Neutrons and computational techniques

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Computing for Science

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Aims

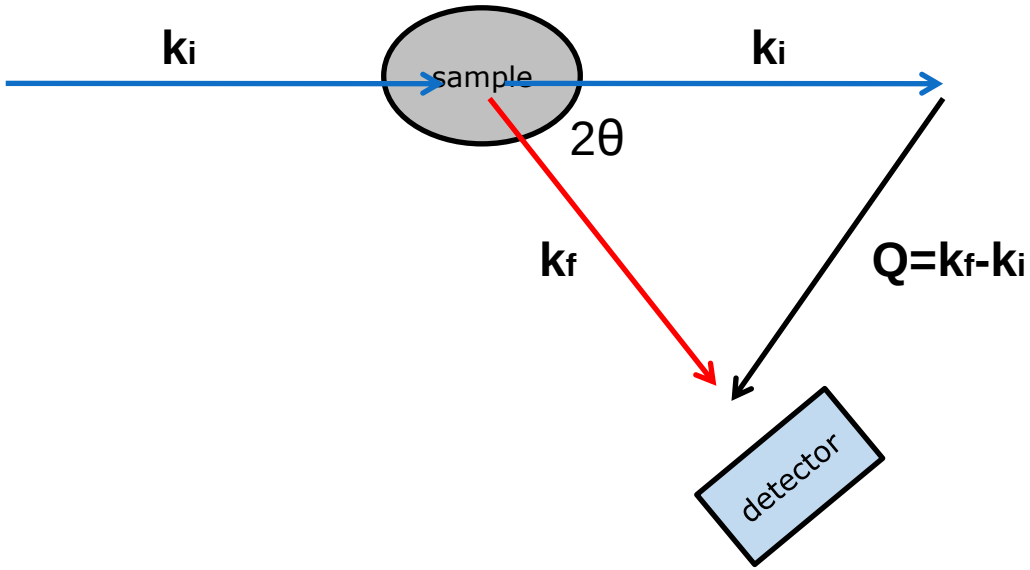
- Neutrons and atomistic simulations – why ?
- Potential Energy – how to calculate it
- Potential Energy Surface (PES) – how to explore it
  - Single point energy (SPE) calculations
  - Geometry optimisation (GO)
  - Lattice dynamics (LD)
  - Molecular dynamics (MD)

The neutron

- Short range interaction with nuclei $\rightarrow$ no atomic form factor, quantified by scattering length b
- *Neutron energy (E): 1 – 1000 meV*
- Neutron wavelength (λ): 0.5 – 25 Å ($E \cong 81/\lambda^2$)
- *Neutron magnetic moment probes magnetic structure and excitations of unpaired electrons in matter*

Neutron scattering triangle

- Elastic scattering: $k_i = k_f$, $(k = 2\pi/\lambda)$, $E_i = E_f$
- Quasielastic scattering : $k_i \approx k_f$, $E_i \approx E_f$
- Inelastic scattering : $k_i <> k_f$, $E_i <> E_f$



Double differential cross-section

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} N \frac{\sigma_t}{4\pi} S(\vec{Q}, \omega),$$

General scattering function

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar N < \overline{b^2} >} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{k,l}^{N} \overline{b_k b_l} < e^{-i\vec{Q}\cdot\vec{r}_k} e^{i\vec{Q}\cdot\vec{r}_l(t)} >$$

r(t): atom trajectories from Molecular Dynamics

For small amplitude motion – vibrations: $r=r^0+\delta r(t)$

$$S(\vec{Q},\omega) = \frac{1}{2N < \overline{b^2} >} \sum_j \frac{|F_j(\vec{Q})|^2}{\omega_j} \left[(n_j+1)\delta(\omega-\omega_j) + n_j\delta(\omega+\omega_j)\right]$$

$$|F_j(\vec{Q})|^2 = \sum_{k,l}^{N} \frac{\overline{b_k b_l}}{\sqrt{m_k m_l}} e^{-W_k(\vec{Q})-W_l(\vec{Q})} \left(\vec{Q}\cdot\vec{e}_j(k)\right)\left(\vec{Q}\cdot\vec{e}_j(l)\right) e^{i\vec{Q}\cdot(\vec{r}_k^{\,0}-\vec{r}_l^{\,0})}.$$

ω_j and e_j from Lattice Dynamics

Characteristics of NS experiments

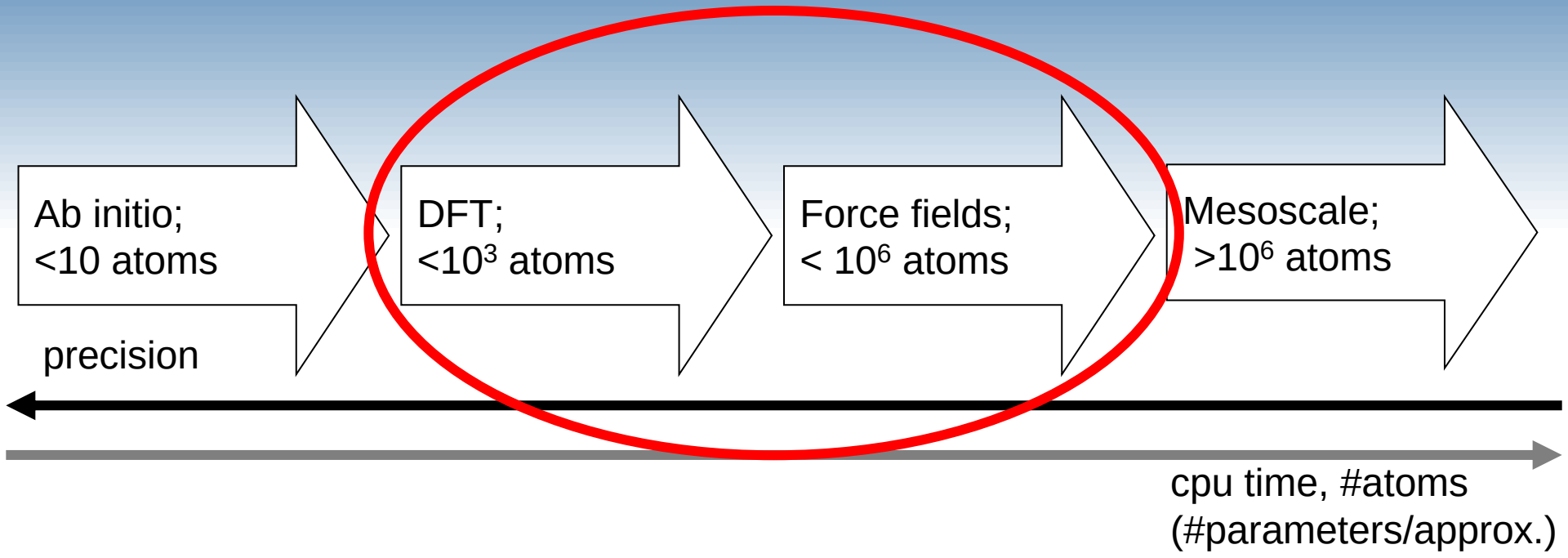
- Probe nuclear (not electron) positions
- *In Q and ω (or t) space*
- Time (<1μs) and length (<100nm) scales
- *Measure 'directly' structure, diffusion and excitations*
- No selection rules (cf. IR/Raman)
- *Neutron magnetic moment probes magnetic order and excitations*

Characteristics of atomistic simulations

- Can simulate nuclei and electrons or just nuclei
- *In real space (r, t): FT → (Q, ω)*
- Time (<1μs) and length (<100nm) scales match NS experiments
- *Calculate structure, diffusion and excitations*
- Electronic calculations probe magnetic order and excitations

Calculating energy (and forces)

Methods of potential energy calculation



Nobel prizes for DFT (1998) and classical MD (2013)

Density functional theory

- *Density Functional Theory (Hohenberg, Kohn, Sham)*
  - $E_{ks}[\rho(x)] = T[\rho(x)] + E_{es}[\rho(x)] + E_{ext}[\rho(x)] + E_{xc}[\rho(x)]$
  - where $\rho(x) = (\Psi\ \Psi^*)$ is position-dependent, electron density ($\rightarrow$ linear scaling)
  - $\rho(x)$ constructed from localised orbitals (H-atom or Gaussian) or plane waves for periodic systems
  - But E_{xc} unknown - LDA, GGA functionals
  - Corrections for long-range dispersive (VDW) interactions
  - Scaling: N (linear) $\rightarrow$ N^2 - N^3

- Practical limits:
  - ~500 atoms for one calculation, 200-300 atoms if many calculations have to be performed
  - Timescale: ~50 ps from ~20 000 simulation steps

Classical force field methods

$E =$

$K_s(l-l_0) +$

$K_b(\theta-\theta_0) +$

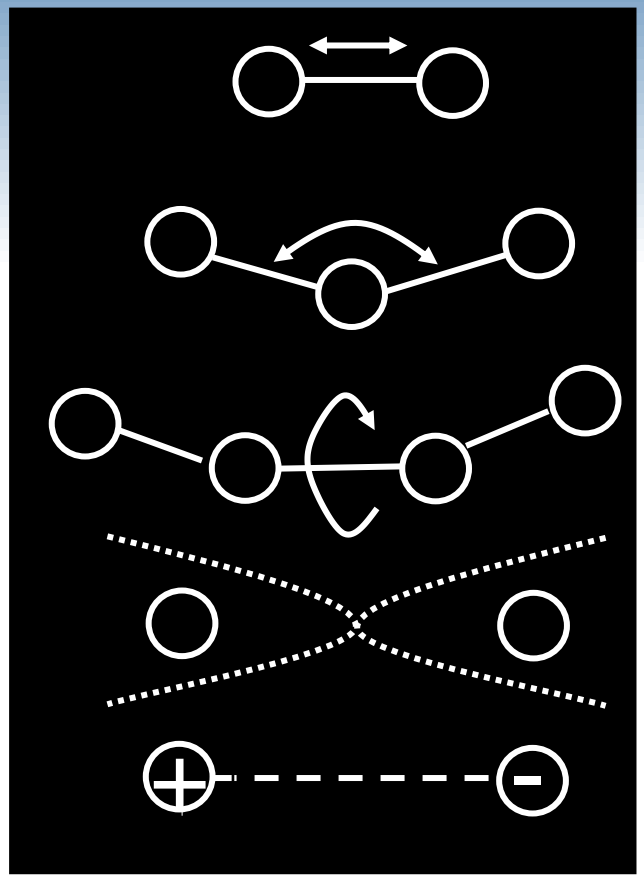
$K_t(\omega-\omega_0) +$

(cross terms +)

$a/r^{12}-b/r^6 +$

q_iq_j/Dr (+

hydrogen bonds etc)

