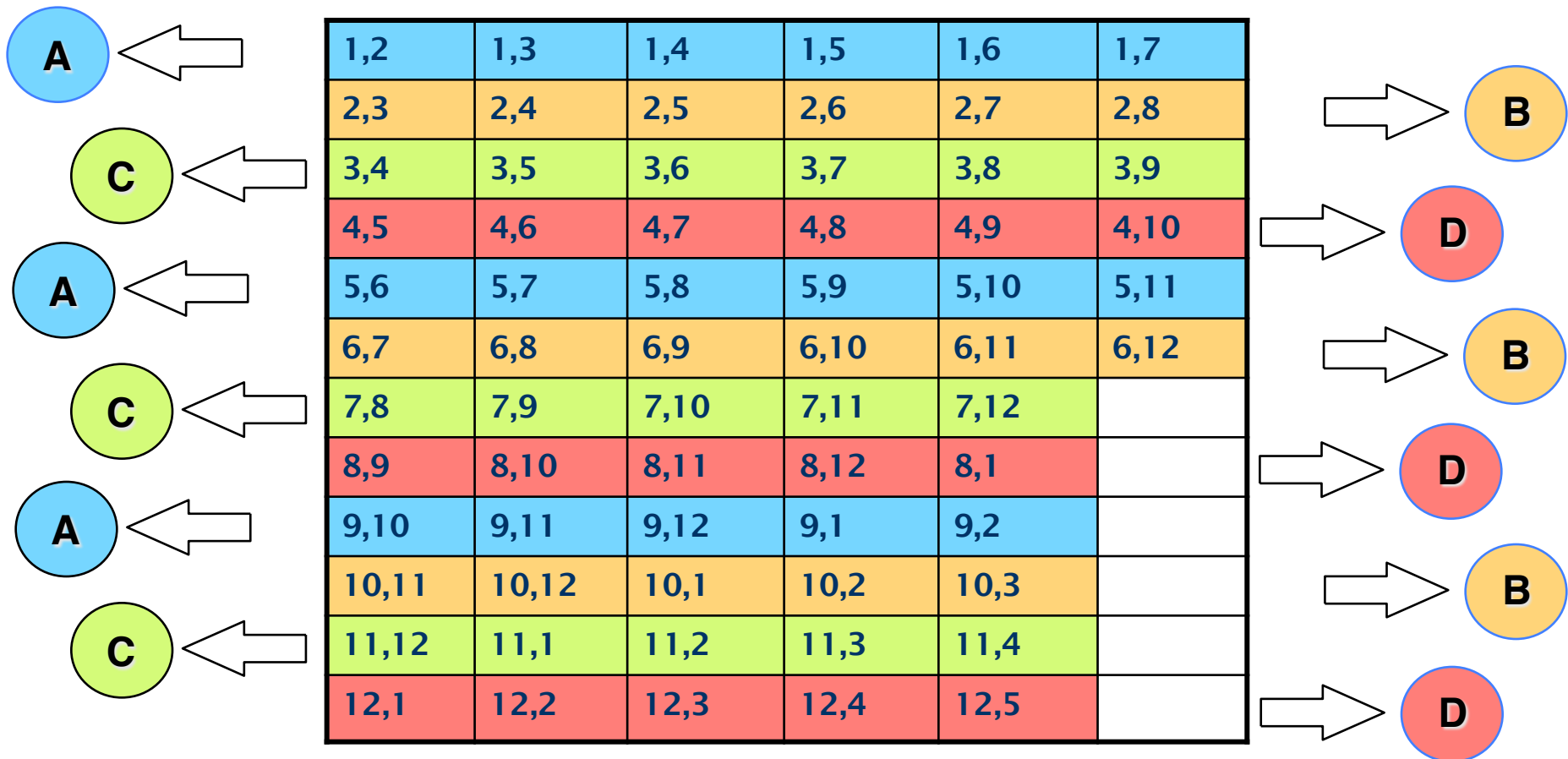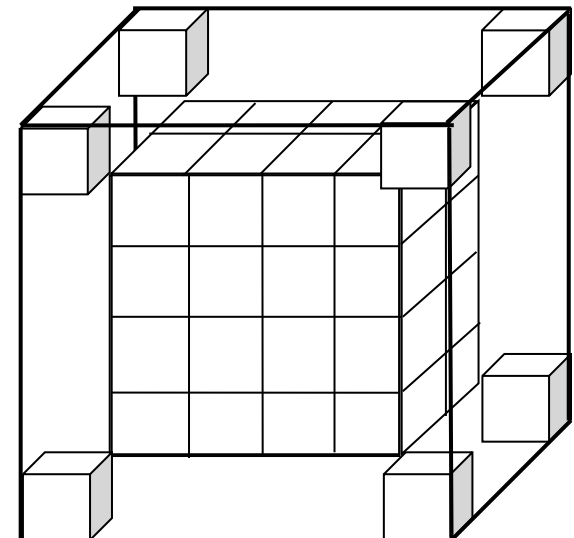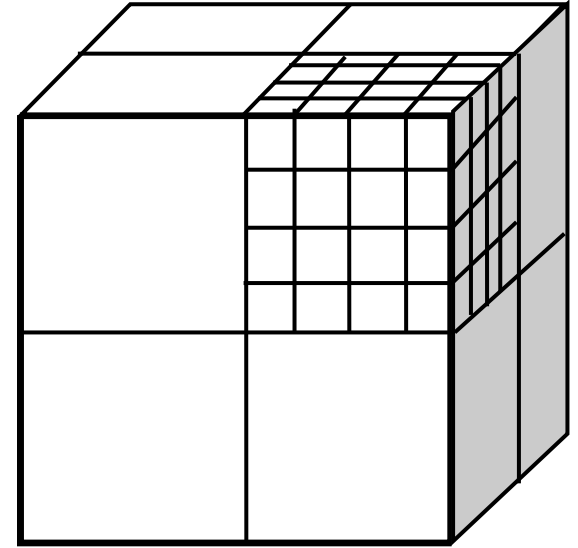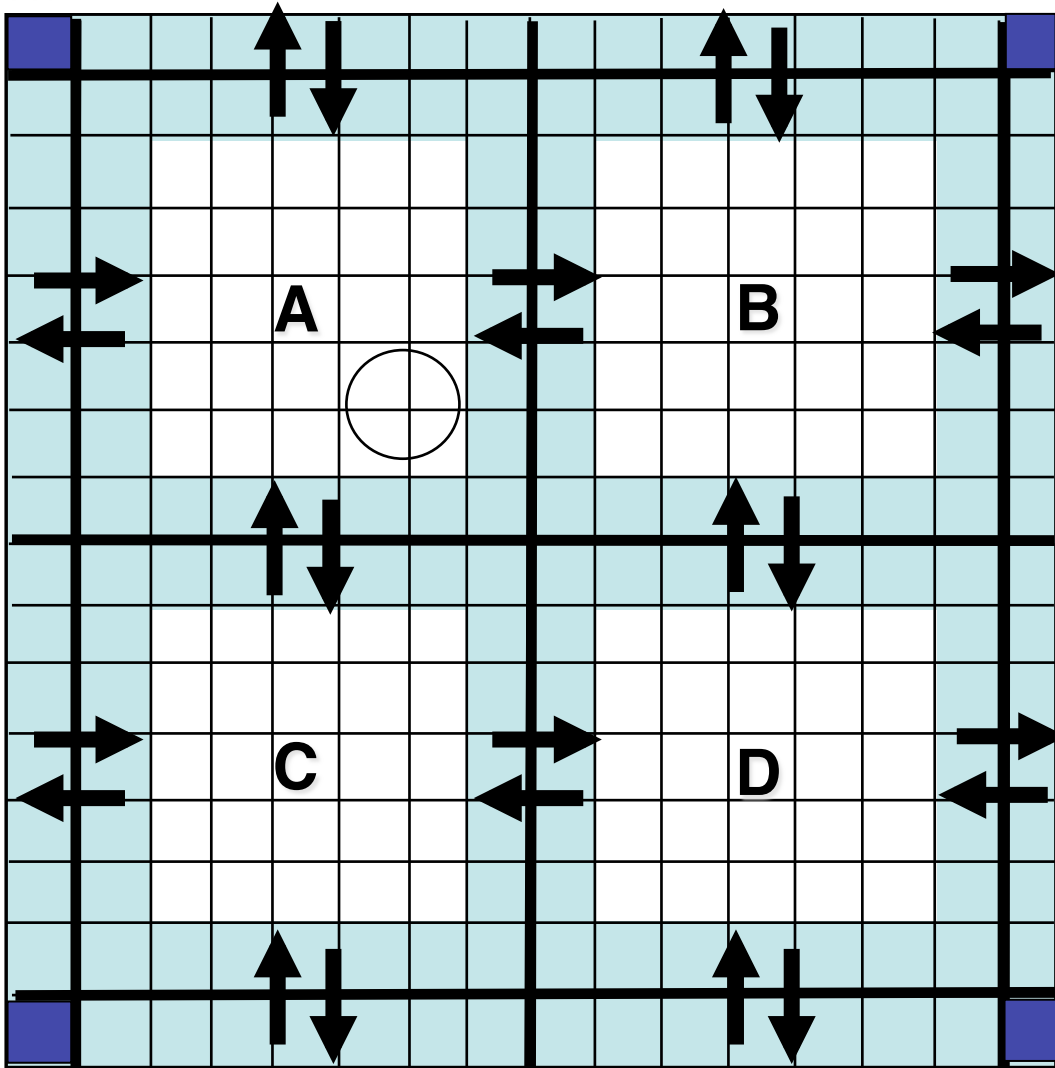
- Linked lists provide an elegant way to scale short-ranged two body interactions from $O(N^2/2)$ to $\approx O(N)$. The efficiency increases with increasing link cell partitioning – as a rule of thumb best efficacy is achieved for cubic-like partitioning with number of link-cells per domain ≥ 4 for 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.

Cell number

1 2 3 4 5

Head of Chain List

| | 6 | | | |

Link Cell 2

6 12
17
16 10

Link List

| | | | | | 10 | | | | 12 | | 16 | | | | 17 | 0 | | | |

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Atom number
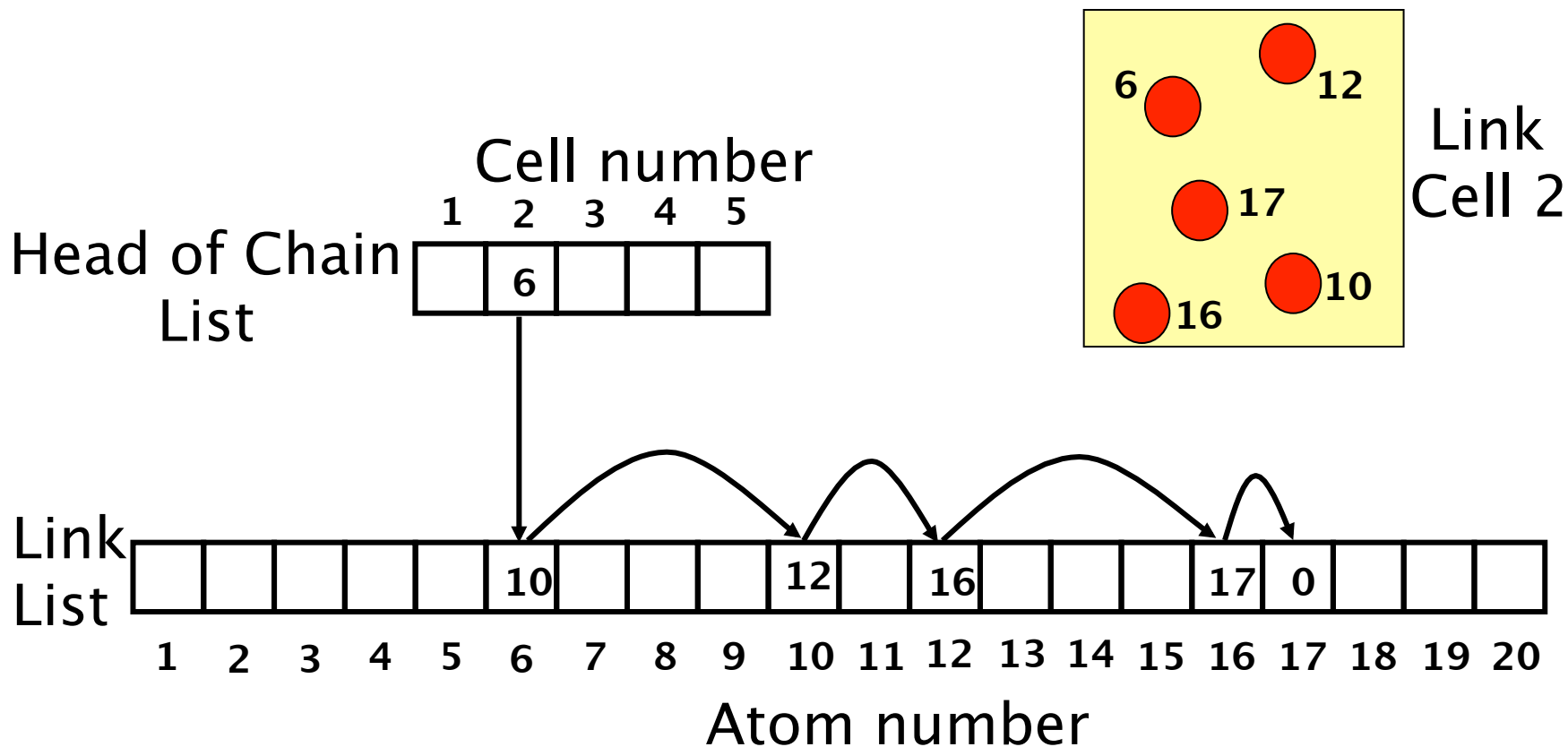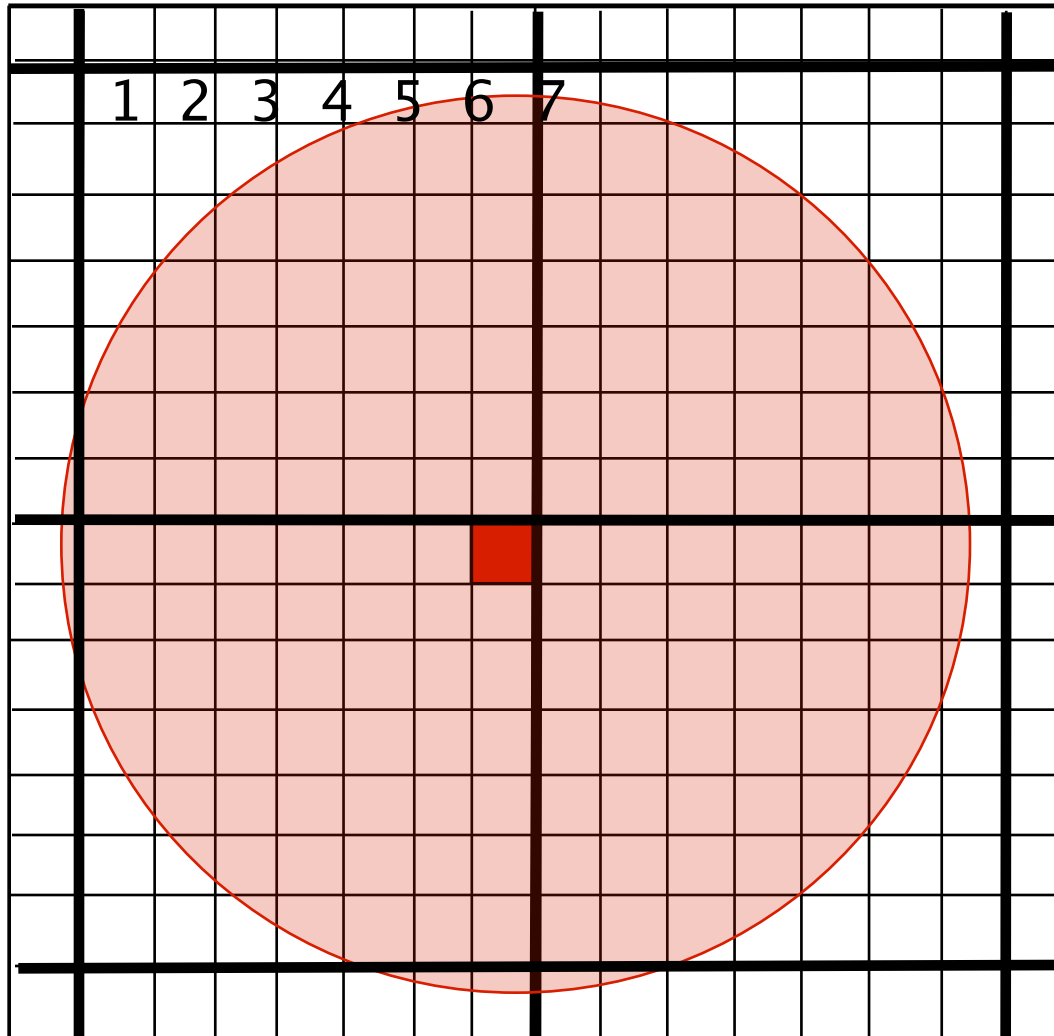
- Provides dynamically adjustable workload for variable local density and VNL speed up of ≈ 30% (45% theoretically).

- 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.

- **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 $\delta r/r_{cut}\approx 5-15\%$.

- **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 $\delta r/r_{cut}\approx 1-5\%$.

- 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%.