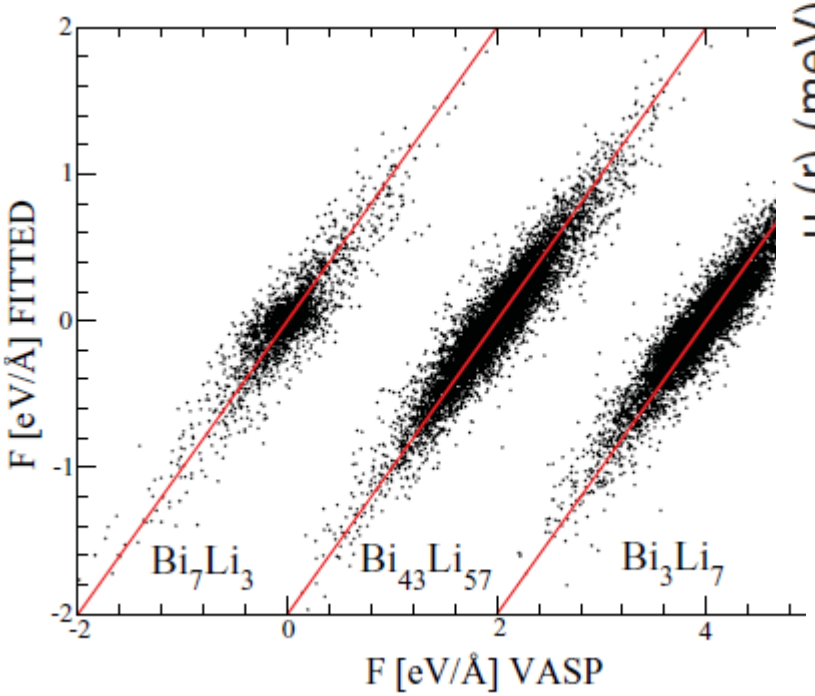


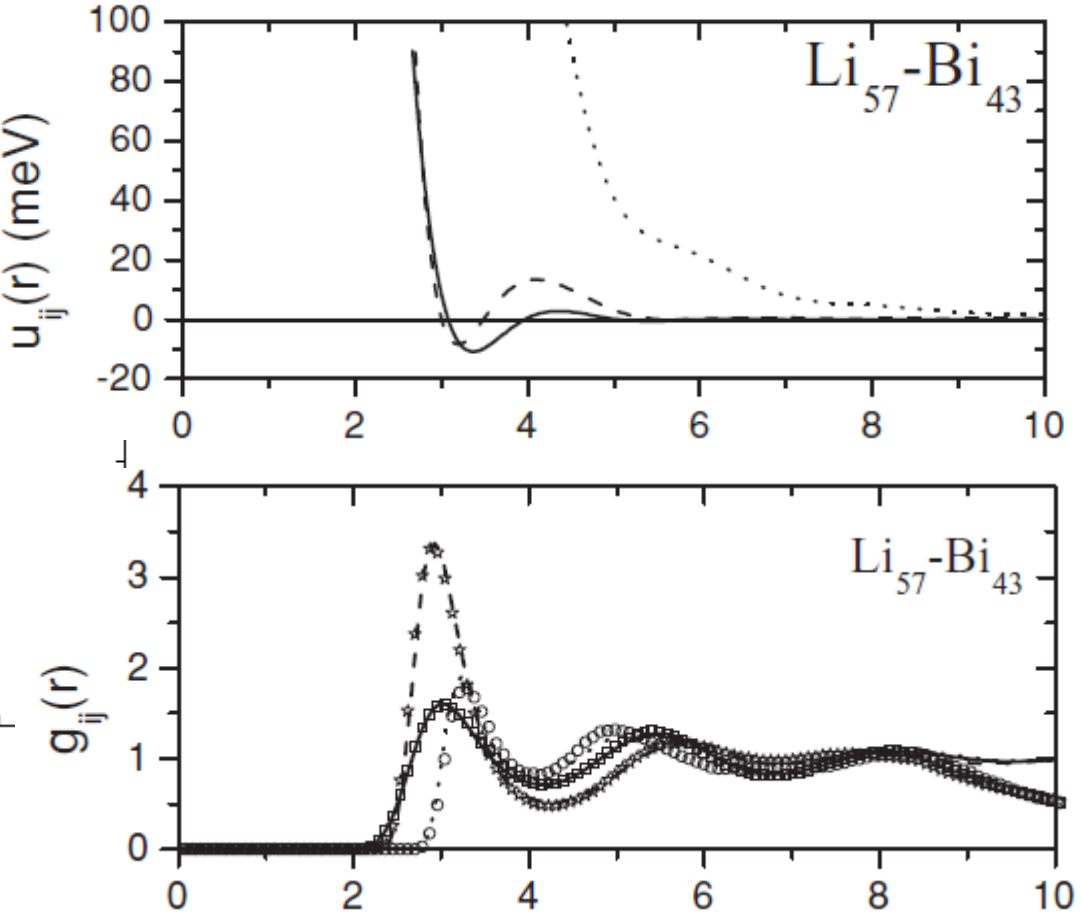
Practical limits:

< 10^6 atoms depending on number of simulations (composition, P, T, ...)

Timescale: 100 ns on 10^5 atoms

Determining empirical potentials (force matching)

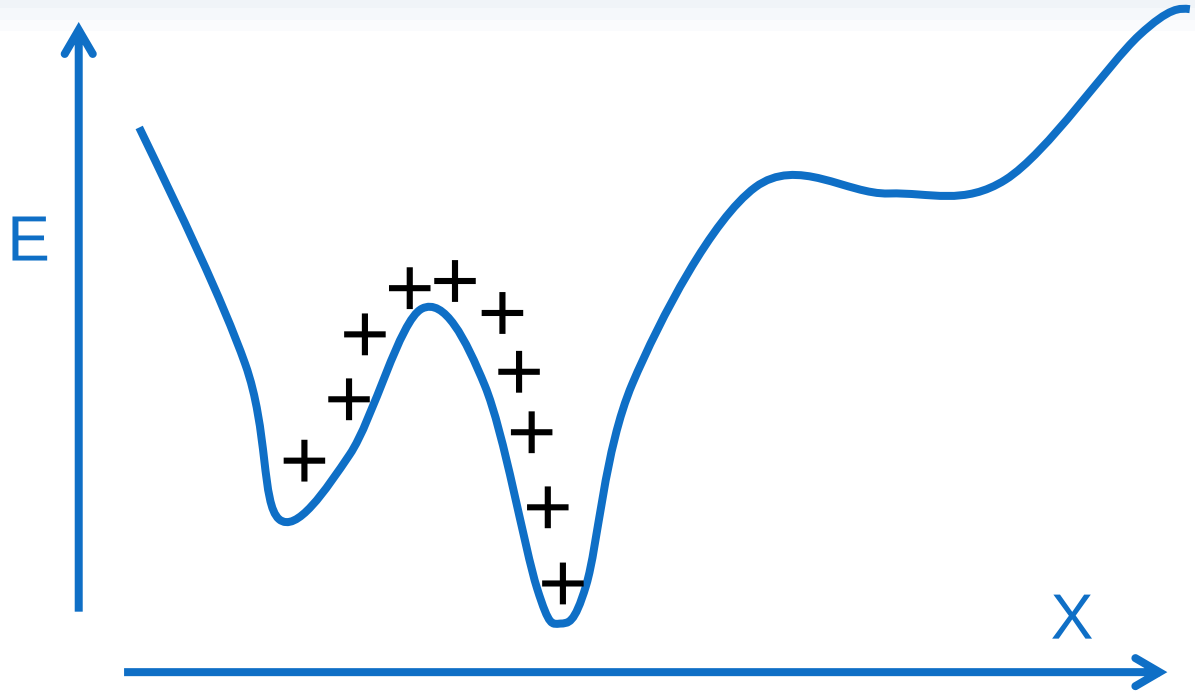




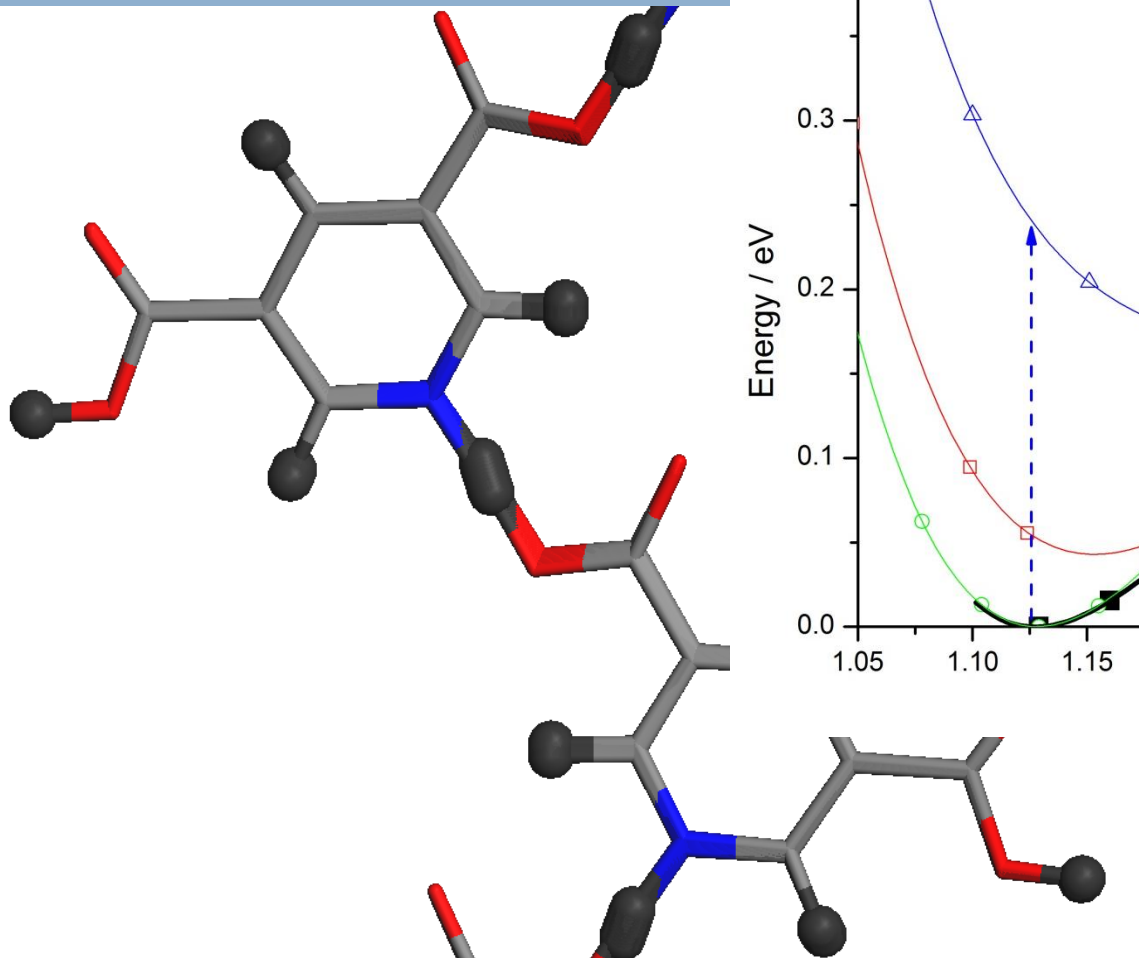
Simulation methods – Exploring the Potential Energy Surface

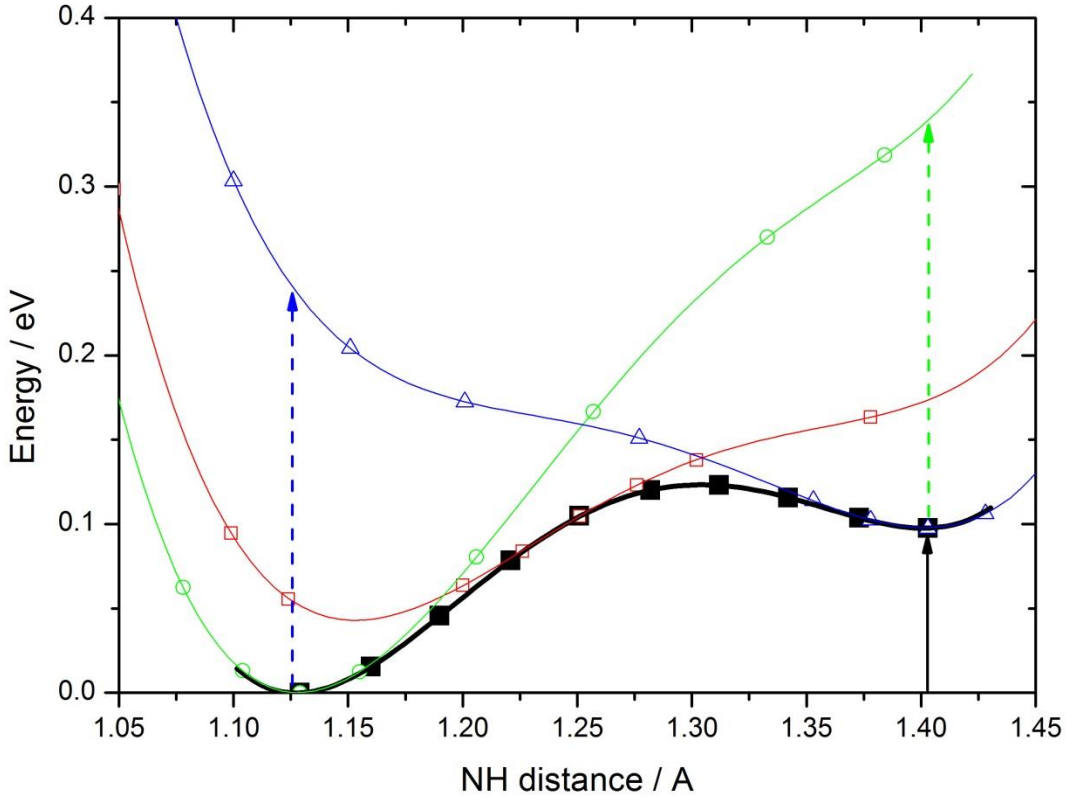
Potential energy surface

- Energy calculations and mapping

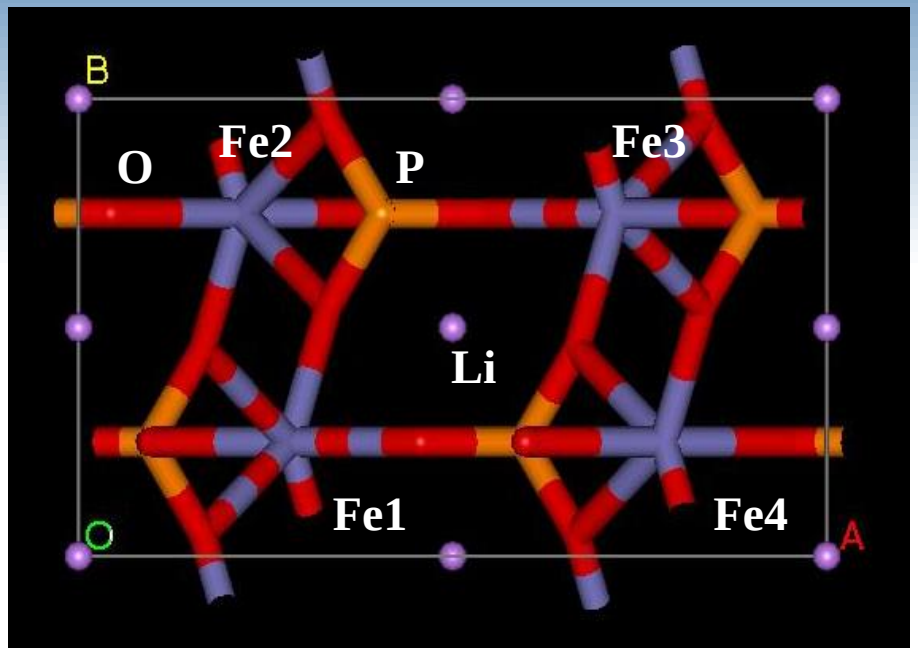


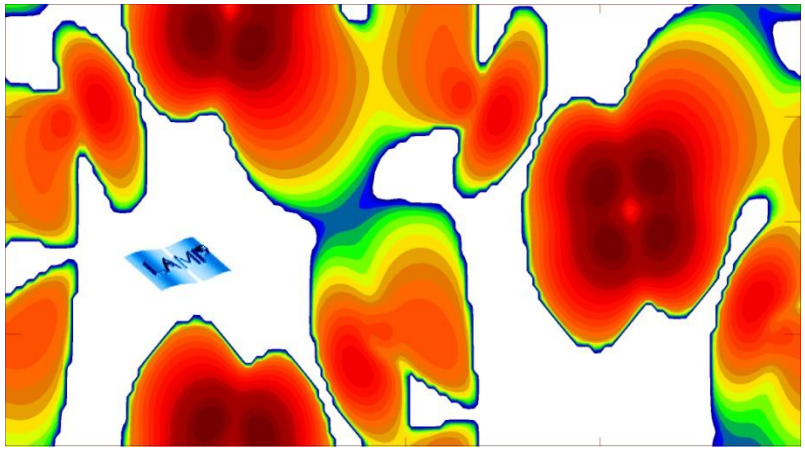
Mapping the PES – PDCA





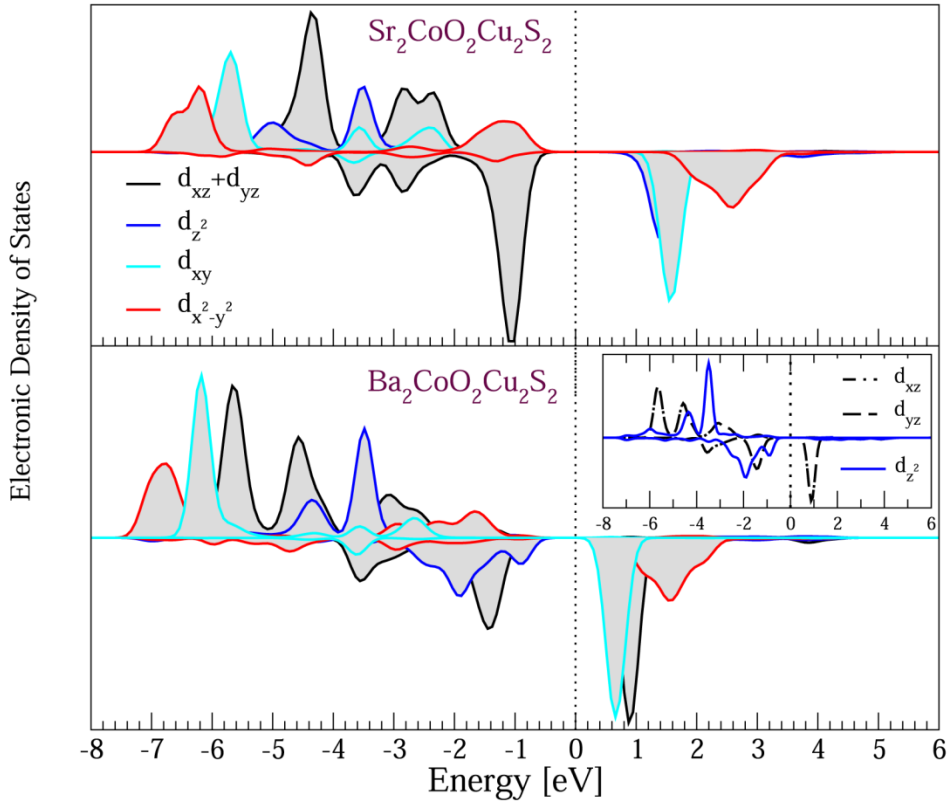
Ab initio energy calculation

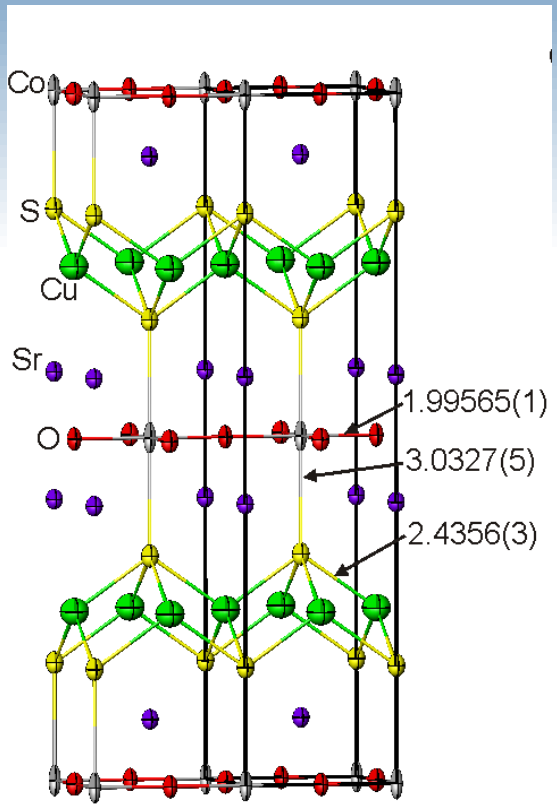




Spin density of $LiFePO_4$ in the a-c plane

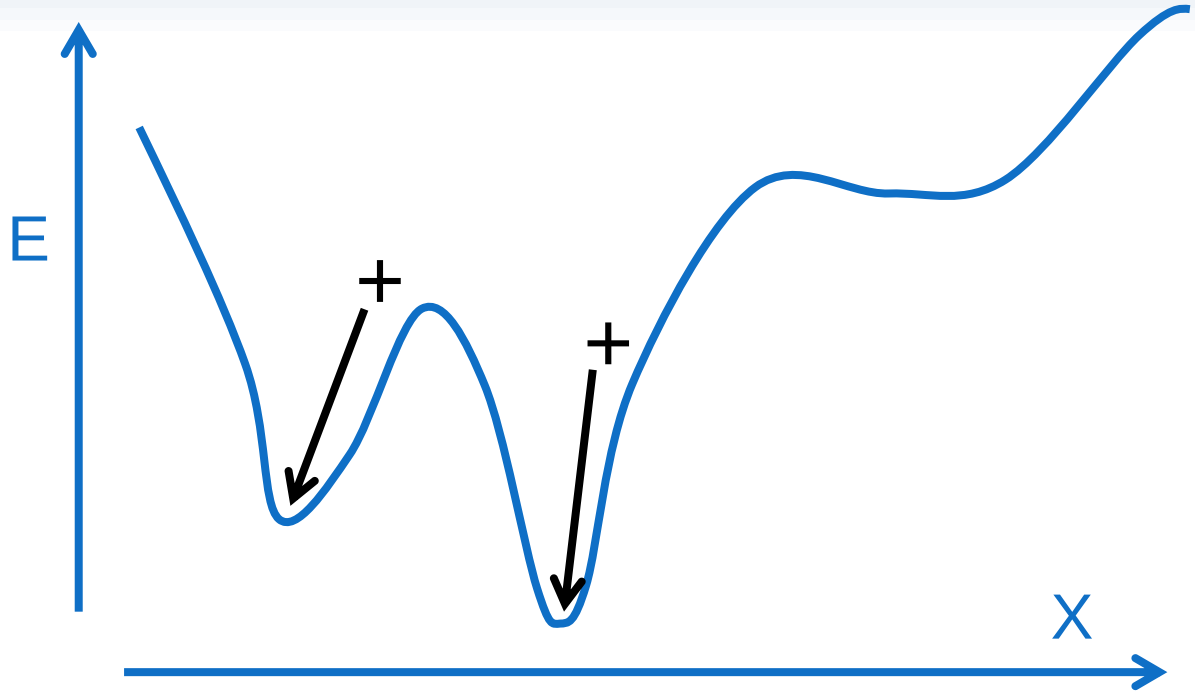
Ab initio energy calculation





Potential energy surface