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- 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!
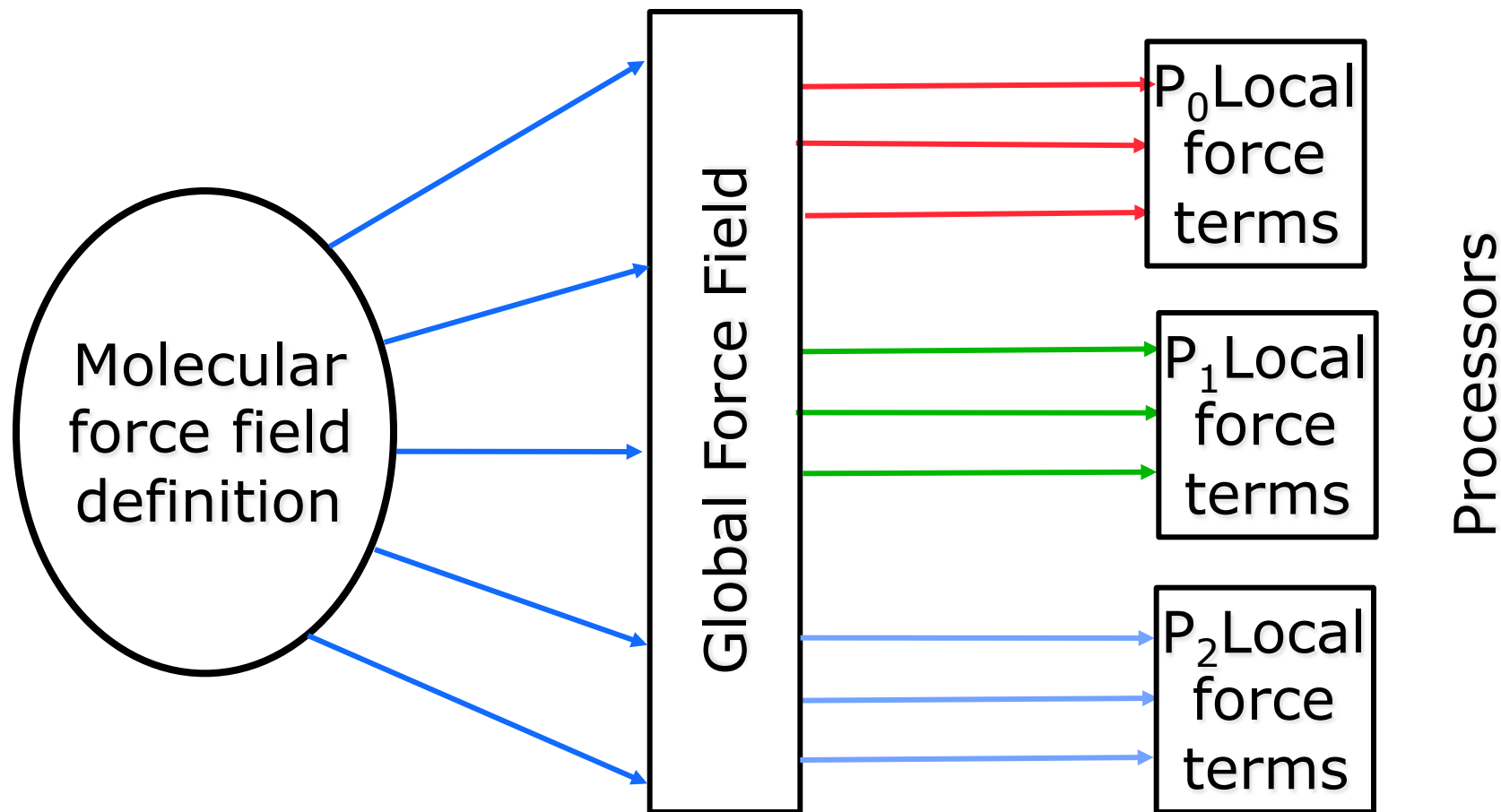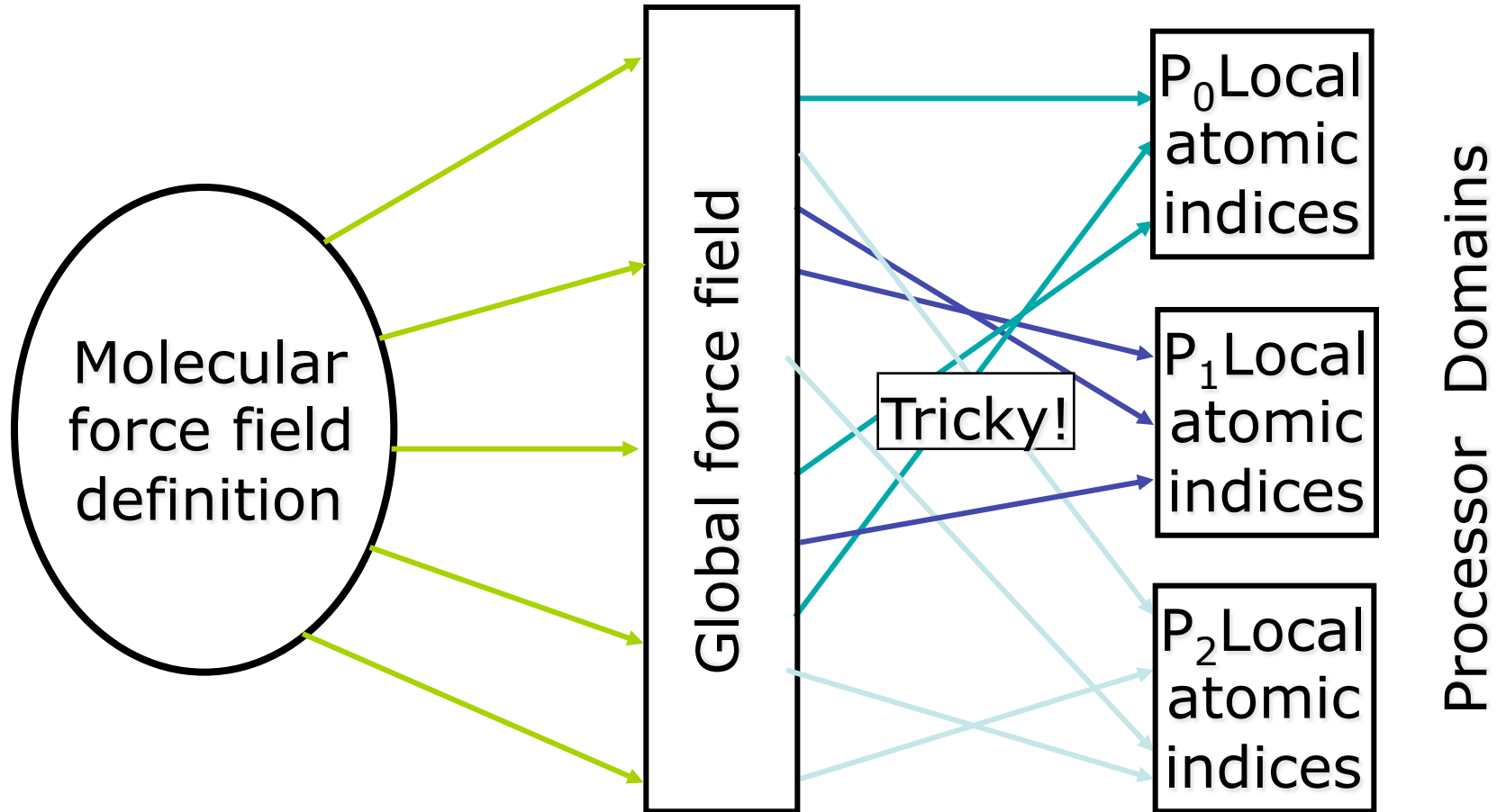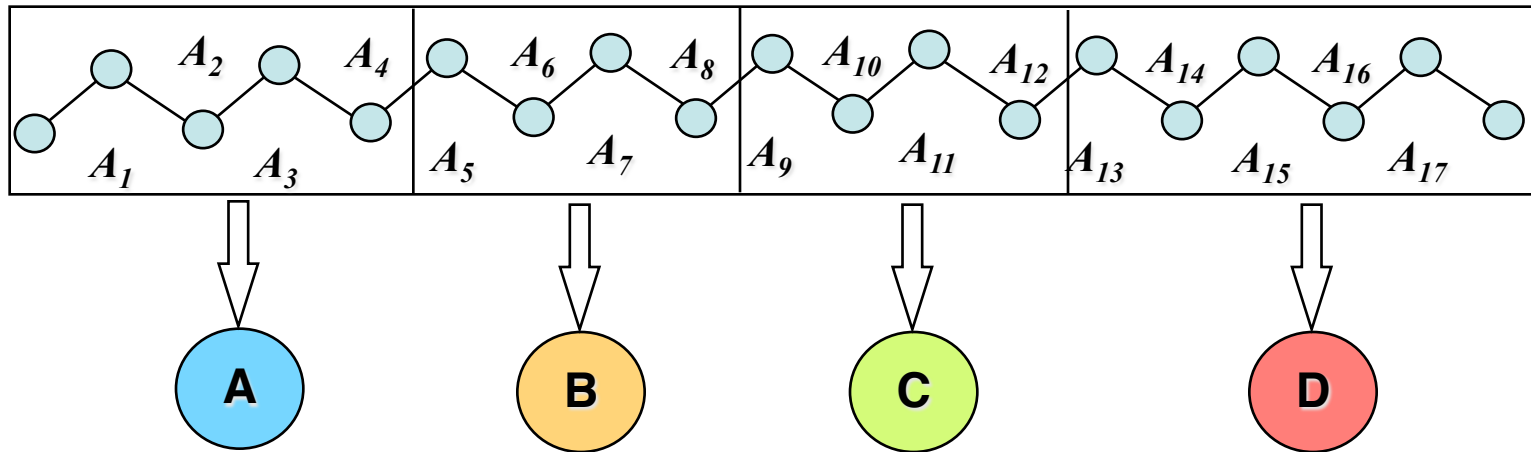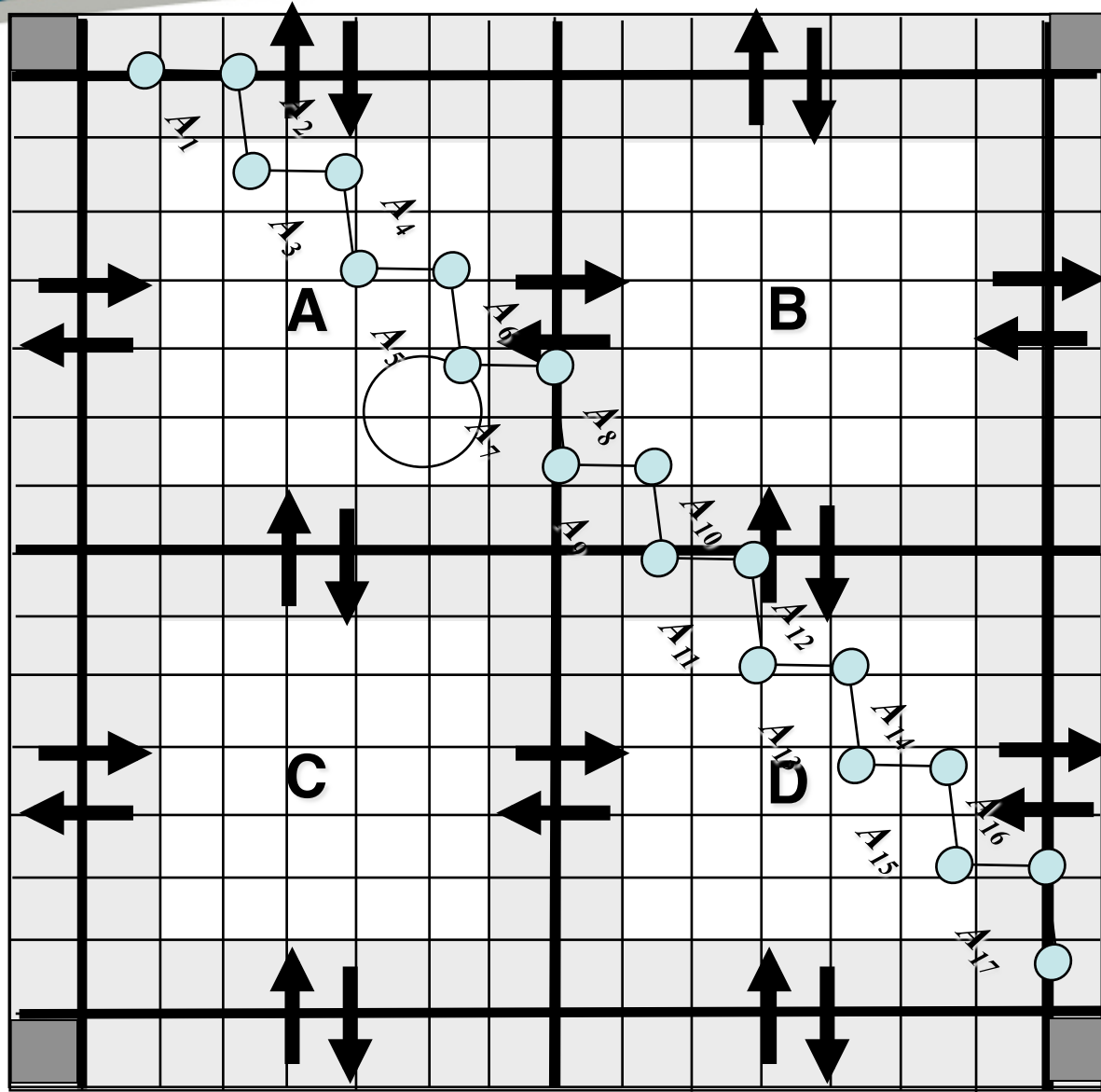
Integration:

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^

Constraints & Rigid Body Solvers:

- **VV dependent – RATTLE, No_Squish, QSHAKE***

- **LFV dependent – SHAKE, Euler-Quaternion, QSHAKE***

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

$\underline{r}'\ (t+\Delta t)$

$\underline{v}\ (t)\Delta t$

Net displacement

$\underline{r}\ (t+\Delta t)$

$\underline{r}\ (t)$

$\underline{f}(t)\Delta t^2/m$

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

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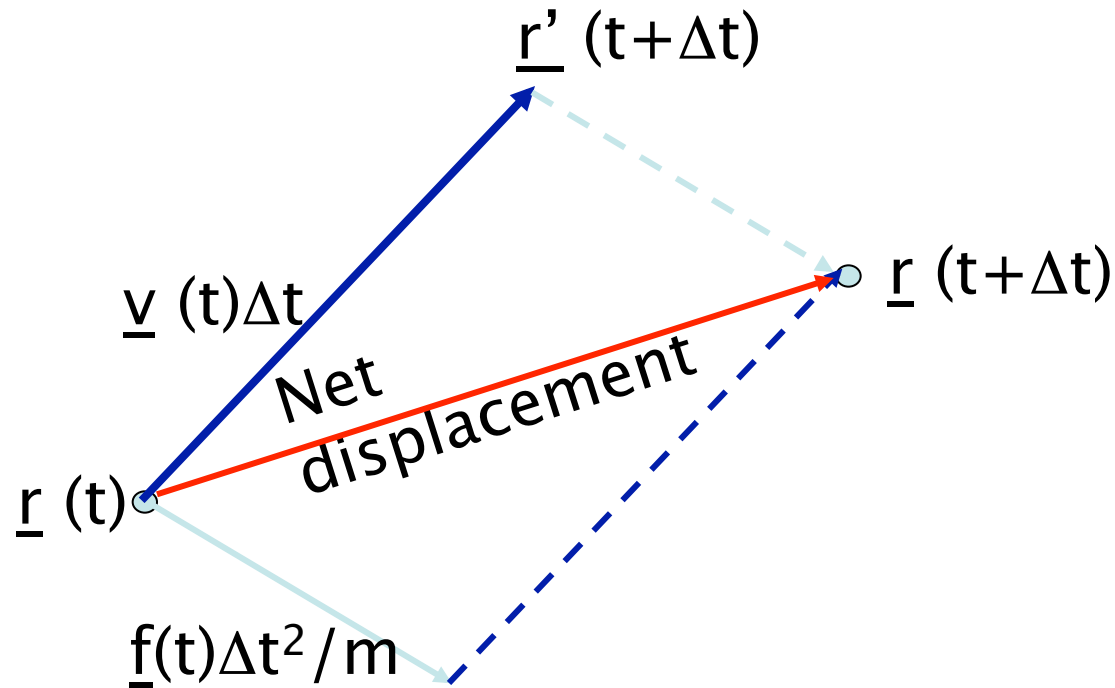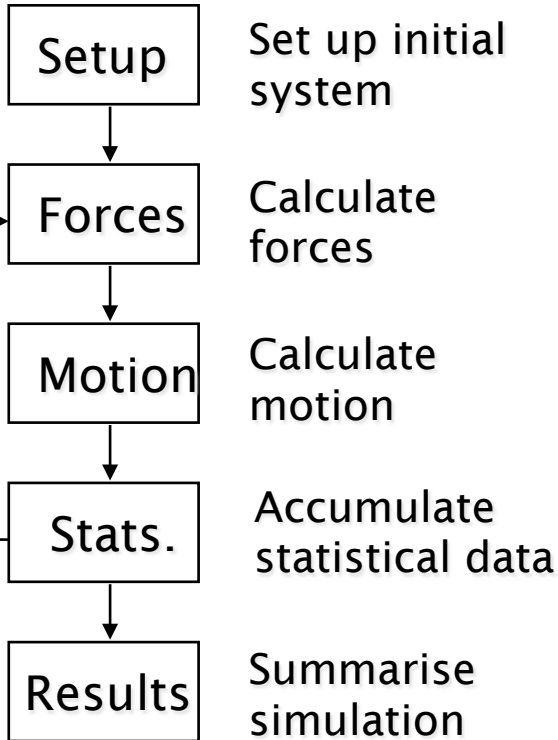
Taylor expansion: $r_{n+1} = r_n + \Delta t\, v_n + \dfrac{\Delta t^2}{2}\dfrac{f_n}{m} + O\!\left(\Delta t^3\right)$

Setup	Set up initial system
Forces	Calculate forces
Motion	Calculate motion
Stats.	Accumulate statistical data
Results	Summarise simulation

Leapfrog Verlet (LFV) **Velocity Verlet (VV)**

0. $x_i(t),\, v_i(t - \tfrac{1}{2}\Delta t)$

1. $f_i(t) - calculated\ \ afresh$

2. $v_i(t + \tfrac{1}{2}\Delta t) = v_i(t - \tfrac{1}{2}\Delta t) + \Delta t\dfrac{f_i(t)}{m_i}$

3. $x_i(t + \Delta t) = x_i(t) + \Delta t\, v_i(t + \tfrac{1}{2}\Delta t)$

VV1.0. $x_i(t), v_i(t), f_i(t)$

VV1.1. $v_i(t + \tfrac{1}{2}\Delta t) = v_i(t) + \dfrac{\Delta t}{2}\dfrac{f_i(t)}{m_i}$

VV1.2. $x_i(t + \Delta t) = x_i(t) + \dfrac{\Delta t}{2}v_i(t + \tfrac{1}{2}\Delta t)$

VV2.0. $f_i(t + \Delta t) - calculated\ \ afresh$

VV2.1. $v_i(t + \Delta t) = v_i(t + \tfrac{1}{2}\Delta t) + \dfrac{\Delta t}{2}\dfrac{f_i(t + \Delta t)}{m_i}$

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

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

f $^{n-2}$	f $^{n-1}$	f ^{n}	
r^{n-2}	r^{n-1}	r^{n}	r^{n+1}
	v$^{n-3/2}$	v$^{n-1/2}$	v$^{n+1/2}$

Discrete time

Application in Practice

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

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

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

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

$$\vec{v}_i^{\,n+1} = \vec{v}_i^{\,n} + \frac{\Delta t}{2m_i}(\vec{F}_i^{\,n} + \vec{F}_i^{\,n+1}) + \vartheta(\Delta t^2)$$

$f^{\,n-2}$	$f^{\,n-1}$	$f^{\,n}$	$f^{\,n+1}$
r^{n-2}	r^{n-1}	r^{n}	r^{n+1}
v^{n-2}	v^{n-1}	v^{n}	v^{n+1}

Application in Practice

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

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

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

Discrete time

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Taylor expansions:

$$r_{n+1} = r_n + \Delta t\, v_n + \frac{\Delta t^2}{2} \frac{f_n + g_n}{m} + O\!\left(\Delta t^3\right)$$

$$v_{n+1} = v_{n+\frac{1}{2}} + \frac{\Delta t}{2} \frac{f_n + h_n}{m} + O\!\left(\Delta t^3\right)$$

<u>SHAKE</u>

$$\vec{G}_{ij} = -\,\vec{G}_{ji} \approx g_{ij}\,\vec{d}^{\,o}_{ij}$$

$$g_{ij} = \frac{\mu_{ij}}{2\Delta t^2} \frac{(\vec{d}^{\,2}_{ij} - \vec{d}^{\,u\,2}_{ij})}{\vec{d}^{\,o}_{ij} \cdot \vec{d}^{\,u}_{ij}}$$
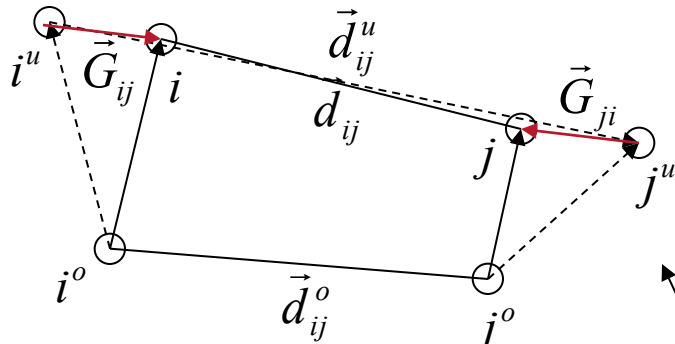
$$\frac{1}{\mu_{ij}} = \frac{1}{m_i} + \frac{1}{m_j}$$

<u>RATTLE</u>
RATTLE_R (SHAKE)

$$g_{ij} = \frac{\mu_{ij}}{\Delta t^2} \frac{(\vec{d}^{\,o\,2}_{ij} - \vec{d}^{\,u\,2}_{ij})}{\vec{d}^{\,o}_{ij} \cdot \vec{d}^{\,u}_{ij}}$$

RATTLE_V

$$\vec{H}_{ij} = -\vec{H}_{ji} = h_{ij} \cdot \vec{d}^{\,o}_{ij}$$

$$h_{ij} = \frac{\mu_{ij}}{\Delta t} \frac{(\vec{v}_i - \vec{v}_j)\cdot \vec{d}^{\,o}_{ij}}{d^2_{ij}}$$

Proc A

Proc B

MU_1

MU_2

MU_3

MU_4

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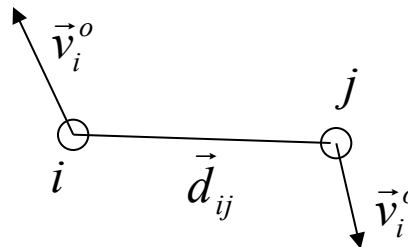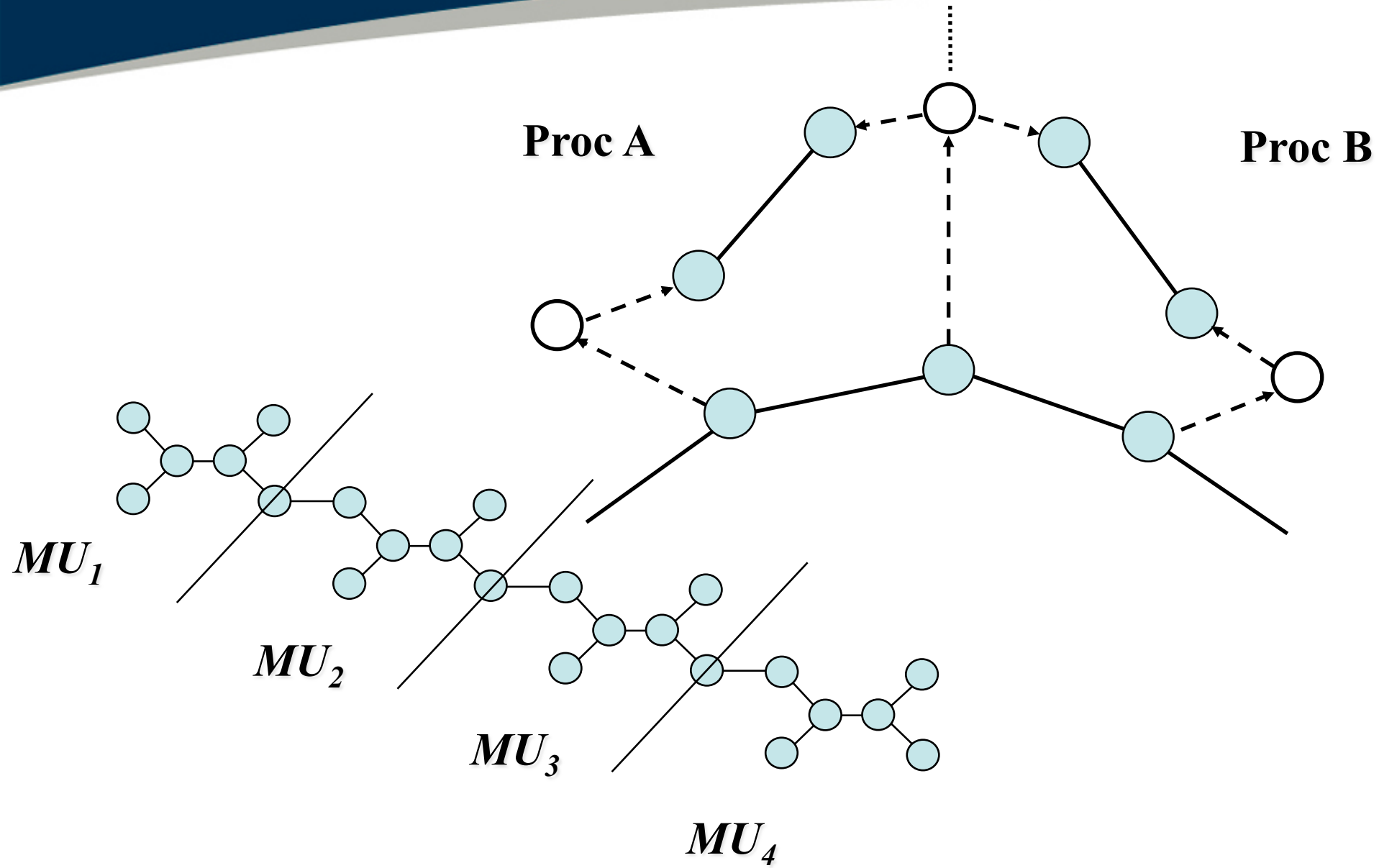
Velocity Verlet integration algorithms can be naturally derived from the non-commutable Liouvile evolution operator by using a second order Suzuki-Trotter expansion. Thus they are symplectic/true ensembles (with conserved quantities) warranting conservation of the phase-space volume, time-reversibility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

Examplary VV Expansion of NVE to NVE$_{kin}$, NVT, NPT & NσT

VV1:

$$x_i(t), v_i(t), f_i(t)$$

$$Thermostat(t \to t + \tfrac{1}{4}\Delta t) \qquad : \tfrac{1}{4}\Delta t$$

$$Barostat(t \to t + \tfrac{1}{2}\Delta t) \qquad : \tfrac{1}{2}\Delta t$$

$$Thermostat(t + \tfrac{1}{4}\Delta t \to t + \tfrac{1}{2}\Delta t) \quad : \tfrac{1}{4}\Delta t$$

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

$$x_i(t + \Delta t) = x_i(t) + \frac{\Delta t}{2} v_i(t + \tfrac{1}{2}\Delta t) \ : \Delta t$$

$$RATTLE\_R(t \to t + \Delta t) \qquad : \Delta t$$

VV2:

$$x_i(t + \Delta t), v_i(t + \tfrac{1}{2}\Delta t), f_i(t + \Delta t) - afresh$$

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

$$RATTLE\_V(t + \tfrac{1}{2}\Delta t \to t + \Delta t) \qquad : \Delta t$$

$$Thermostat(t + \tfrac{1}{2}\Delta t \to t + \tfrac{3}{4}\Delta t) \qquad : \tfrac{1}{4}\Delta t$$

$$Barostat(t + \tfrac{1}{2}\Delta t \to t + \Delta t) \qquad : \tfrac{1}{2}\Delta t$$

$$Thermostat(t + \tfrac{3}{2}\Delta t \to t + \Delta t) \qquad : \tfrac{1}{4}\Delta t$$

- 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 force:

Relative velocity between particles

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

Distance-based screening function

- Random force:

Gaussian random number (zero mean, unity variance)

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

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

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

  – Dissipative force parameter related to fluid viscosity

- Conservative force <u>often</u> 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'

- 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)
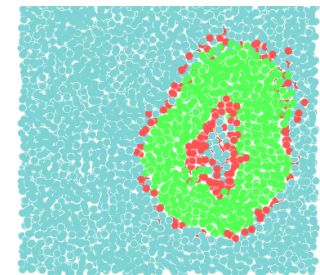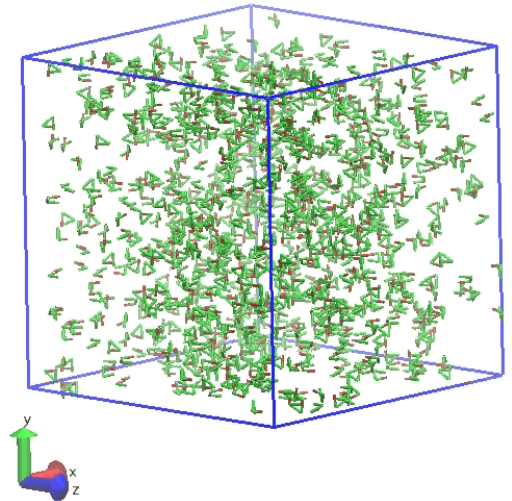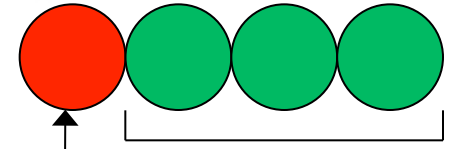
– Example: formation of water drops on hydrophobic surface under influence of gravity
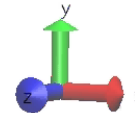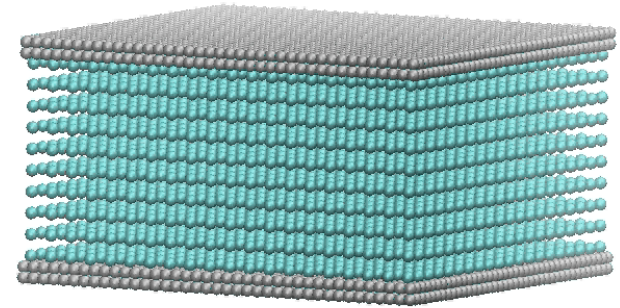
Source: Johansson, *Simulating fluid flow and heat transfer using dissipative particle Dynamics*, Dept. Energy Sci., Lund University (2012)

- **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.

- 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

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- **Radiation damage driven features:**
  - defects analysis
  - boundary thermostats
  - volumetric expansion
  - 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**
- **Direct Metal**
- **Force shifted VdW**
- **I/O driven features Parallel I/O & netCDF**
- **Extra Reporting**

Part 4

DL_POLY I/O Files

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

- **Tabulated interactions**

- **Restart data**

```
           ┌──────────────────────► REVCON
CONFIG ◄────┘
                                     CFGMIN*
REFERENCE*
                                     OUTPUT
HISTORY*
                                     HISTORY*, HISTORF*
CONTROL
                                     DEFECTS*
FIELD
                                     STATIS
TABLE*
                                     MSDTMP*, RSDDAT*
TABEAM*
                                     VAFDAT_*
TABBND*
                                     BNDDAT*, BNDPMF*, BNDTAB*
TABANG*
                                     ANGDAT*, ANGPMF*, ANGTAB*
TABDIH*
                                     DIHDAT*, DIHPMF*, DIHTAB*
TABINV*
                                     INVDAT*, INVPMF*, INVTAB*
REVOLD*
                                     RDFDAT*, VDWPMF*, VDWTAB*
                                     ZDNDAT*
                                     REVIVE
```

DL_POLY_4 I/O FILES
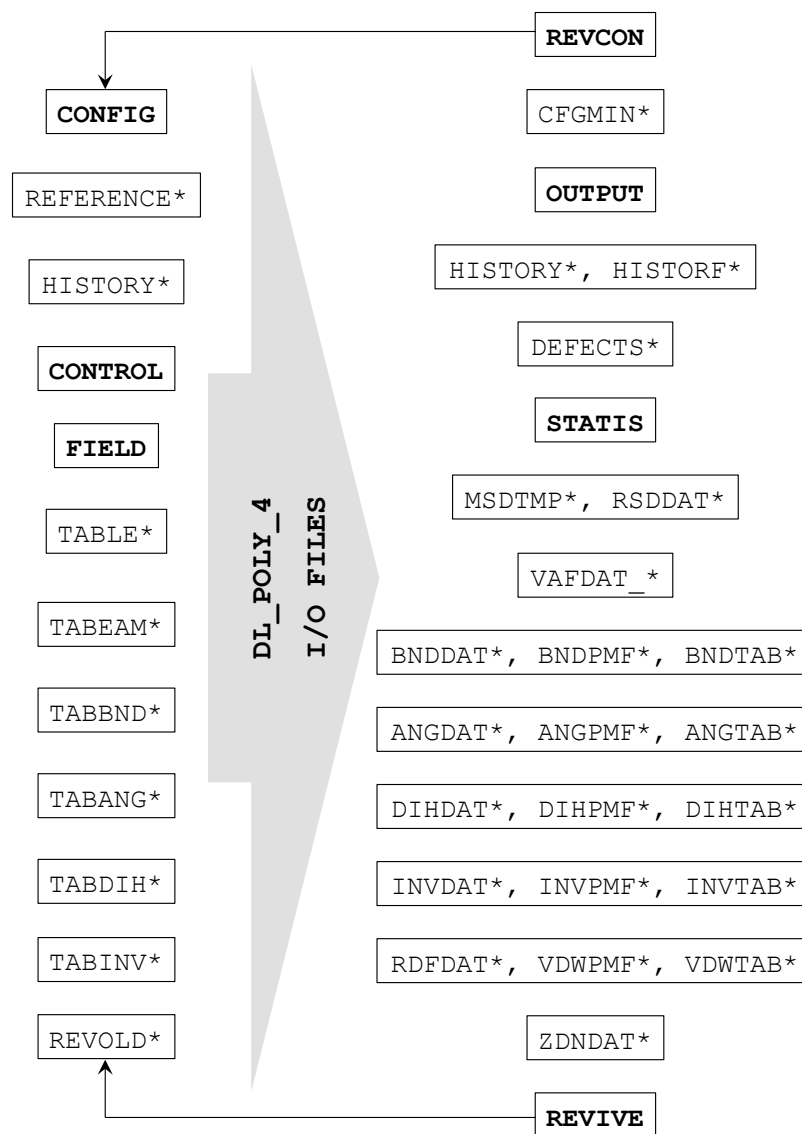
- **Final & CGM configurations**
- **Best CGM configuration**
- **Simulation summary data**
- **Trajectory data**
- **Defects data**
- **Statistics data**

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

- **Intra PDF data**

- **Inter PDF/RDF data**

- **Z density data**
- **Restart data**

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}]

pressure is expressed in k-atm for I/O
angles are expressed in degrees (not radians)

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!