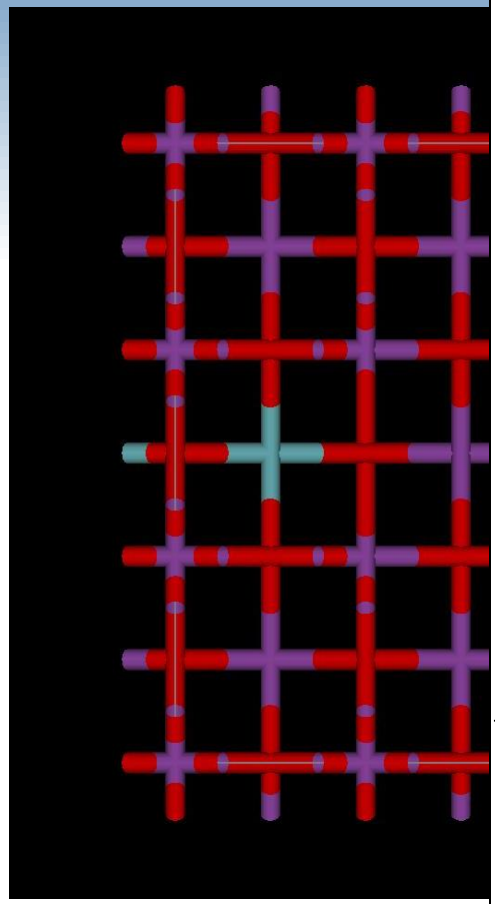
- Stable & metastable structures – finding them

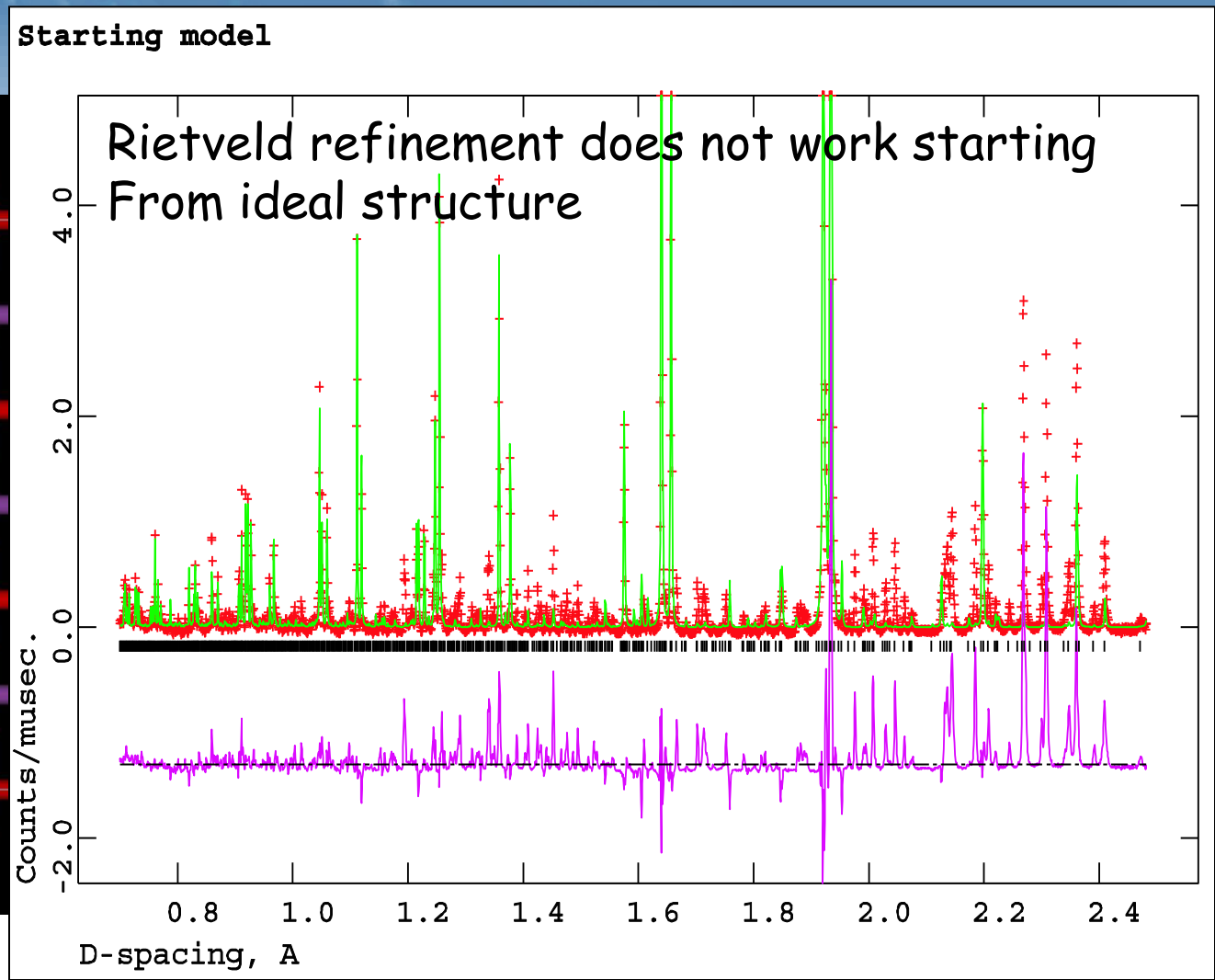


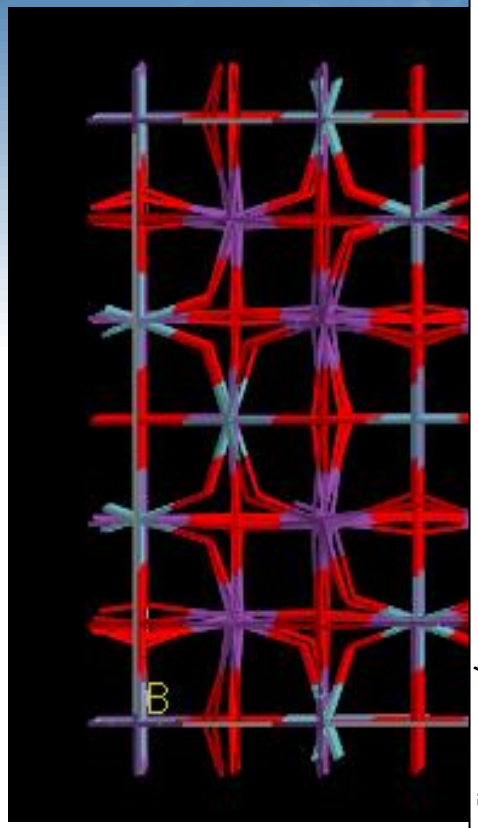
Optimised structures

- Energy $\rightarrow$ minimum
- *Forces $\rightarrow$ 0 ($\pm\delta$)*
- Determines crystal structure if starting model is 'good'
- *May need to explore PES more thoroughly/widely using eg. MD or Monte Carlo methods to find global minimum*
- Removes 'close contacts' before a MD simulation

Optimised structures



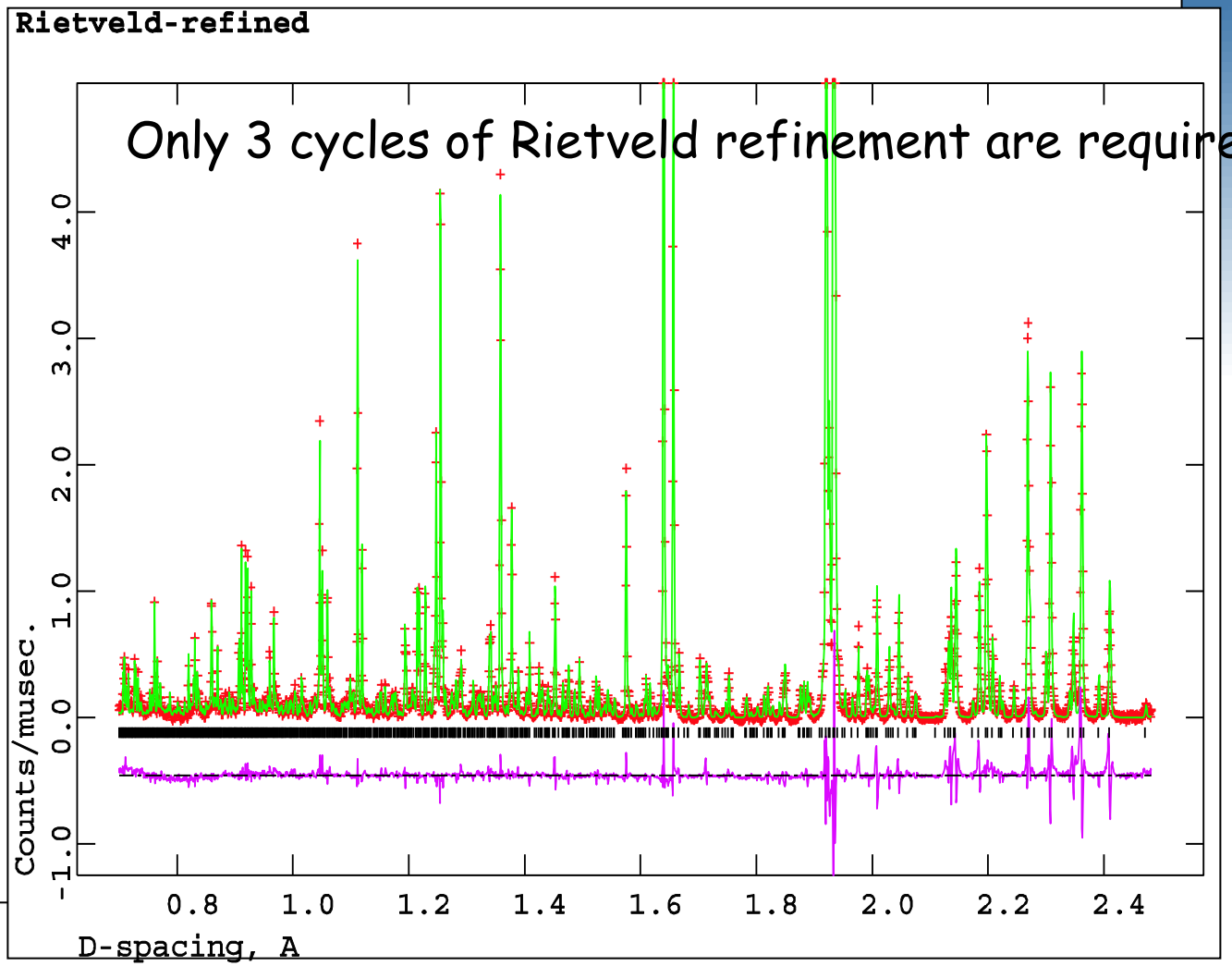




VASP-optimised

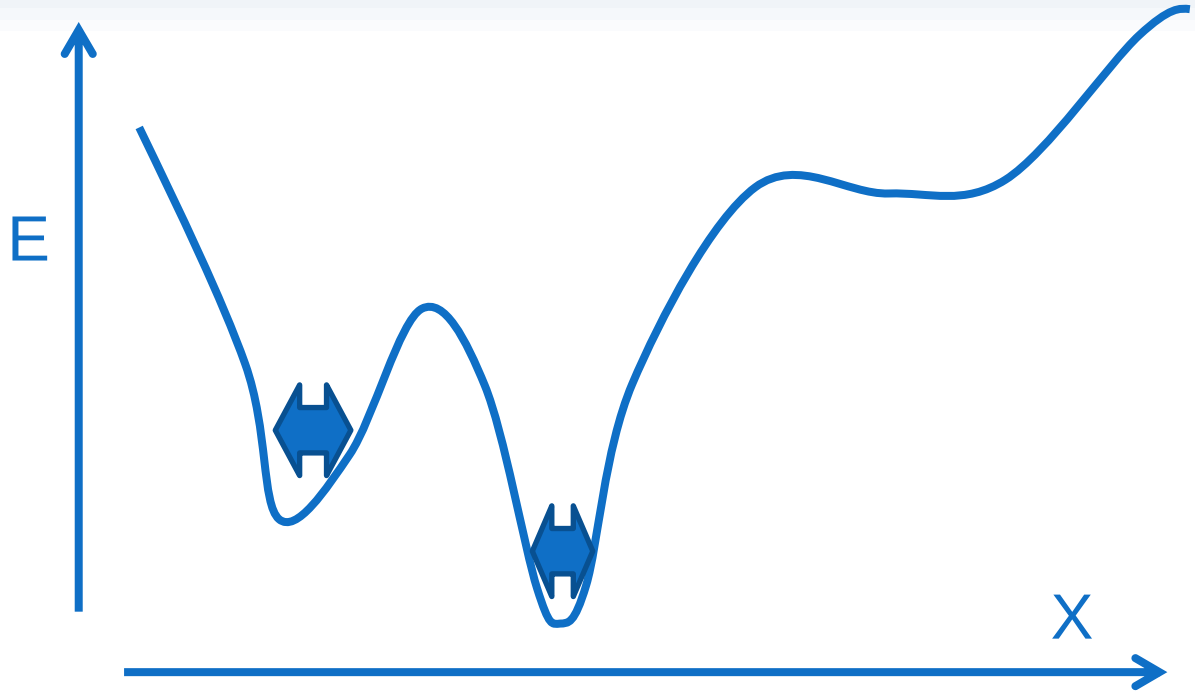
Rietveld-refined

Only 3 cycles of Rietveld refinement are required



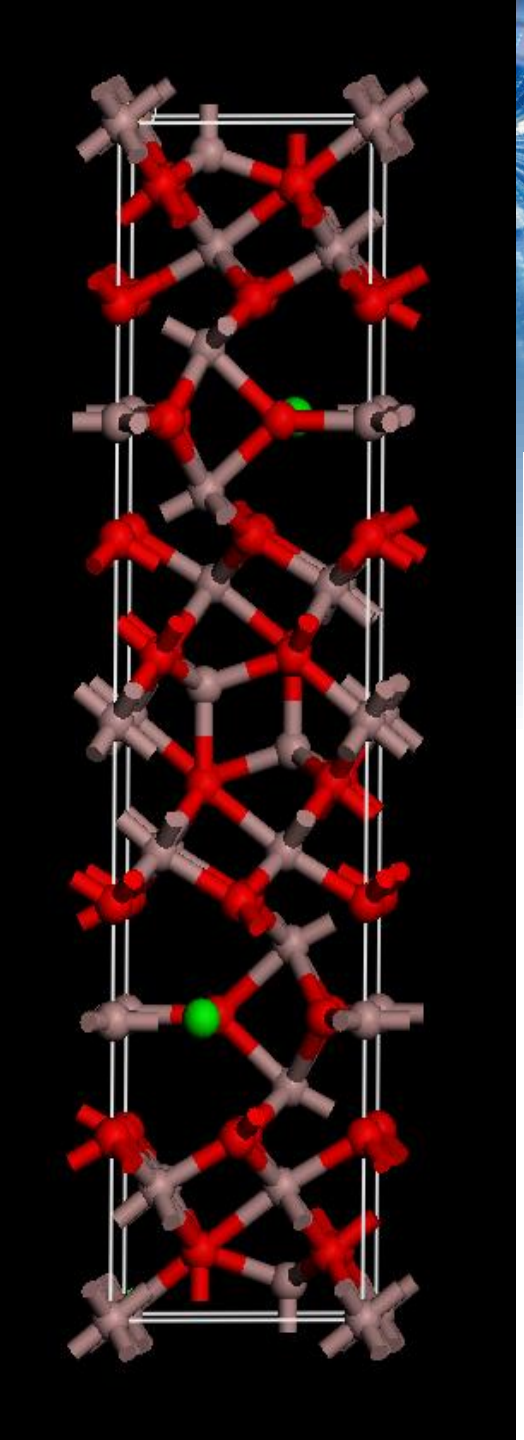
Potential energy surface

- Small amplitude vibrations



Lattice dynamics simulations

- Small amplitude dynamics (vibrations) about minima of the potential energy surface
- *Hessian is matrix of inter-atomic force constants (FC)*
- Dynamical matrix introduces atomic masses (m) and wavevector (Q) – it is a generalisation of solving the equations of motion for a monatomic chain
  - $DM_{ij}(\mathbf{Q}) = FC_{ij.}\exp[i\mathbf{Q}(\mathbf{r}_i-\mathbf{r}_j)]/\sqrt{(m_i m_j)}$
- *Eigenvalues and eigenvectors of DM give Q-dependent vibration frequencies (squared) and displacement vectors*



DOS & dispersion relations

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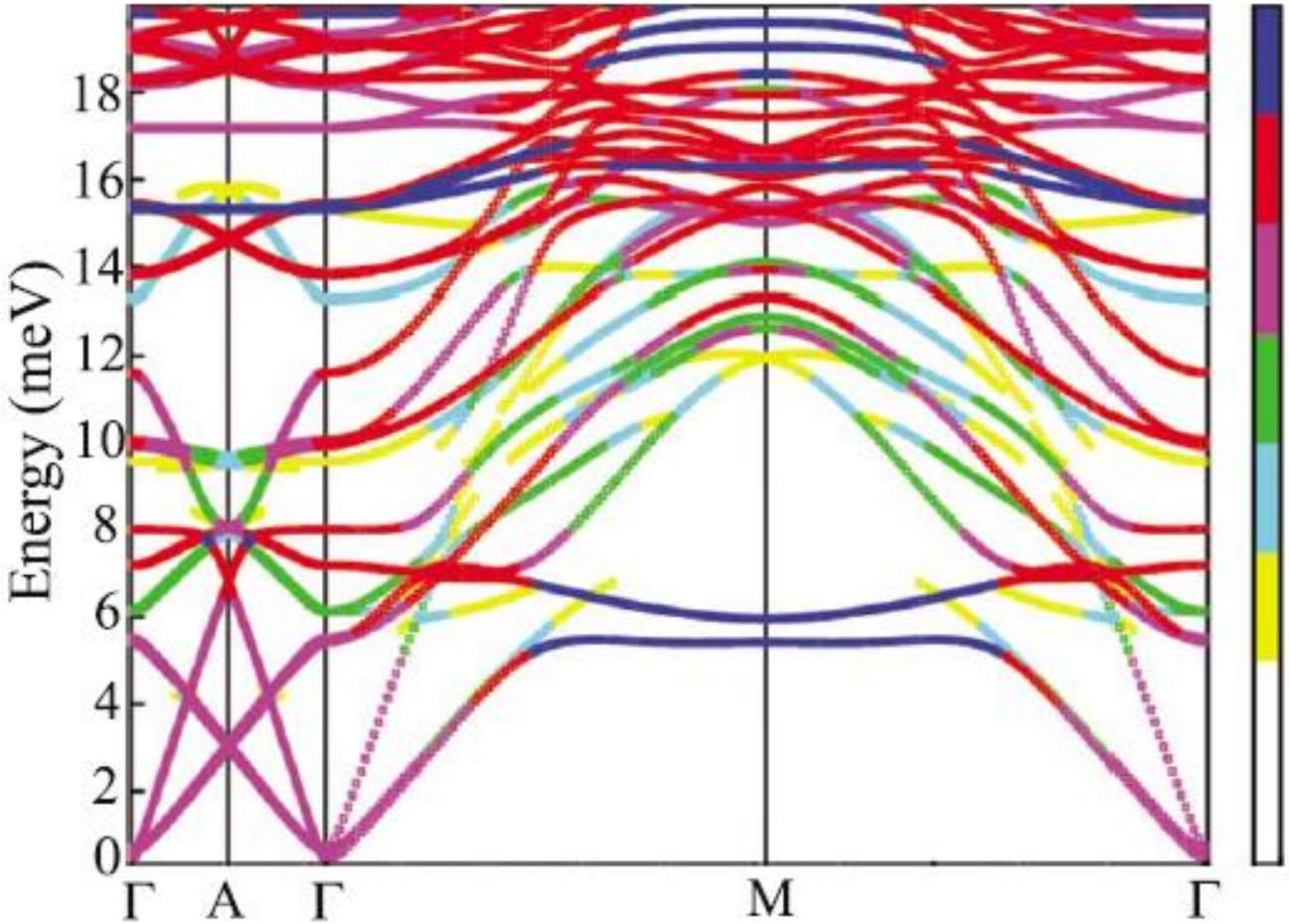
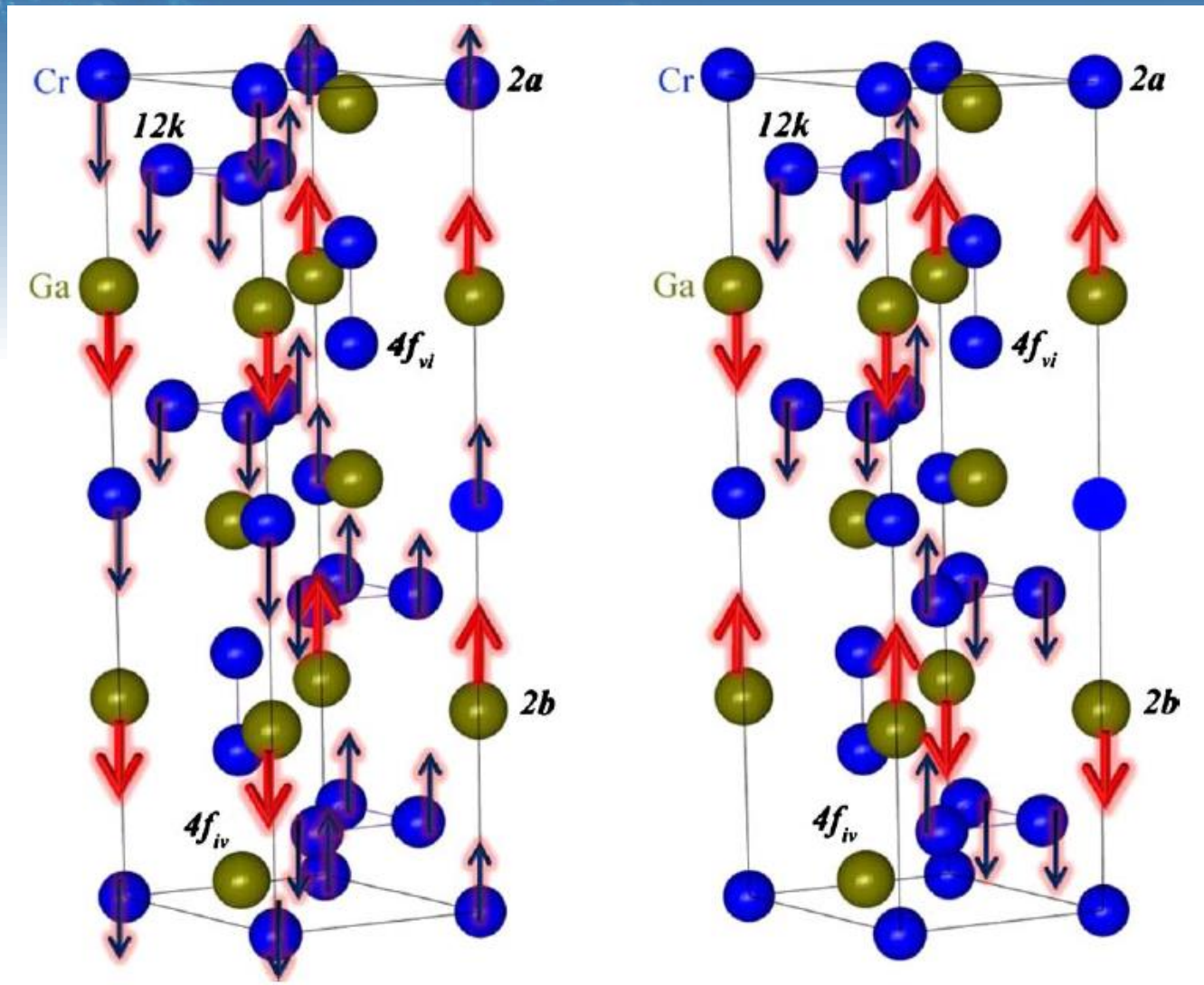