- **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
```

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- **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
```

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- **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
```

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- 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

- **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)**

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- **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, CFG and relaxed shell model iteration data**
  - **Warning & Error reports**

- **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
```

- **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)**

- 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
```

- 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

300,763,000 NaCl with full SPME electrostatics evaluation on 1024 CPU cores
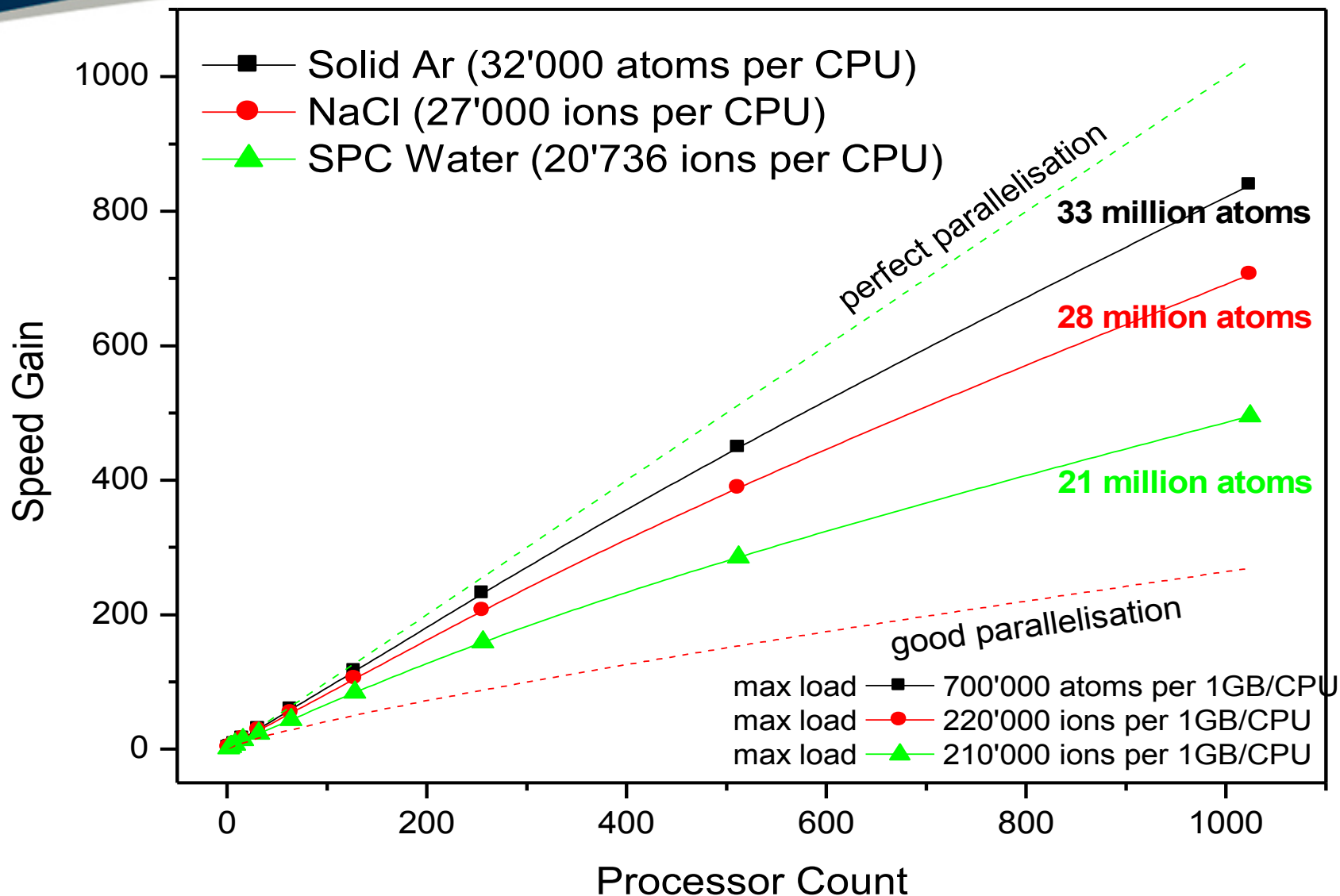
		HECToR (2013 – Cray XE6)
Start-up time	$\approx$ 60 min	$\approx$ 15 min
Timestep time	$\approx$ 68 sec	$\approx$ 23 sec
FFT evaluation	$\approx$ 55 sec	$\approx$ 18 sec

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 $2\,\mu$m along the side and as the wavelength of the visible light is $0.5\,\mu$m so it should be theoretically possible.
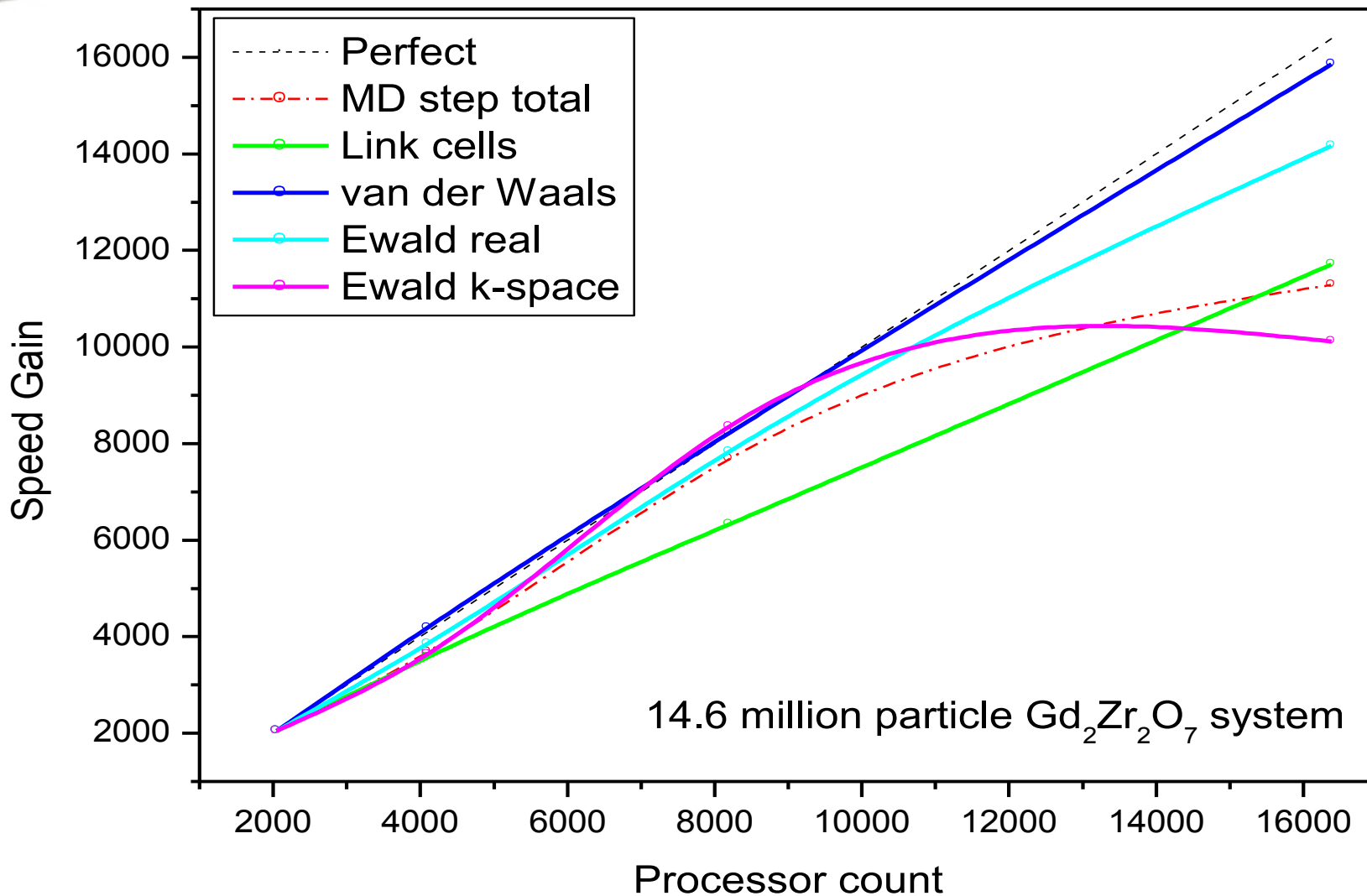
Weak Scaling
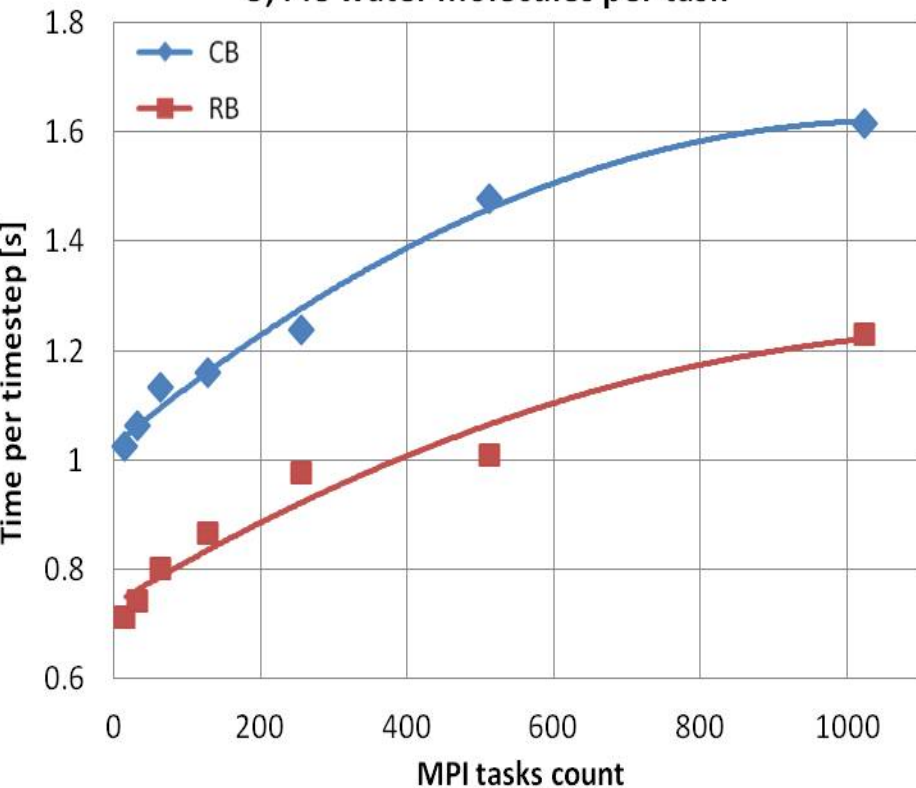
Science & Technology
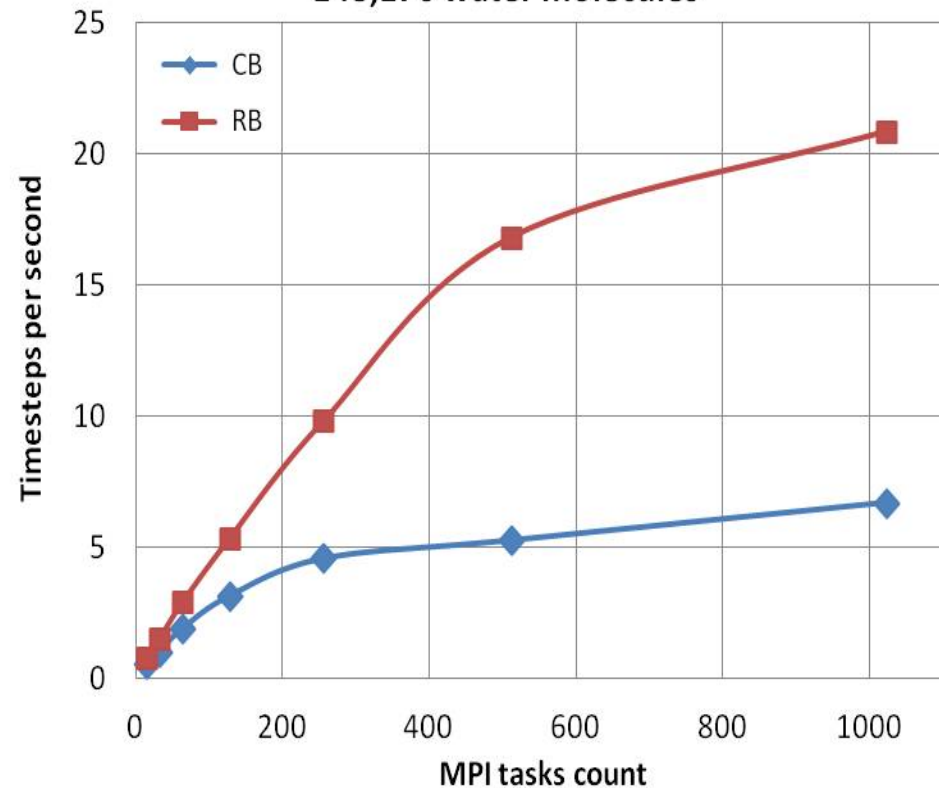Facilities Council

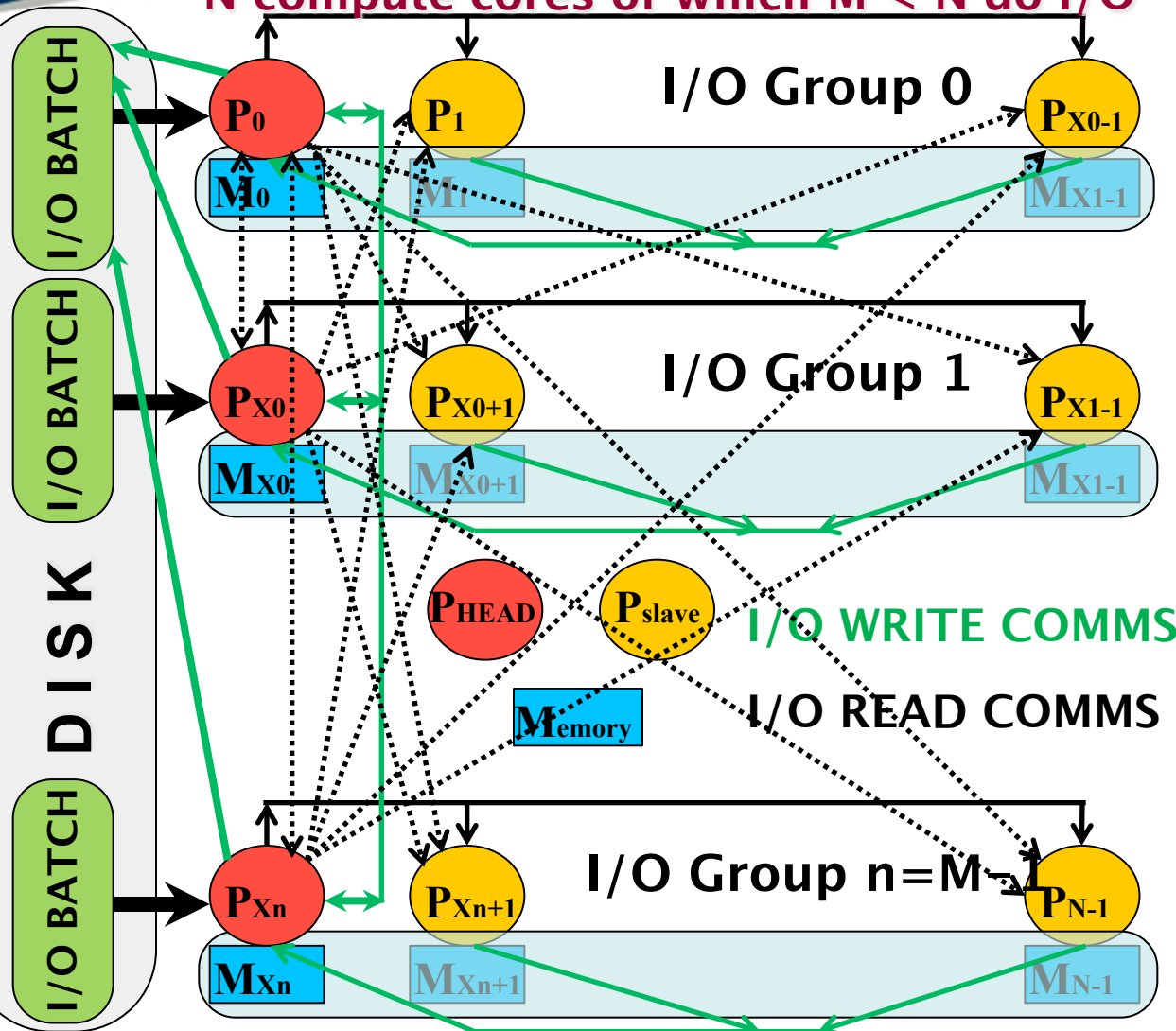# HECToR (Cray XE6) 2013

HECToR (Cray XE6) 2013
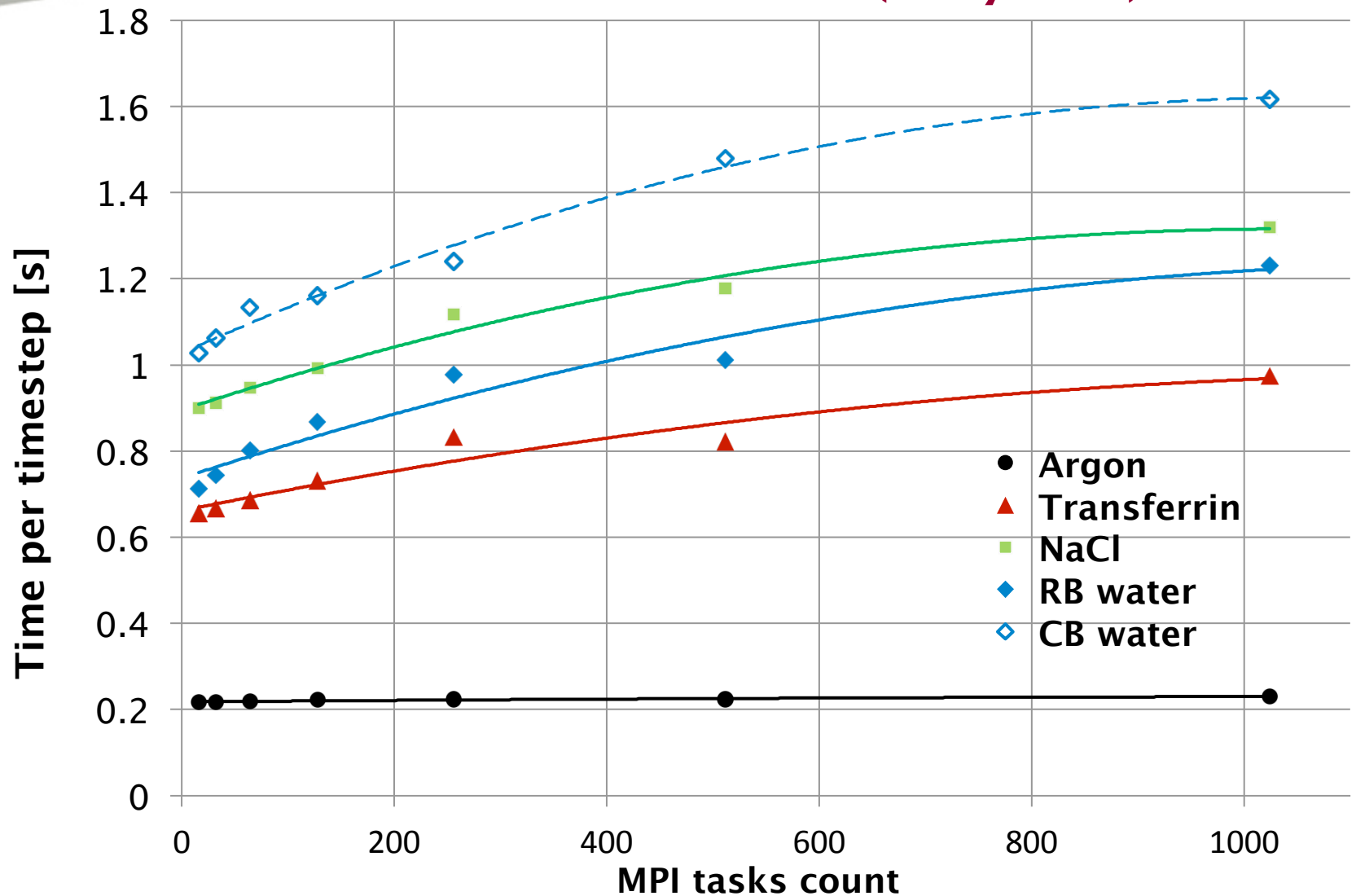
1. **Serial read and write (sorted/unsorted)** – where only a single MPI task, the master, handles it all and all the rest communicate in turn to or get broadcasted to while the master completes writing a configuration of the time evolution.

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

N compute cores of which M < N do I/O

I/O Group 0

I/O Group 1

P_{HEAD} P_{slave} I/O WRITE COMMS

M_{emory} I/O READ COMMS

I/O Group n=M-1

- 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

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

- Register at **http://www.ccp5.ac.uk/DL_POLY/**

- Registration provides the decryption - procedure and password (sent by e-mail)

- Source is supplied by anonymous FTP

- Source is in an encrypted zip file

- Successful unpacking produces a unix directory structure

- Test and benchmarking data are also available on the FTP

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

WWW:

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

FTP:

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

PORTAL:

http://community.hartree.stfc.ac.uk/portal/site/DL_SOFTWARE/

- **Downloads are available from CCPForge at http://ccpforge.cse.rl.ac.uk/gf/project/dl_poly_classic/**

- **No registration required – BSD licence**

- **Download source from: CCPForge: Projects: DL_POLY Classic: Files: dl_poly_classic: dl_poly_classic1.9**

- **Sources is a in tarred and gzipped form**

- **Successful unpacking produces a unix directory structure**

- **Test data are also available**

DL_POLY

- **build** — Home of makefiles
- **source** — DL_POLY source code
- **execute** — Home of executable & Working Directory
- **java** — Java GUI source code
- **utility** — Utility codes
- **data** — Test data

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The slide content:

DL_POLY_C v/s DL_POLY_4 Usage
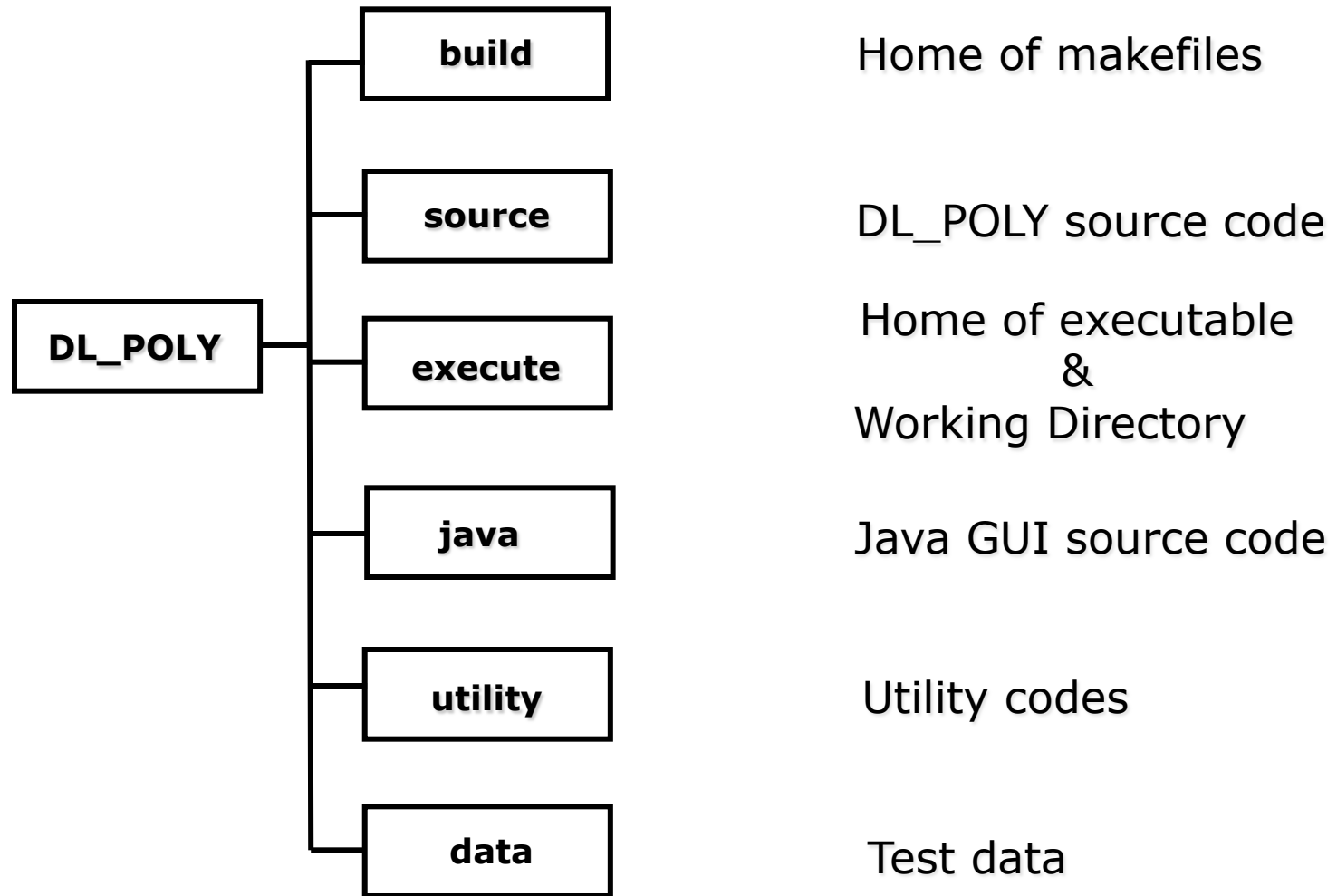
1. Note differences in capabilities (e.g. linked rigid bodies) !!!
2. Less than 10,000 atoms (if in parallel)? – DL_POLY Classic
3. More than 30,000 atoms? – DL_POLY_4
4. Ratio cell_width/r_{cut} < 3 (in any direction)? – DL_POLY_Classic
5. Less than 500 particles per processor? – DL_POLY_Classic

DL_POLY_Classic

Simple molecules (no SHAKE):
- 8 or less, 10,000 atoms
- 16 or less, 20,000 atoms
- 32 or less, 30,000 atoms

Simple ionics:
- 16 or less, 10,000 atoms
- 64 or less, 20,000 atoms
- 128 or less, 30,000 atoms

Molecules (with SHAKE):
- 64 max!

DL_POLY_4

- Golden Rule 1: No fewer than 3x3x3 link cells per processor (if in parallel)