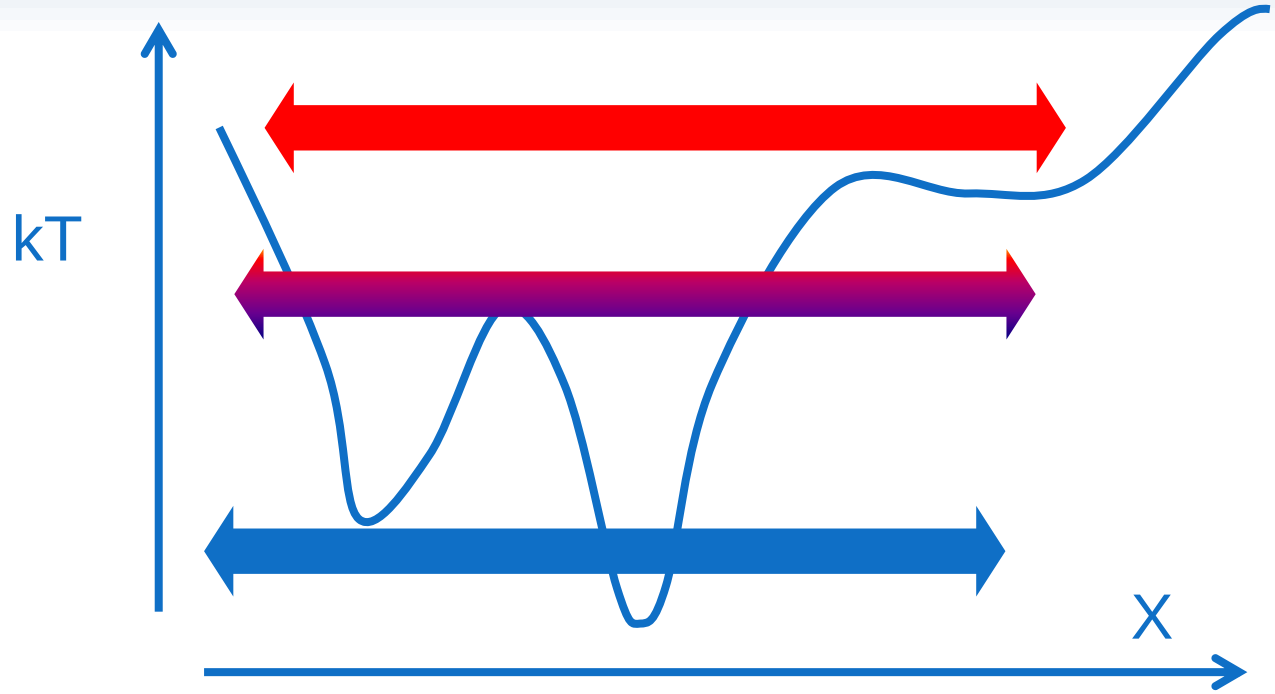
Displacement vectors

- Strong Ga displace-ment
- But Kagome triangles rock and drive relaxation
- Contrast with Γ point modes



Potential energy surface

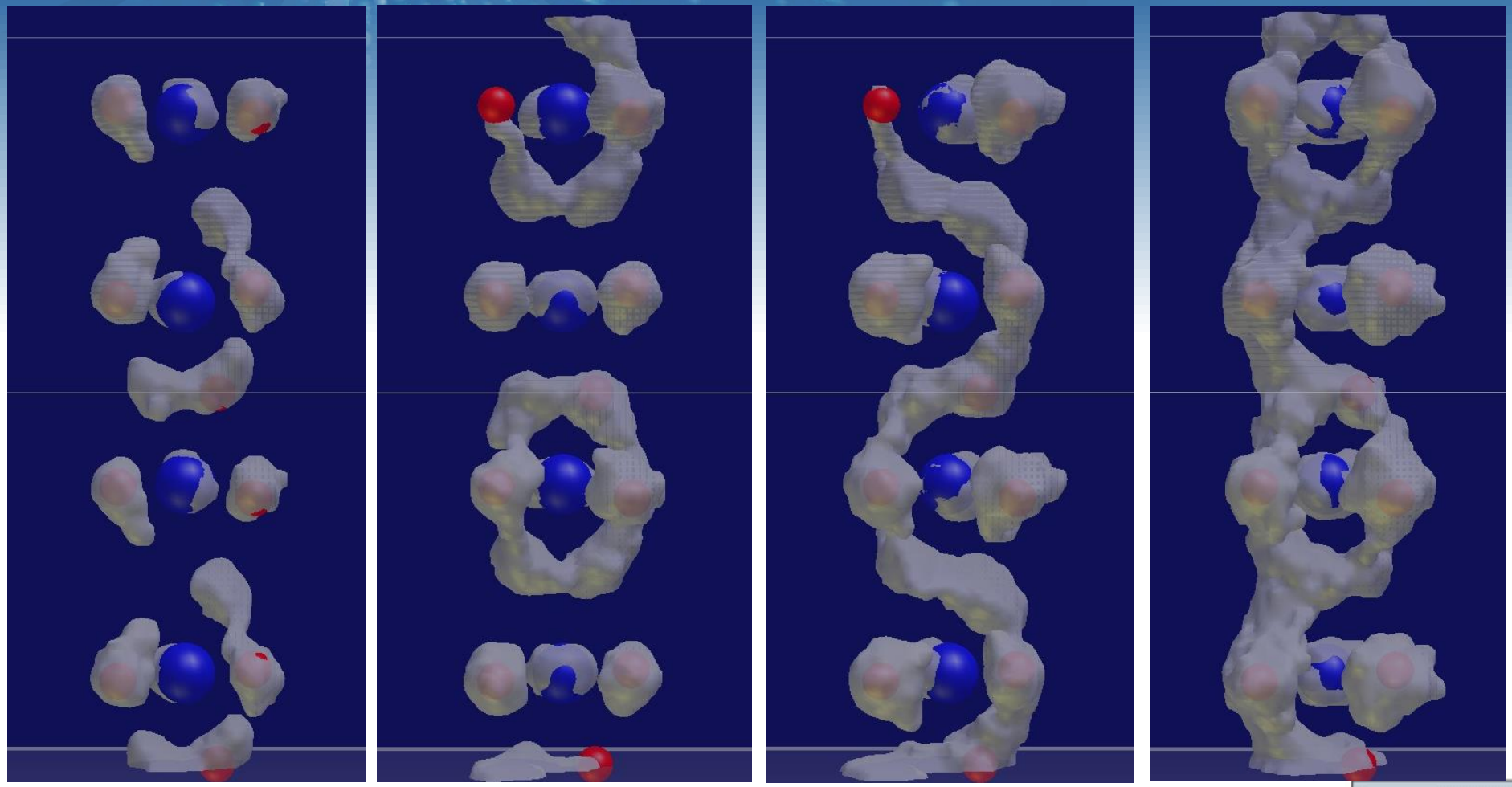
- Kinetic energy to explore all (thermally accessible) degrees of freedom



Molecular dynamics simulations

- Exploring small and large amplitude motions in the PES
- Simple equations intelligently implemented
  - $F \rightarrow a=F/m \rightarrow r'=r+v.dt$ & $v'=v+a.dt$
  - Initial velocities from requested temperature
    - $\Sigma mv^2/2=3kT/2$
  - Total time = n.dt
- Potential & kinetic energy will exchange resulting in a new temperature
  - Thermostat: NVE $\rightarrow$ NVT
  - Barostat: NVT $\rightarrow$ NPT

Understanding experimental data...

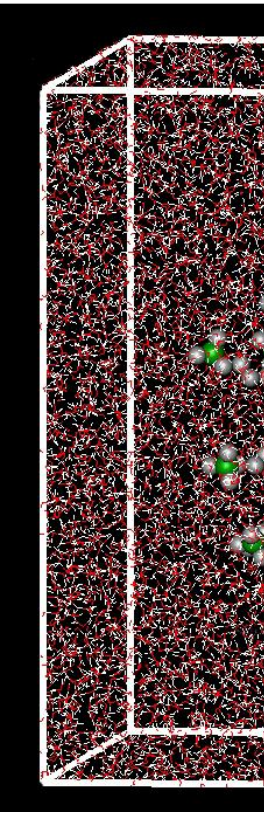


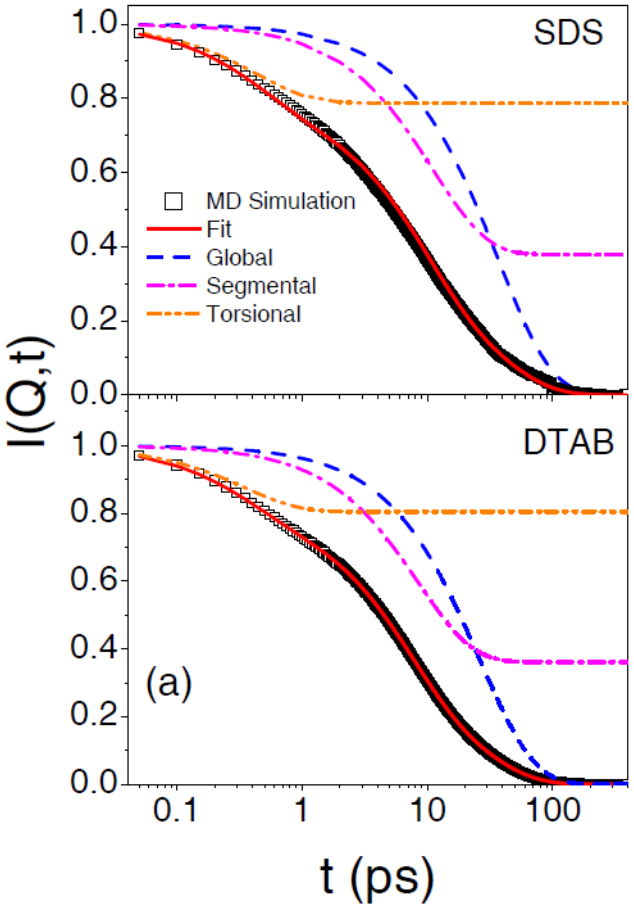
Temperature

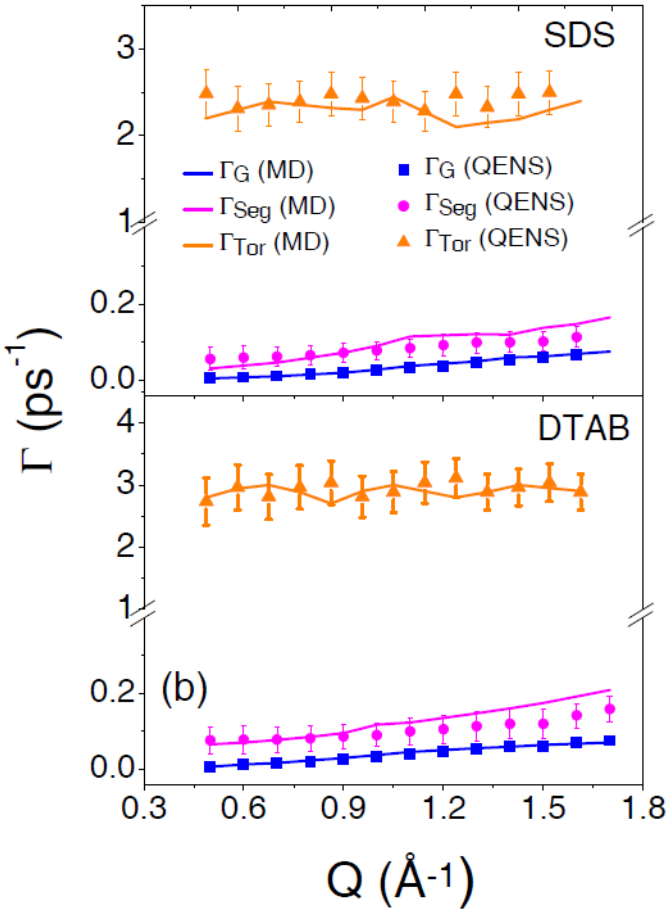
Molecular dynamics output

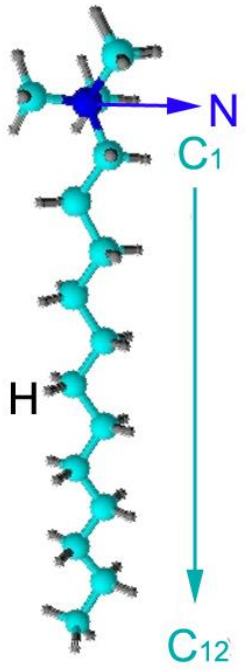
- Time-averaged structure – S(Q,ω=0), S(Q)=I(Q,t=0)
- *Vibrational density-of-states – FT of the velocity auto-correlation function*
- I(Q,t) & S(Q, ω): coherent and incoherent
  - *Intensity-weighted dispersion relations from supercell simulations – excitations must be commensurate with simulation box*
- *Diffusion constants*
- *Disorder: dynamic or static?*
- Normal modes from principle component analysis
- …

MD output – I(Q,t)