- Golden Rule 2: No fewer than 500 particles per processor (if in parallel)!

Part 6

DL_POLY_Classic Functionality
W. Smith

- Hyperdynamics
  - Bias potential dynamics
  - Temperature accelerated dynamics
  - Nudged elastic band
- Solvation properties:
  - Energy decomposition
  - Spectroscopic solvent shifts
 - Free energy of solution
- Metadynamics

I/O Files

Standard Input	Special Input	Standard Output	Special Output
CONFIG	REVOLD	OUTPUT	HISTORY
FIELD	TABLE	STATIS	RDFDAT
CONTROL	TABEAM	REVIVE	ZDNDAT
		REVCON	
	HYPOLD		HYPRES
			EVENTS
			CFGBSNnn
			CFGTRAnn
			PROnn.XY
			SOLVAT
			FREENG
	STEINHARDT		METADYNAMICS
	ZETA		
			CFGMIN

Operation Type:
Standard use
Hyperdyn./TAD
Solvation
Metadynamics
Optimisation

- Molecular Solvation Energy
  - Energy decomposition
  - Energy distribution functions
- Free Energy of Solvation
  - Mixed Hamiltonian method
  - Thermodynamic Integration
- Solution Spectroscopy
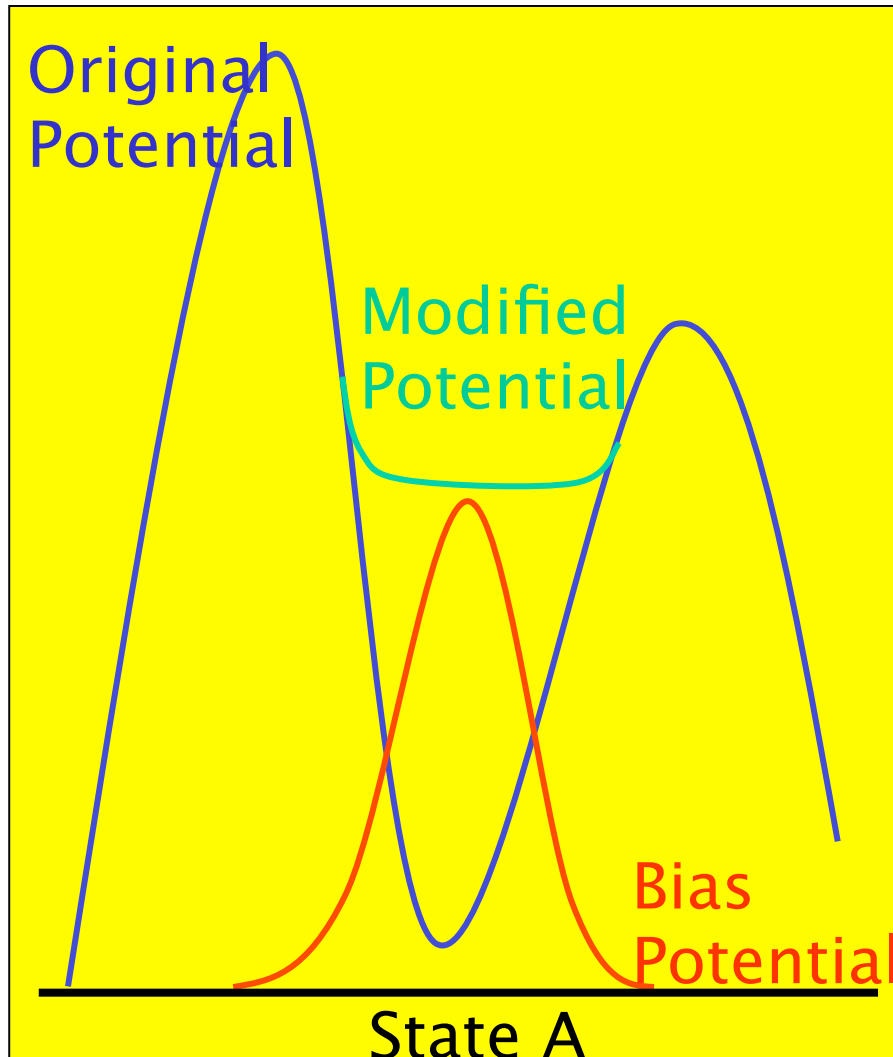 - Solvent induced shifts
  - Solvation relaxation
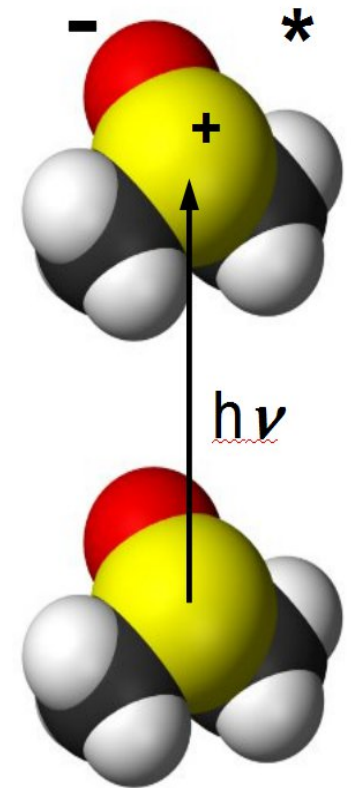
- SOLVAT
  - Breakdown of system energy based on molecular types
  - Energies of ground and excited states

- FREENG
  - Energy data for thermodynamic integration

- Bias Potential Dynamics

- Temperature Accelerated Dynamics

- Metadynamics

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Original Potential

Modified Potential

Bias Potential

State A

- Construct bias potential to reduce well depth of state A.

- Bias potential is zero at saddle point.

- Ratios of rates from state A to states B, C, etc. preserved:

$$\frac{k_{TST}^{A \to B}}{k_{TST}^{A \to C}} = \frac{k_{TST}^{A_b \to B}}{k_{TST}^{A_b \to C}}$$

- Suitable bias potential:

$$V_b(R^N) = \frac{(E - V(R^N))^2}{(\lambda + E - V(R^N))}$$

$$\langle f \rangle_A = \frac{\iint f(\Gamma^N)\exp(-\beta H(\Gamma^N))d\Gamma^N}{\iint \exp(-\beta H(\Gamma^N))d\Gamma^N}$$

$$\langle f \rangle_A = \frac{\iint f(\Gamma^N)\exp(-\beta[H(\Gamma^N)+V_b(R^N)-V_b(R^N)])d\Gamma^N}{\iint \exp(-\beta[H(\Gamma^N)+V_b(R^N)-V_b(R^N)])d\Gamma^N}$$

$$\langle f \rangle_A = \frac{\langle f(\Gamma^N)\exp(\beta V_b[R^N])\rangle_{A_b}}{\langle \exp(\beta V_b[R^N])\rangle_{A_b}}$$

Now $\quad k_{TST} = \langle |\underline{V}_N|\delta(R^*)\rangle_A$

So $\quad k_{TST} = \langle |\underline{V}_N|\delta(R^*)\exp(\beta V_b[R^N])\rangle_{A_b} / \langle \exp(\beta V_b[R^N])\rangle_{A_b}$

and $\quad k_{TST} = \langle |\underline{V}_N|\delta(R^*)\rangle_{A_b} / \langle \exp(\beta V_b[R^N])\rangle_{A_b}$ if $V_b[R^*]=0$

or $\quad k_{TST} = k_{TST}^{A_b} / \langle \exp(\beta V_b[R^N])\rangle_{A_b}$

First order reactions:
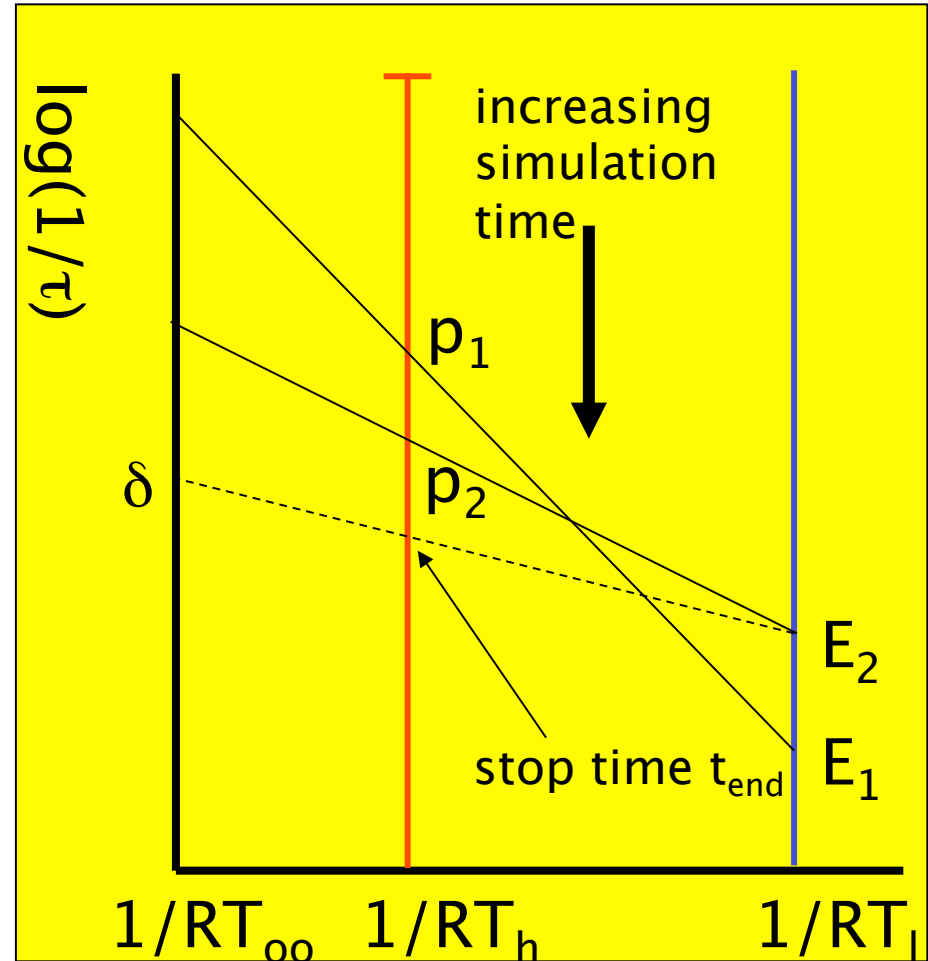
Hopping probability:

$$P \, dt = k \exp(-kt) \, dt$$

Lifetime of state: $\tau = 1/k$

Arrhenius:

$$k = A \exp(-E^*/RT)$$
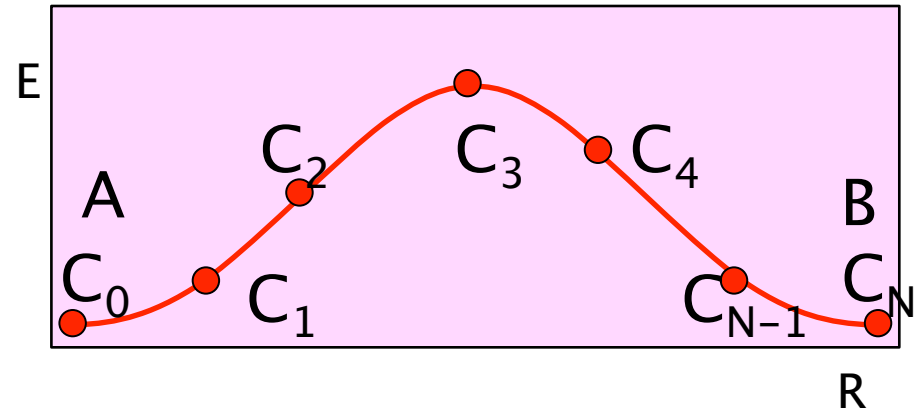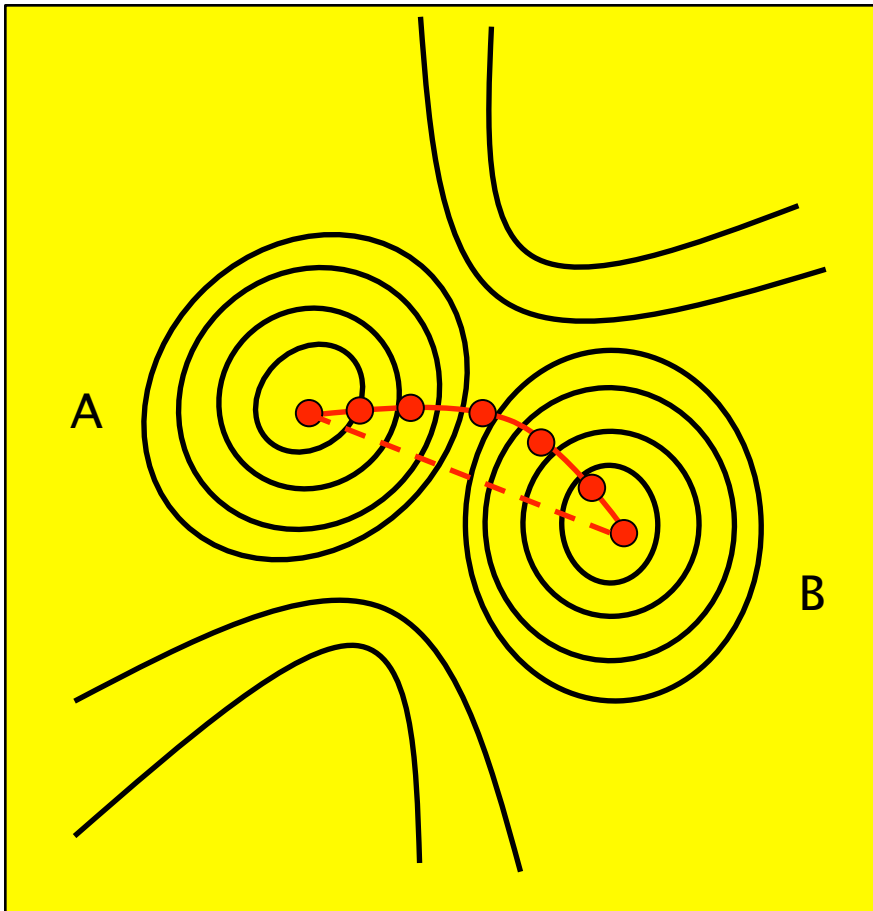
$$\log(1/\tau) = \log A - E^*/RT$$

- Simulate system at high T & watch for transitions
- When transition found, stop simulation and:
  - Determine activation energy using nudged elastic band
  - Record transition time, save `new' state configuration
- Restart simulation in original state with new velocities.
- Search for new transitions. Hence build `library' of transition data.
- Stop searching after time t_{end} given by:

$$t_{end}=\exp[E_2+(T_h-T_l)(E_2-\delta)/T_h]$$

- Commence new search from `first' low T state.

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E

C_2 C_3 C_4

A   B

C_0 C_1 C_{N-1} C_N

R

A

B

- N+1 configs (C_0…C_N) linearly interpolated From A to B
- Connect by spring (stiffness K)
- Remove `off tangent' forces
- Minimise all configs subject to presence of spring forces
- Resulting path is reaction path through saddle point

- Simulate set of competing processes $\left\{p_i; i = 1, \cdots, N\right\}$
- Rate of process p_i is r_i (make a list).
- Define sum of rates

$$R = \sum_{i=1}^{N} r_i$$

- Generate random number

$$u : 0 < u \leq 1$$

- Select process

$$p_i : \left\{\sum_{j=1}^{i-1} r_j\right\} < uR < \left\{\sum_{j=1}^{i} r_j\right\}$$

$$R$$

$$p_i$$

- Advance time

$$uR$$
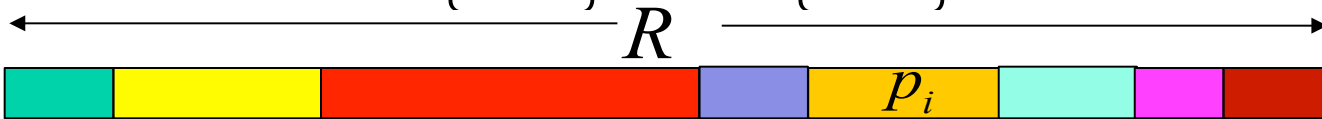
- Repeat!

$$\Delta t = -\log(u) / R$$

In the CONTROL file:

```
tad
units kJ
num_block      500
num_track      10
blackout       1000
catch_radius   3.5
neb_spring     10.0
deltad         6.91
low_temp       40.0
force          0.0025
endtad
```

OR

```
bpd path
units eV
vmin  –3.9935E03
ebias –3.5000E03
num_block      300
num_track      10
catch_radius   3.5
neb_spring     1.0
force          0.00025
endbpd
```
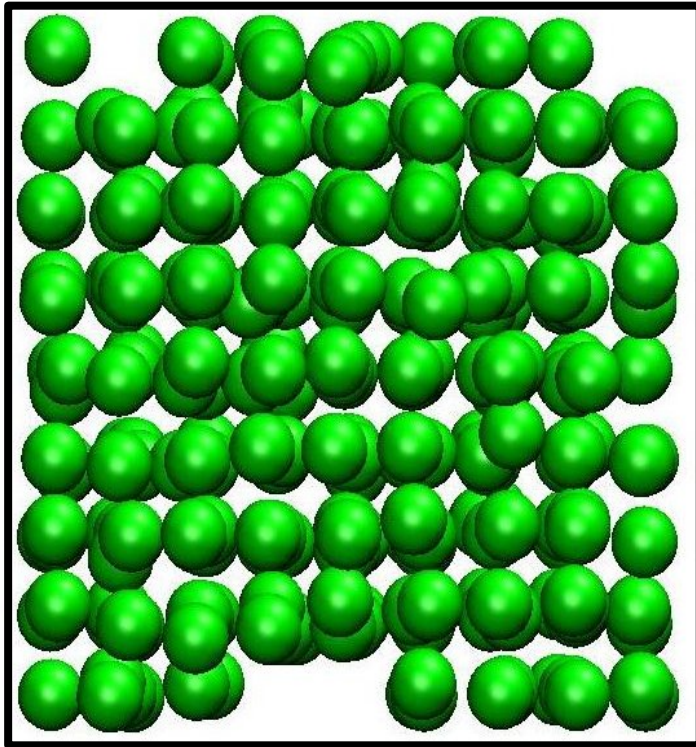
Additional files for TAD and Bias potential dynamics:

- HYPRES/HYPOLD – restart files
- EVENTS –program activity report
- CFGBSNnn – Basin CONFIG files (new states)
- PROnn.XY – Reaction path profiles
- CFGTRAnn – Tracking CONFIG files

Subdirectories required in *execute* directory: BASINS, PROFILES, TRACKS

255 L-J Argon atoms FCC crystal + 1 vacancy

- Atoms `hop' into vacancies
- Each vacancy has 12 nearest neighbour atoms
- So 12 possible escapes from PE basin
- Use TAD to find them!
- Use NEB to find activation energy
- Extrapolate to low temperature for low T rate
- Put results into KMC simulation

EVENTS file extract:

Event	nΔt	Basins	Nt	ΔE	Time(ps)	Extrap.(ps)	Stop time(ps)
TRA	38500	0	1	1	7.28338E+00	3.82250E+01	4.31244E+07	2.04398E+03
TRA	55500	0	2	1	7.20808E+00	5.49650E+01	5.36891E+07	2.04398E+03
TRA	127500	0	3	1	7.28160E+00	1.26145E+02	1.41830E+08	2.04398E+03
TRA	750500	0	4	1	7.19597E+00	7.47515E+02	7.13444E+08	2.04398E+03

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998 NaCl ions rocksalt crystal + 2 vacancies
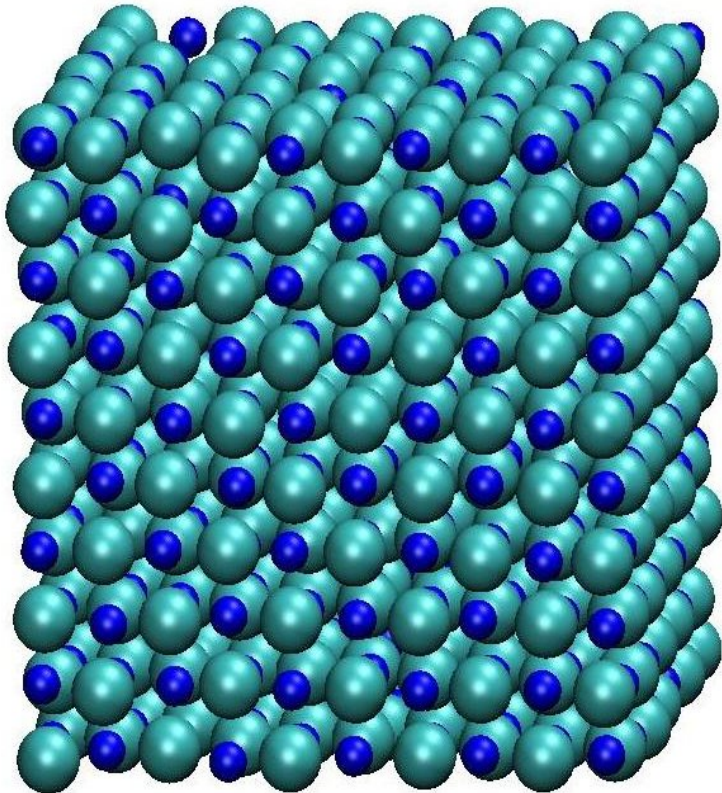
- Overall neutral system
- Ions `hop' into vacancies
- Escapes from PE basin unknown (a priori)
- Use BPD to find them!
- Use NEB to find activation energy
- Extrapolate hopping time for zero bias
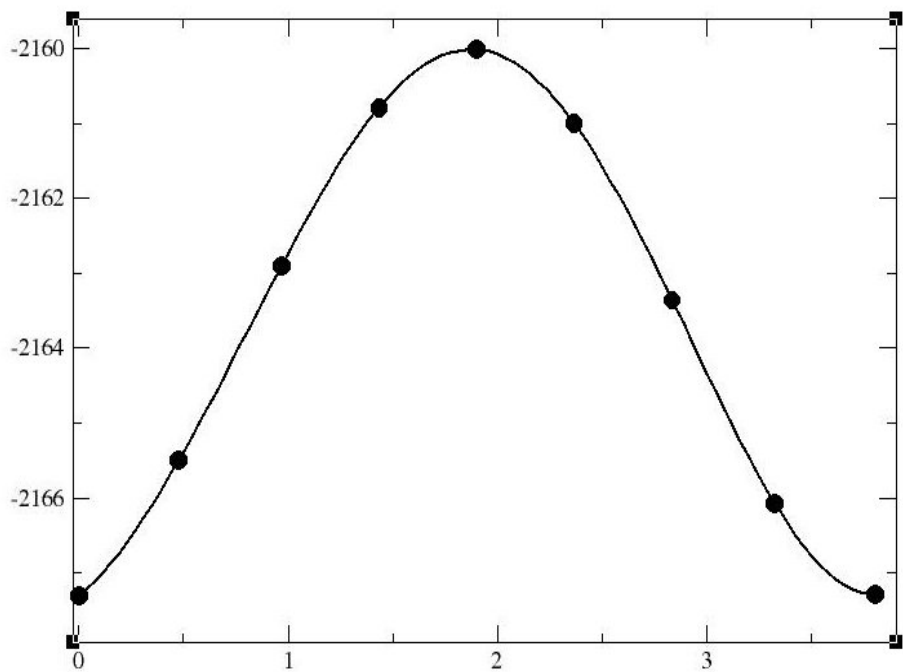- Put results into KMC simulation

EVENTS file extract:

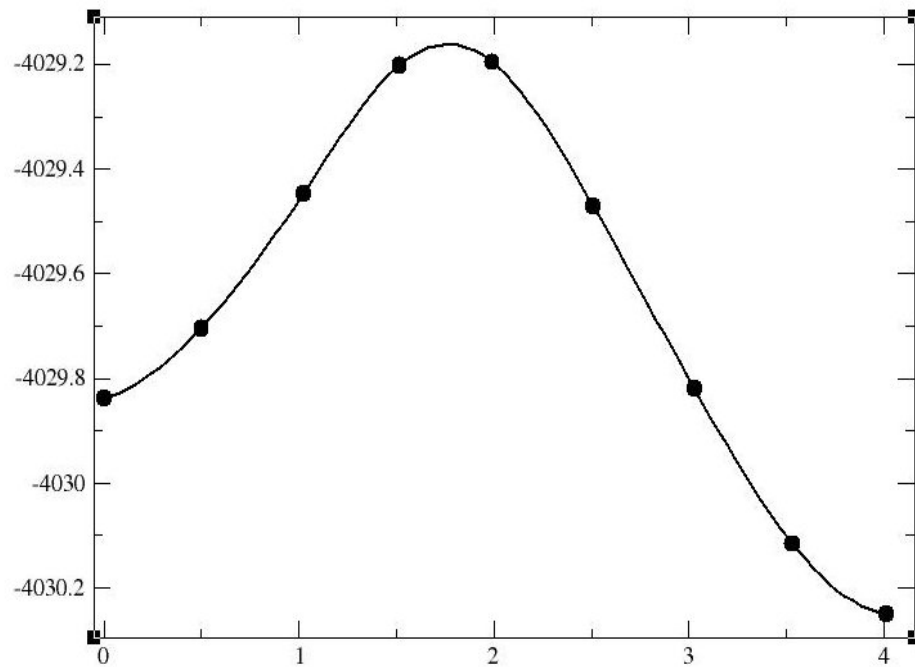| Event	$n\Delta t$	Basins		Nt	ΔE	Time(ps)	Extrap.(ps)
TRA	4500	0	1	1	6.74301E−01	4.39500E+00	7.34793E+03
TRA	399300	1	2	1	1.11127E+00	3.99185E+02	6.45155E+05
TRA	466500	2	3	1	6.57466E−01	4.66495E+02	7.53837E+05

Sodium   Chloride

Lennard Jones Argon

Metadynamics is a method devised by Alessandro Laio and Michele Parrinello for accelerating the exploration of a free energy landscape as the function of *collective* variables.

Method:

- The system potential energy is augmented by a time-dependent bias potential consisting of Gaussian functions of the collective variables

- The longer a simulation remains in a particular free energy minimum, the larger the bias potential becomes – thus forcing the system to seek out a new thermodynamic state.

- The accumulated bias potential provides a description of the free energy surface

A. Laio & M. Parrinello, PNAS **99** (2002) 12562
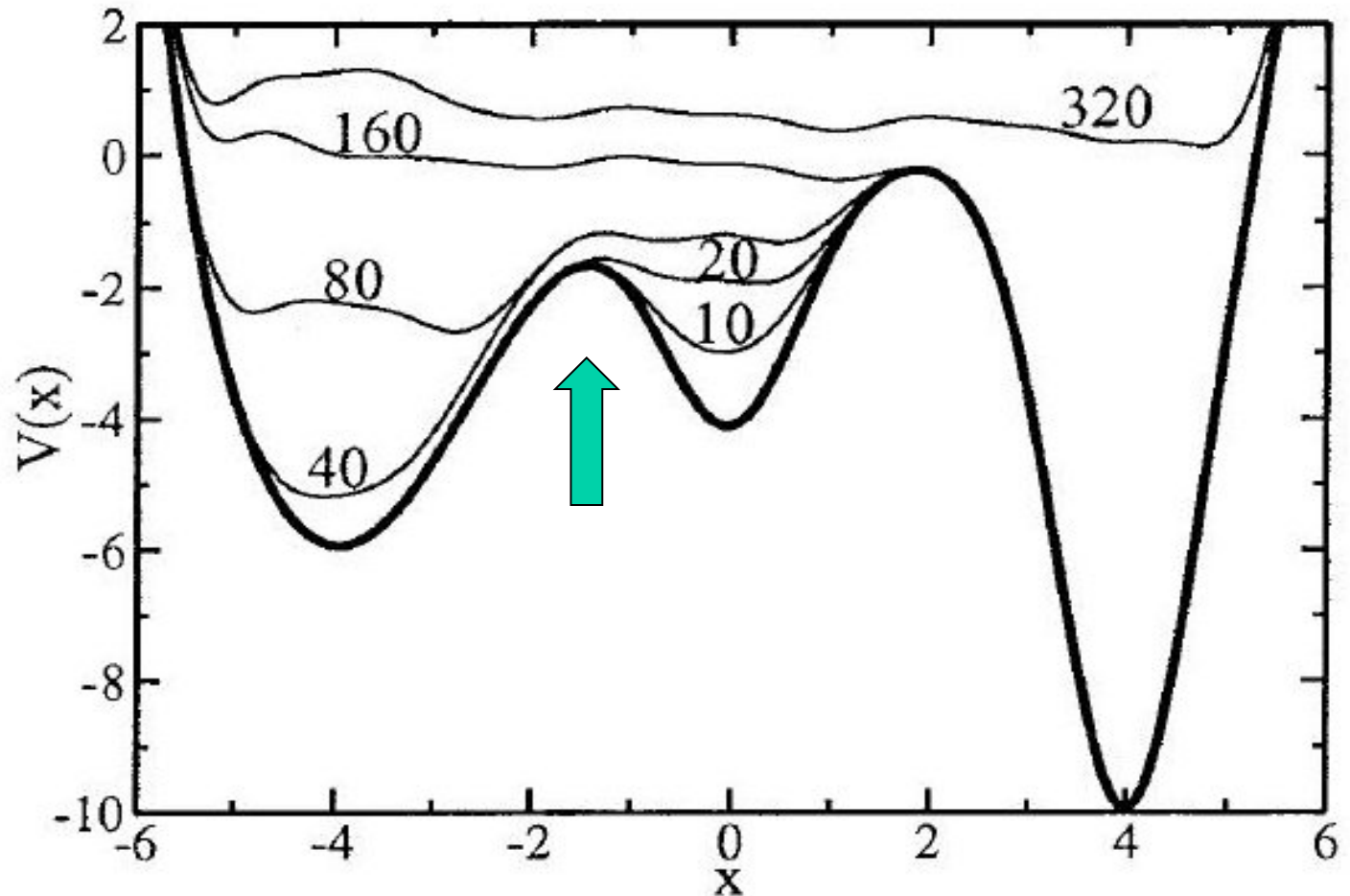
A collective variable is a single number that defines an atomic structure (i.e. it is a function of $\underline{r}^N$). Most often they are called **Order Parameters**. Particular examples used in metadynamics are:

- The system potential energy: $U(\underline{r}^N)$

- Simulation cell vectors: $\underline{\underline{h}} = (\underline{a}, \underline{b}, \underline{c})$

- The Steinhardt order parameters: $Q_\ell^{\alpha\beta}$

- Tetrahedral order parameters: ζ_α

$Q_\ell^{\alpha\beta}$ and ζ_α are maximum for particular structures.
Defining the bias potential in terms of order parameters allows destabilization of particular structural phases.

Metadynamics Formulae

Order parameter vector: $\underline{s}^M(\underline{r}^N) = \left\{ s_1(\underline{r}^N), \cdots, s_M(\underline{r}^N) \right\}$

System Hamiltonian: $H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(\underline{r}^N) + V[\underline{s}^M(\underline{r}^N), t]$

Bias Potential: $V[\underline{s}^M(\underline{r}^n), t] = W \sum_{k=1}^{N_g} \exp\left[-\left| \underline{s}^M(\tau_k) - \underline{s}^M(t) \right|^2 / 2\delta h^2 \right]$

W and δh are chosen to `fill' surface at acceptable rate

Force: $\underline{f}_i = -\underline{\nabla}_i U(\underline{r}^N) - \sum_{j=1}^{M} \frac{\partial V}{\partial s_j} \underline{\nabla}_i s_j(\underline{r}^N)$

Free Energy Surface: $F_g(\underline{s}^M) = -\lim_{t \to \infty} V[\underline{s}^M(\underline{r}^N), t]$

- **METADYNAMICS**
  - Data defining the metadynamics hypersurface
- **STEINHARDT**
  - Defines the Steinhardt order parameters
- **ZETA**
  - Defines the tetrahedral order parameters

$$Q_\ell^{\alpha\beta} = \left[\frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} \left| \frac{1}{N_C N_\alpha} \overline{Q}_{\ell m}^{\alpha\beta} \right|^2 \right]^{1/2}$$

for atom types α and β, with

$$\overline{Q}_{\ell m}^{\alpha\beta} = \sum_{b=1}^{N_b} f_c(r_b) Y_{\ell m}(\theta_b, \phi_b)$$

where b runs over all N_b vectors connecting atom types α and β and

$$f_c(r) = \begin{cases} 1 & \text{if } r \le r_1 \\ \frac{1}{2}\left\{ \cos\left[\frac{(r-r_1)}{(r_2-r_1)} \pi \right] + 1 \right\} & \text{if } r_1 < r \le r_2 \\ 0 & \text{if } r > r_2 \end{cases}$$

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$$T_\alpha = \frac{1}{N_c N_\alpha} \sum_{i=1}^{N_\alpha} \sum_{j \neq i}^{N_\alpha} \sum_{k > j}^{N_\alpha} f_c(r_{ij}) f_c(r_{ik}) (\cos\theta_{jik} + 1/3)^2$$
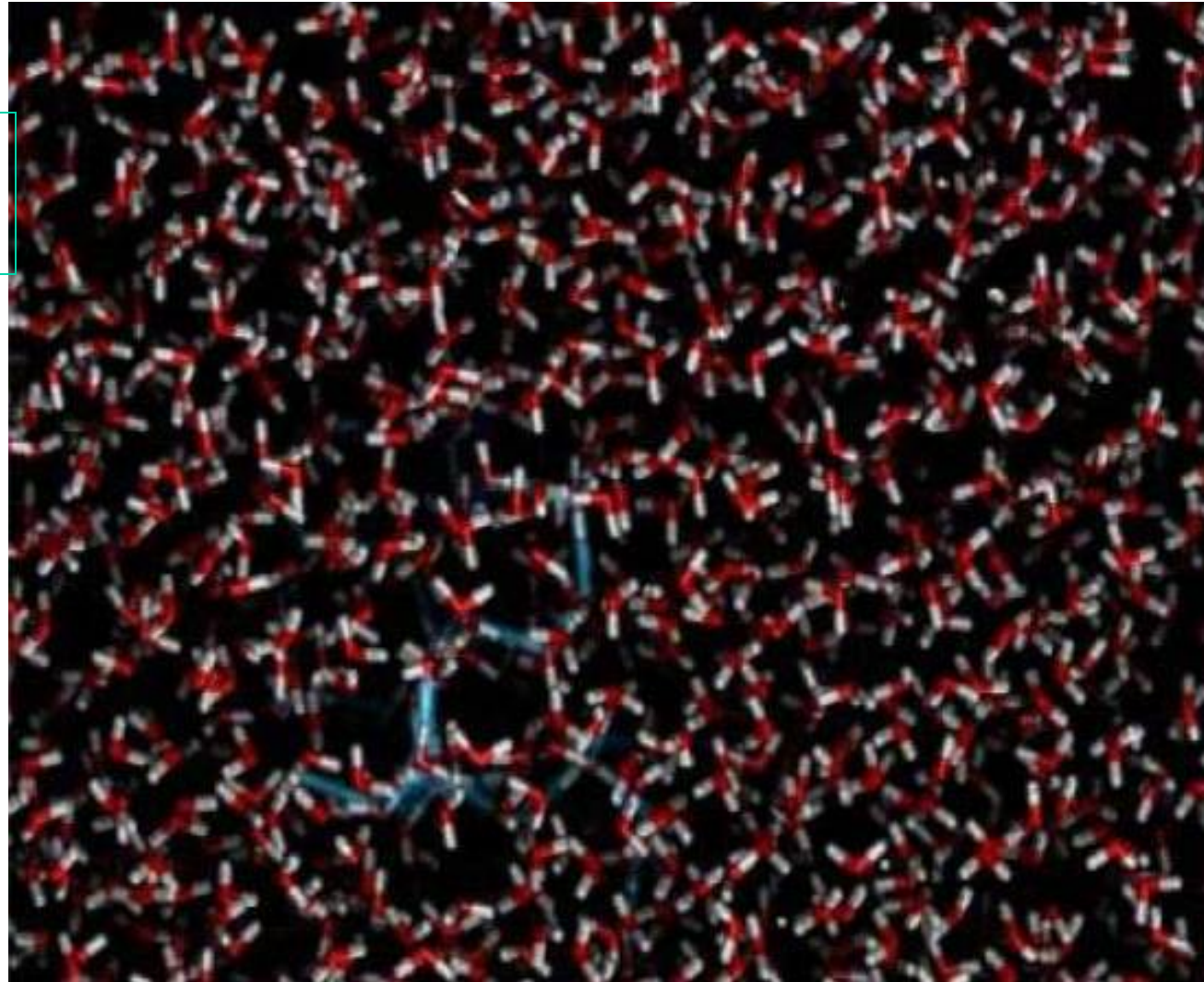
Where i, j, k run over all N_α atoms of species α and N_c is the number of pairs of atoms linked to atom α (assuming all atoms are of type α)

Bias:
Q_4^{OO}, Q_6^{OO}, T & PE

0.5ns

D Quigley and PM Rodger, Molec. Sim. 35 (2009) 613