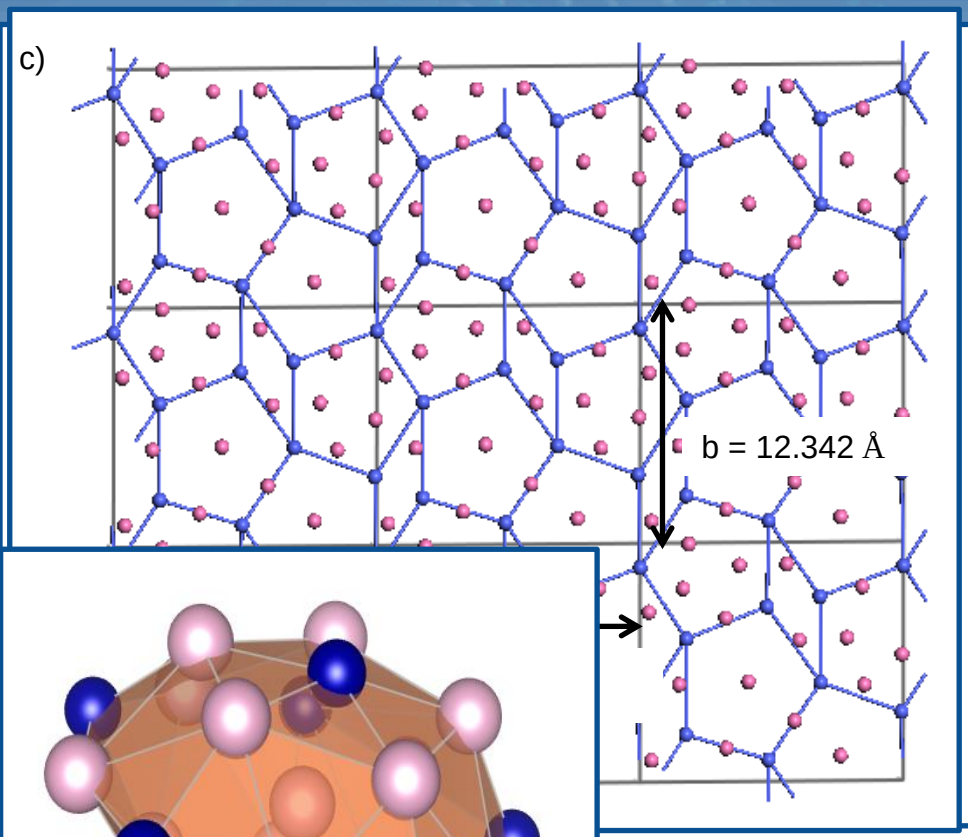


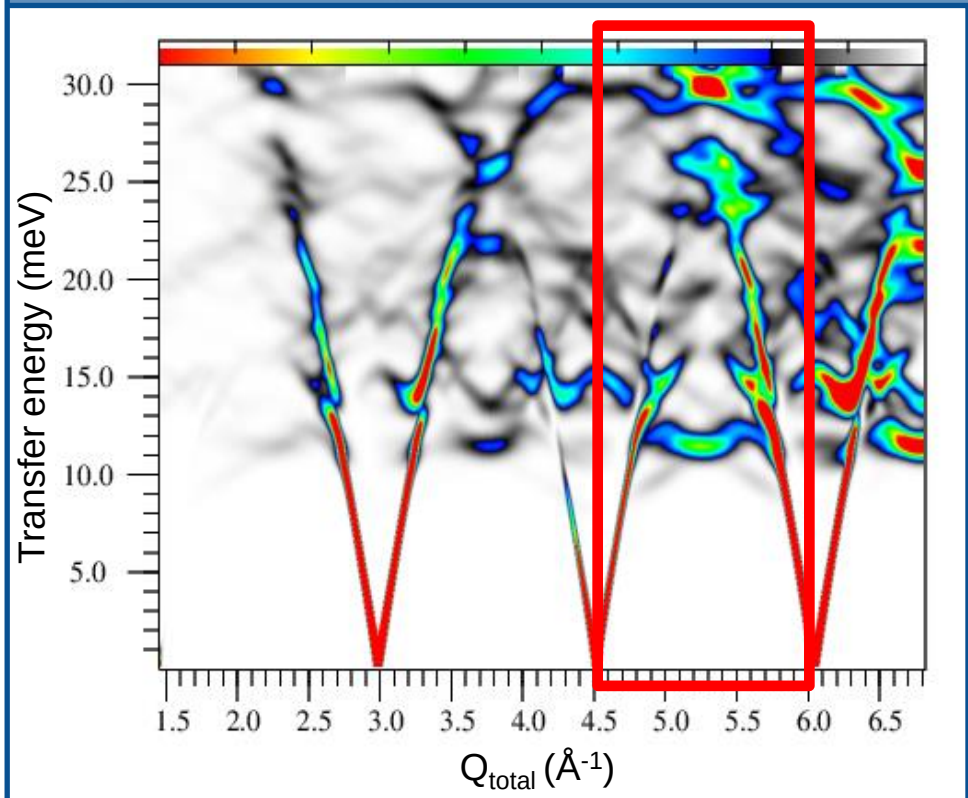






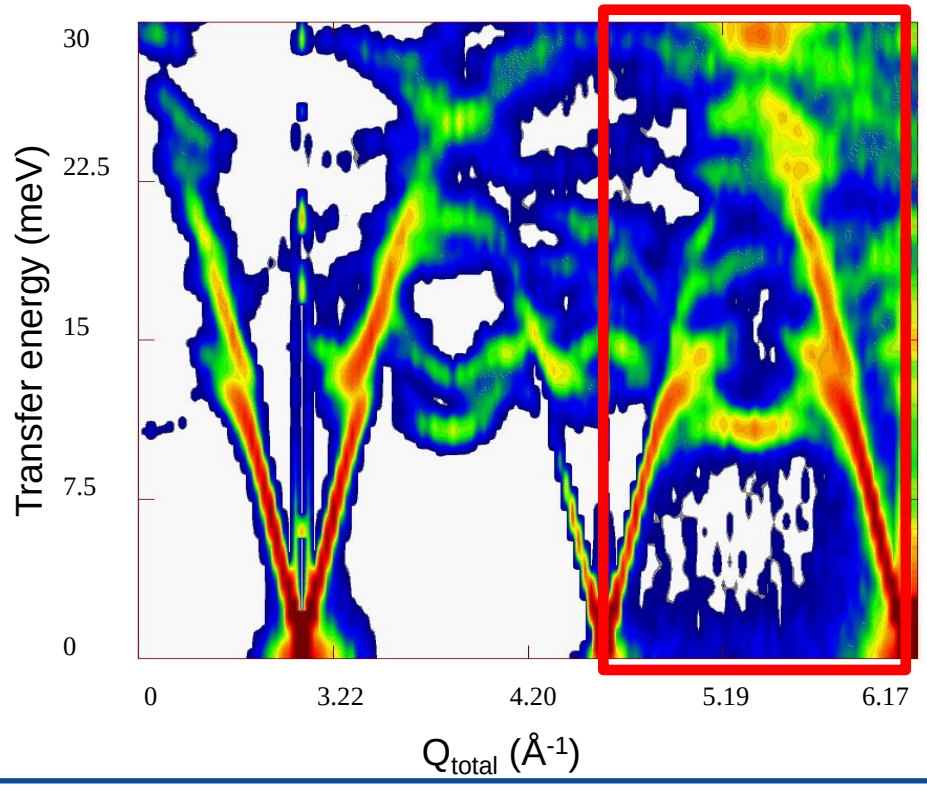
MD output – SQW

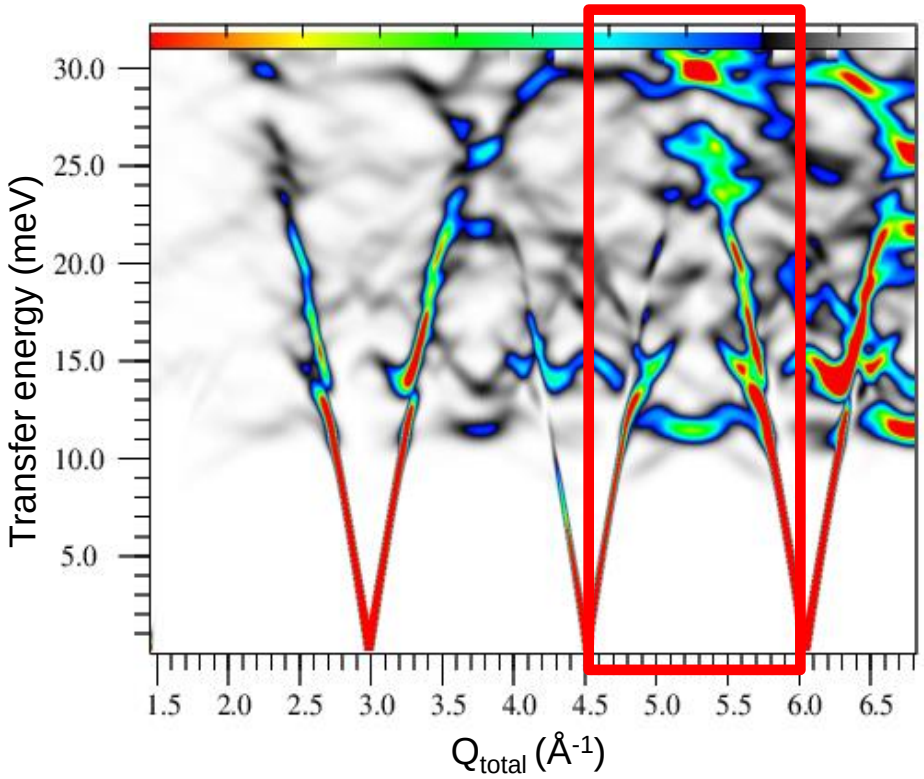




LD – DFT, ~100 atoms, harmonic approx.

MD output – SQW



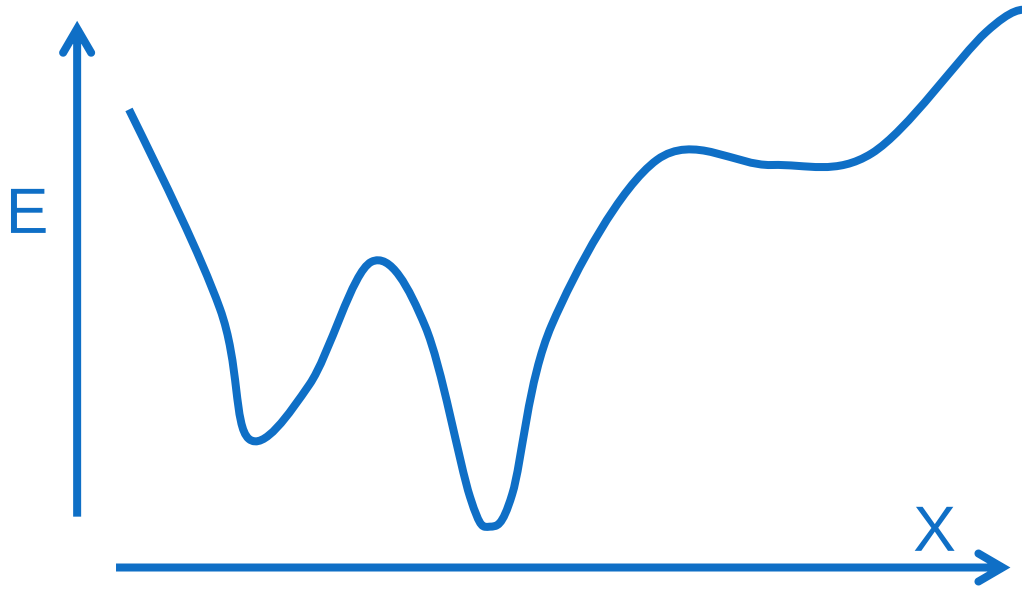


MD – FF, 10^6 atoms, anharmonic and T effects

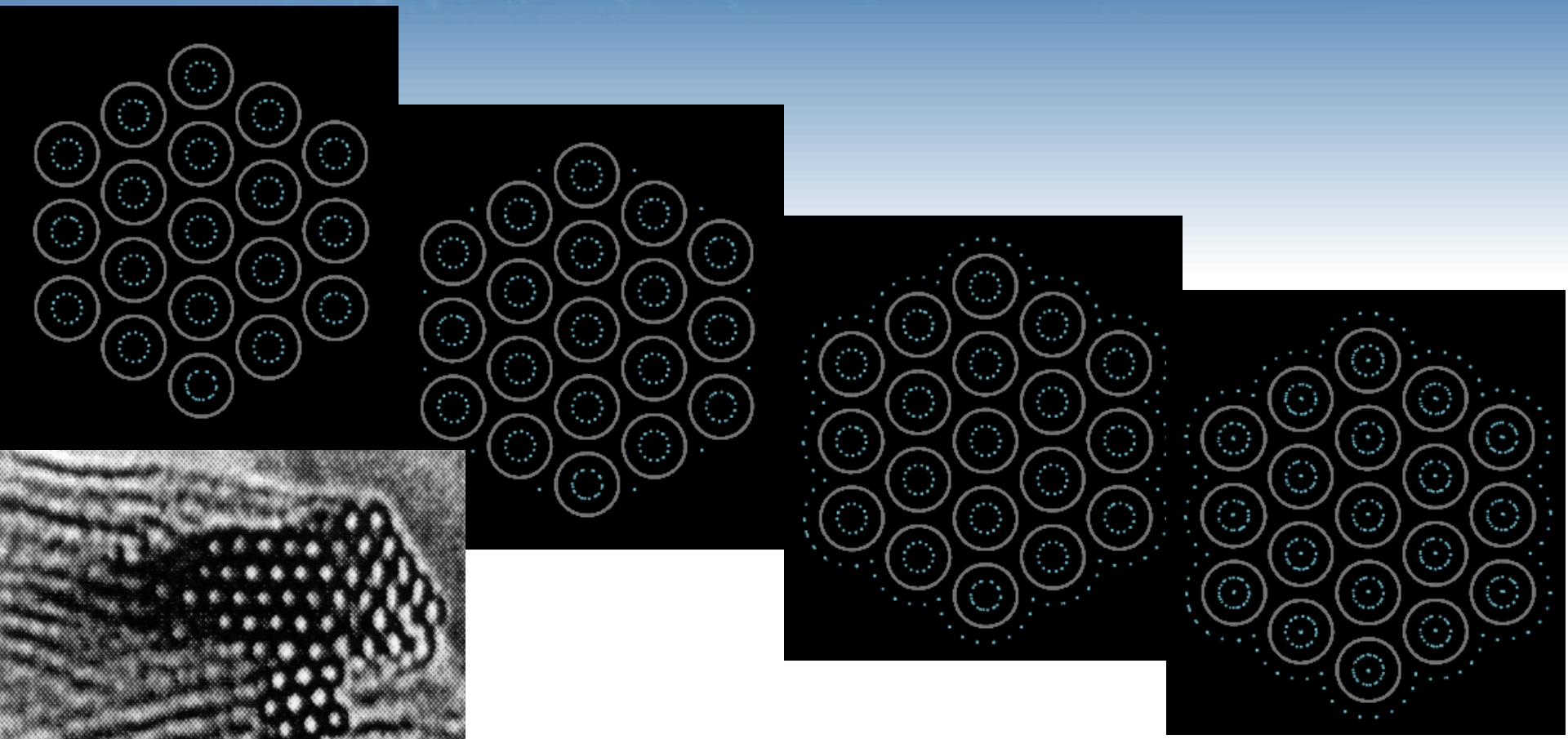
LD – DFT, ~100 atoms, harmonic approx.

Potential energy surface

- Monte Carlo methods may be better for exploring the PES
- *Random displacement*
- ACCEPT if $\Delta E <= 0$
- *$P=exp(-\Delta E/kT)$ if $\Delta E > 0$, then ACCEPT if $P >$ random no.*



MC: structure determination



What to remember…

DFT vs FF

- DFT is much more accurate (unless FF is determined from DFT specifically for a composition/T/P/etc) and transferable than FF methods
- DFT determines electronic & spin structure
- DFT allows bond breaking/formation – chemical reactions
- DFT is 10^6 (10^3 in space & 10^3 in time) times 'slower' than FF methods

Exploring the PES

- Both DFT and FF can be used – the choice depends on the size of the system and what is of interest
- SPE: Mapping
- GO: Find minima – (meta-) stable structures
- LD: Lattice dynamics (vibrations) – harmonic approximation (minimise + mapping)
- MD: Molecular dynamics – anharmonic contributions and temperature

Calculate and compare with experiment

- Ground state structures including magnetic
- Time averaged, liquid-like structures – S(Q)
- Relaxation processes via QENS – S(Q,w) or I(Q,t)
- Quantum excitations from PES & solving Schroedinger's equation
- Vibrational density of states
- Dispersion relations (LD) and phonon lifetimes (MD)

Perspectives

- More accurate electronic methods for magnetic systems
- Approximate electronic methods to bridge the gap in time and length scales between DFT and FF methods
- Coarse grain (mesoscale) methods to explore comformation space of large (polymer, membrane, protein,…) systems
- Refining potentials against experimental data


PES near Grenoble ☺

Further reading…

Presentations from MDANSE schools at ILL in 2012 & 2014

http://www.ill.eu/en/html/instruments-support/computing-for-science/modelling/mdanse-2012/

http://www.ill.eu/en/html/instruments-support/computing-for-science/modelling/mdanse-2014/

Proceedings of SFN French Neutron School 2010 on simulations:

http://www.neutron-sciences.org/index.php?option=com_toc&url=/articles/sfn/abs/2011/01/contents/contents.html