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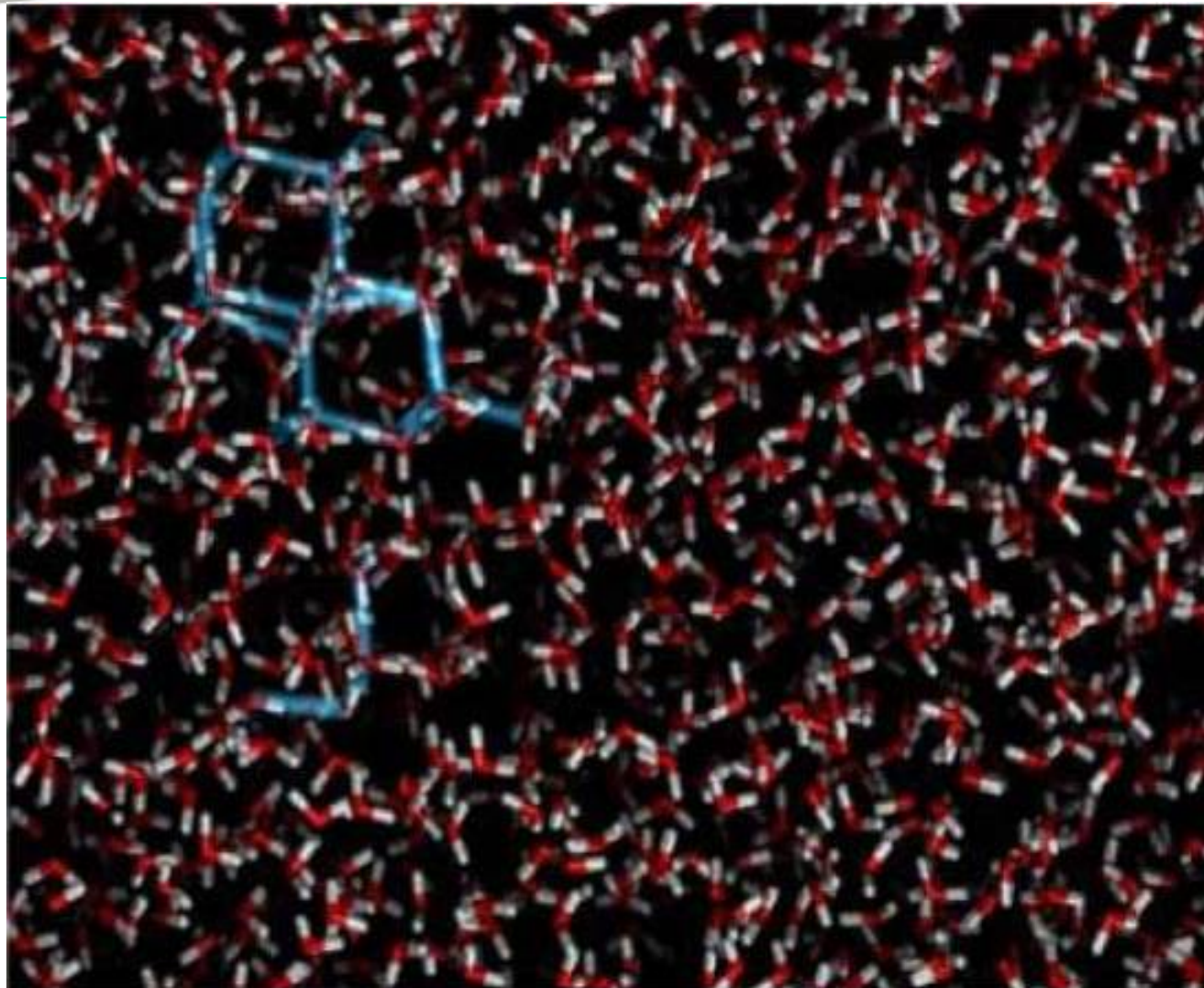**Bias**:
Q_4^{oo}, Q_6^{oo}, T & PE

0.75ns

D Quigley and PM Rodger, Molec. Sim. 35 (2009) 613
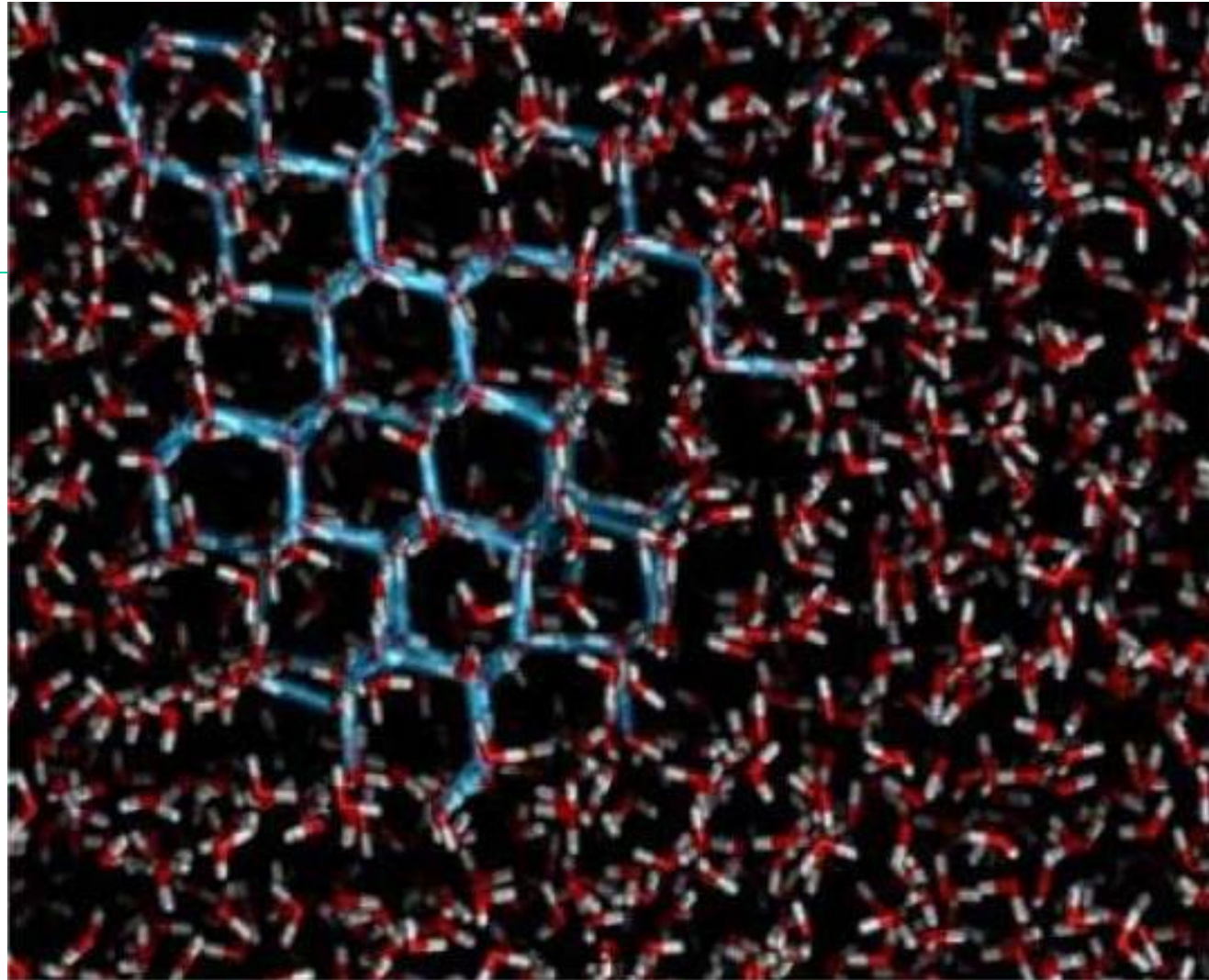
Bias:
$Q_4{}^{OO}$, $Q_6{}^{OO}$, T & PE

1.25ns

D Quigley and PM Rodger, Molec. Sim. 35 (2009) 613

Bias:
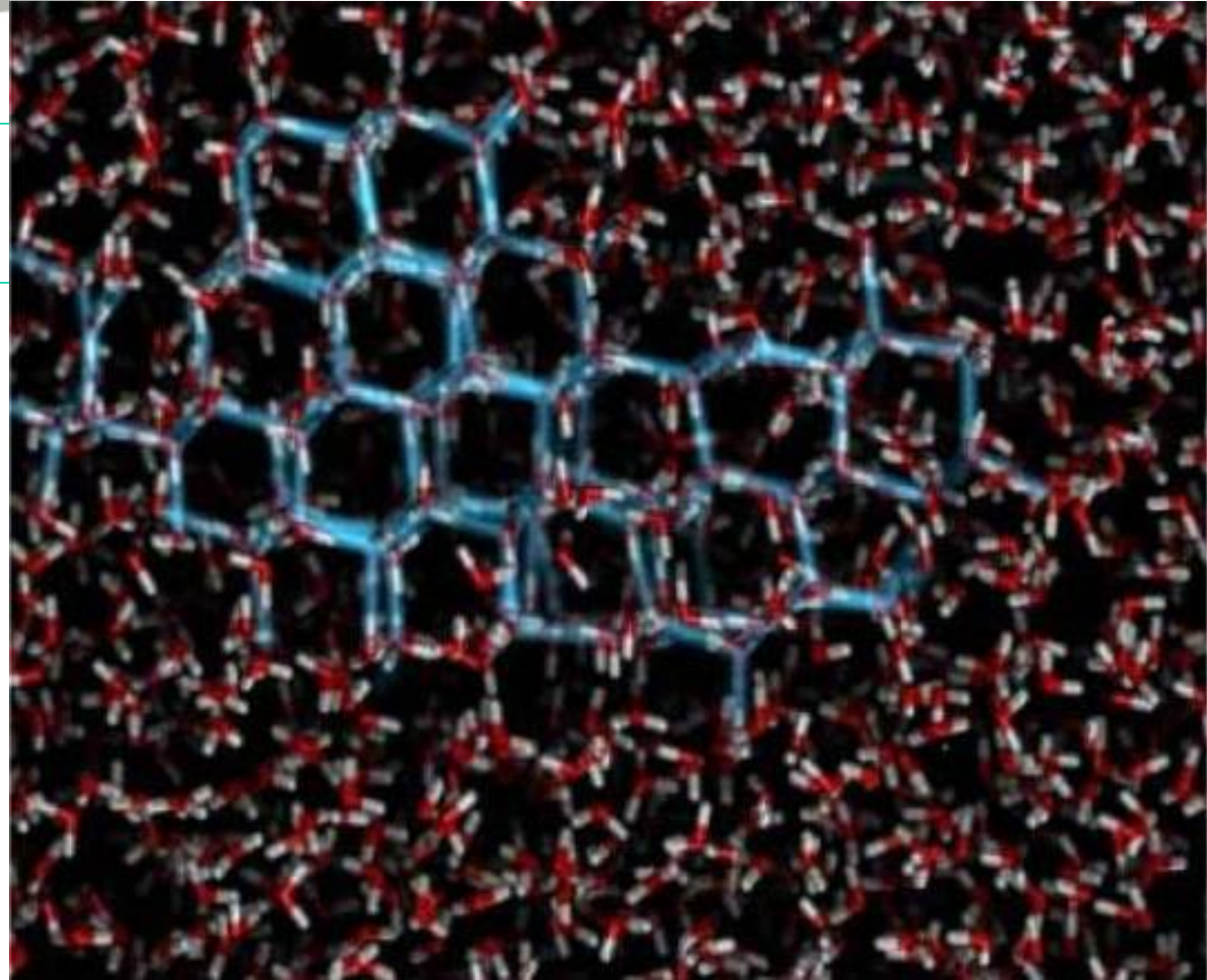Q_4^{OO}, Q_6^{OO}, T & PE

1.5ns

D Quigley and PM Rodger, Molec. Sim. 35 (2009) 613

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- **DL_POLY Classic is free**

- **It's very versatile with advanced features**

- **Go get it!**

Part 7

The DL_POLY Java GUI
W. Smith

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- 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

- 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

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

  java -jar ../java/GUI.jar

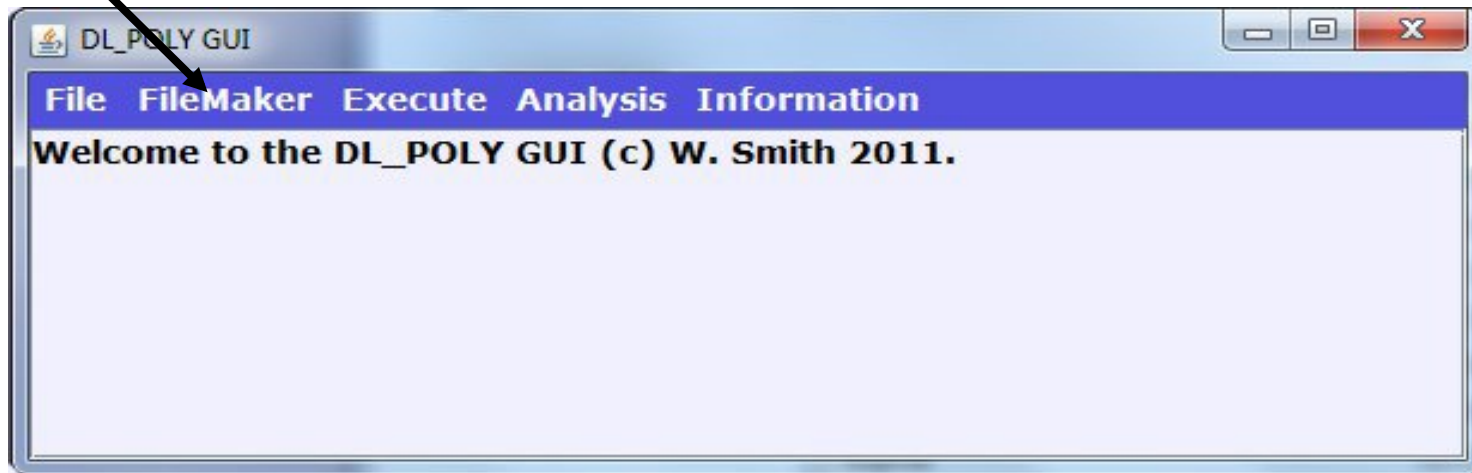- Colour scheme options:

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

with *colourscheme* one of:

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

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Menus

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DL_POLY GUI

| File | FileMaker | Execute | Analysis | Inform |

Welc | CONTROL | POLY GUI (c) W. Smith
Activ | CONFIG ▶ | making ceramic FIELD f
| FIELD ▶ |
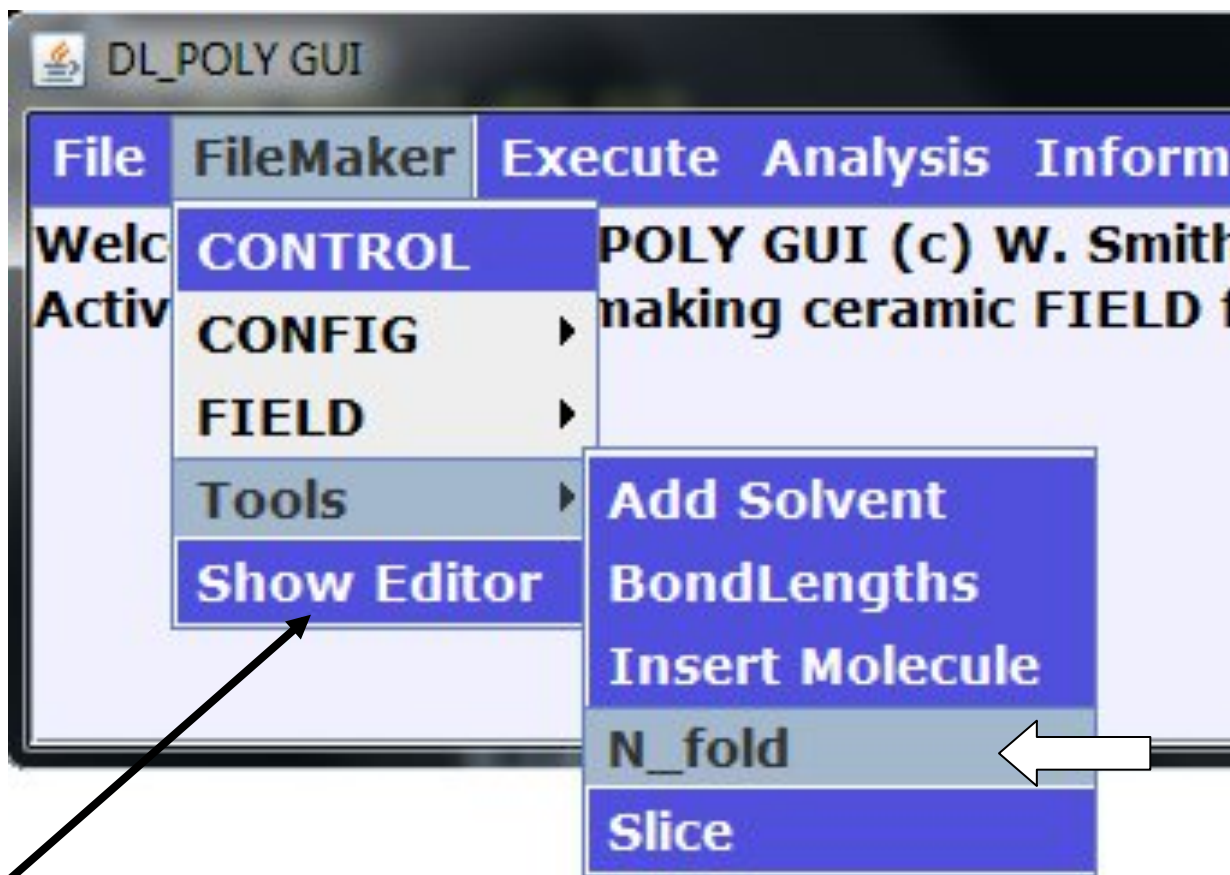| Tools ▶ | Add Solvent
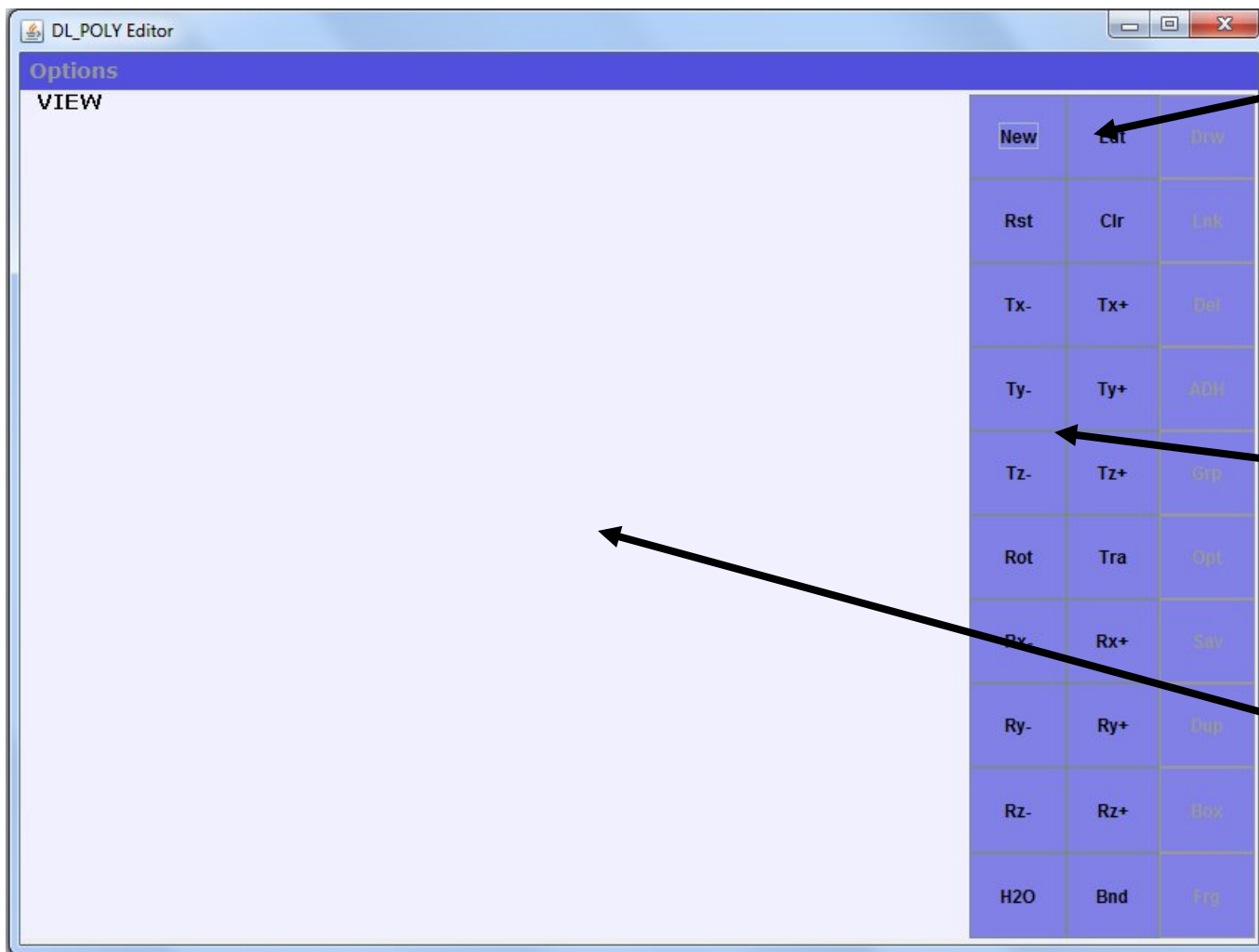| Show Editor | BondLengths
| Insert Molecule
| N_fold
| Slice

Show
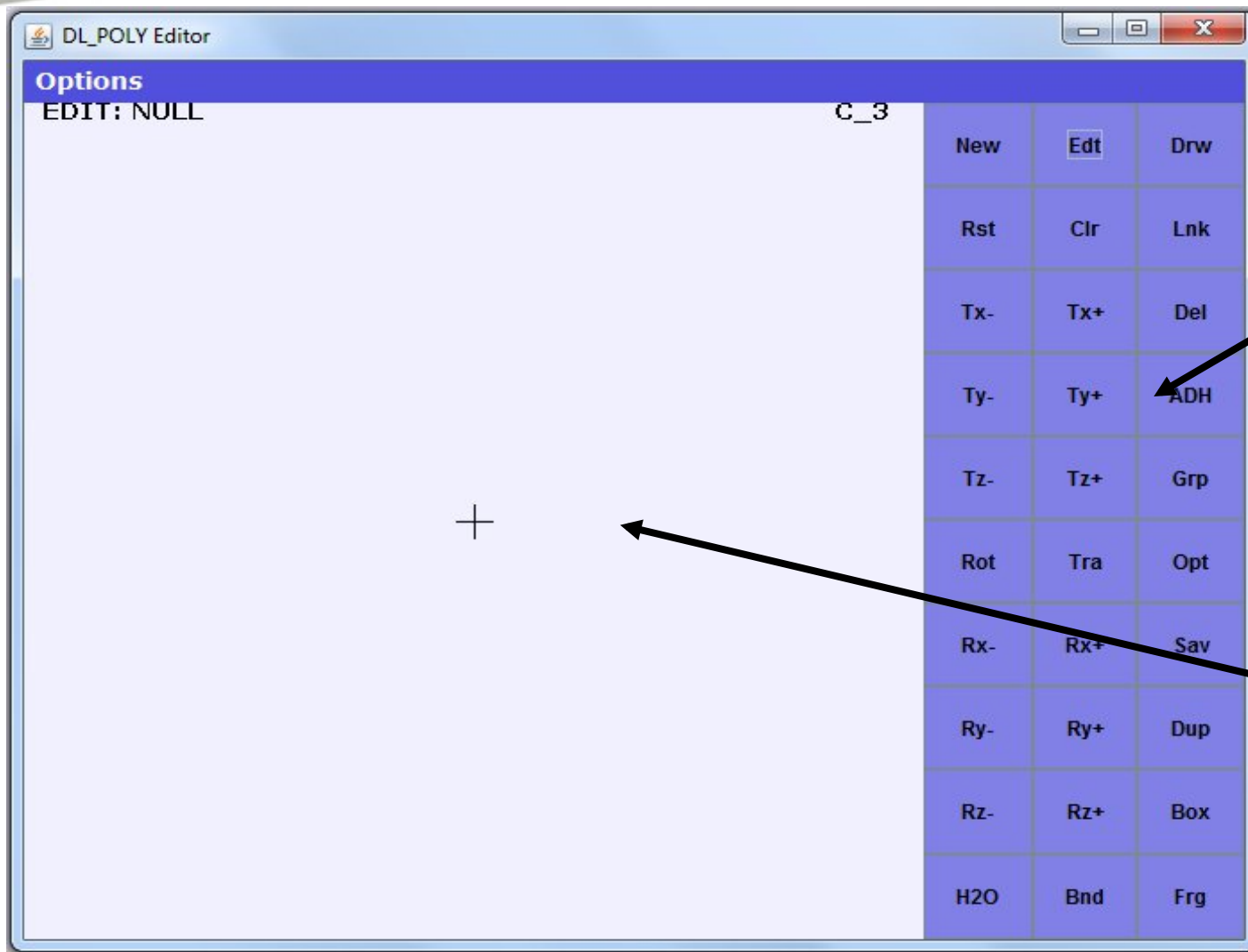Editor
Option

The Molecular Viewer

Editor Button

Graphics Buttons

Graphics Window

The Molecular Editor
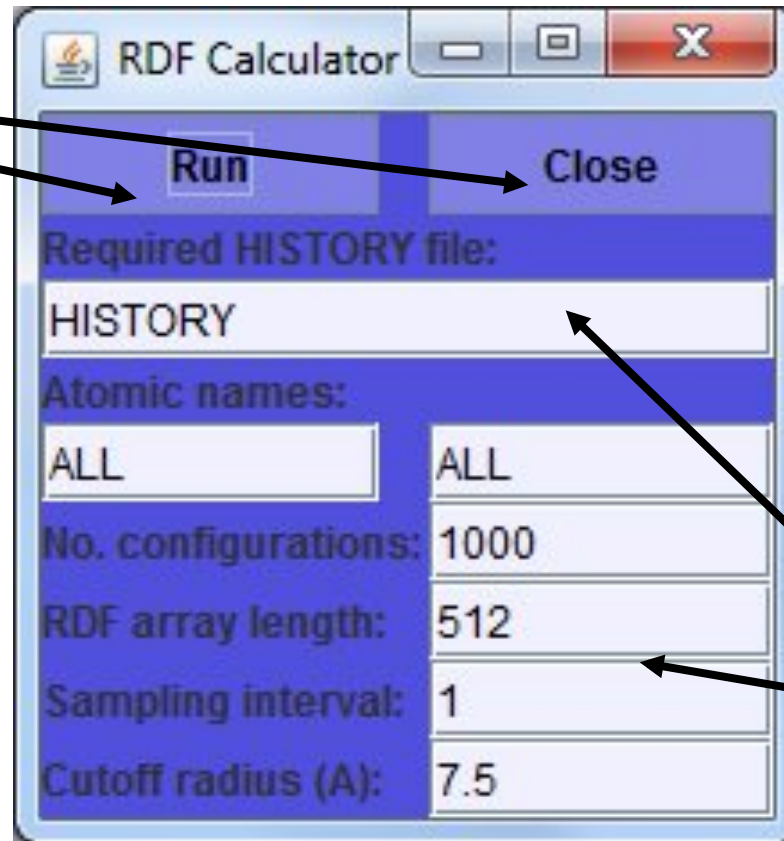

Editor Buttons

Editor Window

- 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.

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Buttons

Text Boxes

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- **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**

Developed by C.W. Yong

- **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

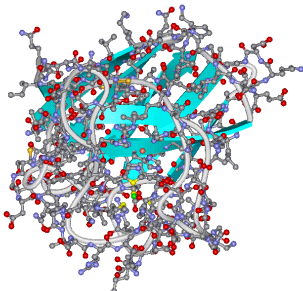- input units freedom and molecular rigidification

| xyz PDB | DL_FIELD → 'black box' | FIELD | CONFIG |

Protonated

SOD

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

This will consist of (up to) five components:

- Download & compile DL_POLY_4&Classic
- A demonstration of the Java GUI
- Trying some DL_POLY simulations:
  - prepared exercises, or
  - creative play
- DL_POLY clinic - what's up doc?
- Group therapy – all for one and one for all …

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DL_POLY Hands-On

http://www.ccp5.ac.uk/DL_POLY/TUTORIAL/EXERCISES/index.html