Plan…

Properties at the nano-scale : quantum theory

Classical Methods (Free Energy and Mol. Dynamics)

Practical quantum mechanics – density functional theory

Implementations

- Plane waves and pseudopotentials
- Local basis sets – all electron calculations

Approximate quantum methods

Some recent progress…

- Spin transport and quantum computing
- New solar cells: quantum dots & wells
- Chemistry at interfaces
- Magnetic carbon polymorphs

Molecular Dynamics

$$F = ma$$

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

What is Molecular Dynamics?

The solution of the classical equations of motion for atoms and molecules to obtain the time evolution of the system **ie: r_i(t)**

Molecular Dynamics Features

Applied to many-particle systems - a general analytical solution not possible. Why ?

Must resort to numerical methods and computers

Classical mechanics only - fully fledged many-particle time-dependent quantum method not yet available

Maxwell-Boltzmann averaging process for thermodynamic properties (time averaging).

Integrating the Equations of Motion

If we know the force on each atom *i* then we can compute its acceleration over a small time step Δt – this yields a new velocity.

If we know the velocity we can compute the change in position over Δt – this yields a new position.

Very roughly…

$$a_i = F_i / m_i$$

$$\Delta v_i = a_i \Delta t$$

$$\Delta r_i = v_i \Delta t$$

The Velocity Verlet Algorithm (~LeapFrog)

For a given set of initial conditions – positions and velocities $(\mathrm{r}_i^{0}, v_i^{0})$

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

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

The use of the average force between timesteps n and n+1 to update v_i and then taking care of some of the acceleration in v_i between timesteps reduces the errors.

How to compute the forces ?

Quantum mechanics (usually density functional theory)

$$\vec{F}_i = \frac{\partial E[\rho]}{\partial \vec{r}_i}$$

Force field methods – eg: if we have a pairwise potential *V*(r_{ij})

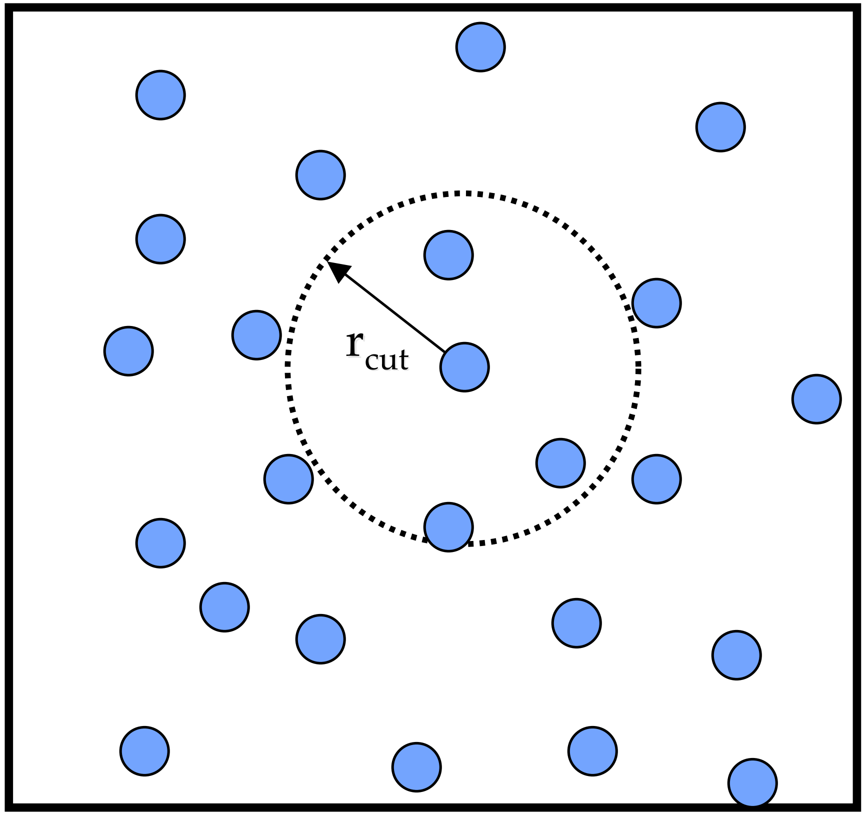
$$\vec{F}_i = \sum_{j \neq i}^{N} \vec{f}_{ij}$$

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

The pair potential can be empirical (fitted to experimental data) or, more often now, determined from QM studies of model systems….

A Simple Example - Pair Interactions

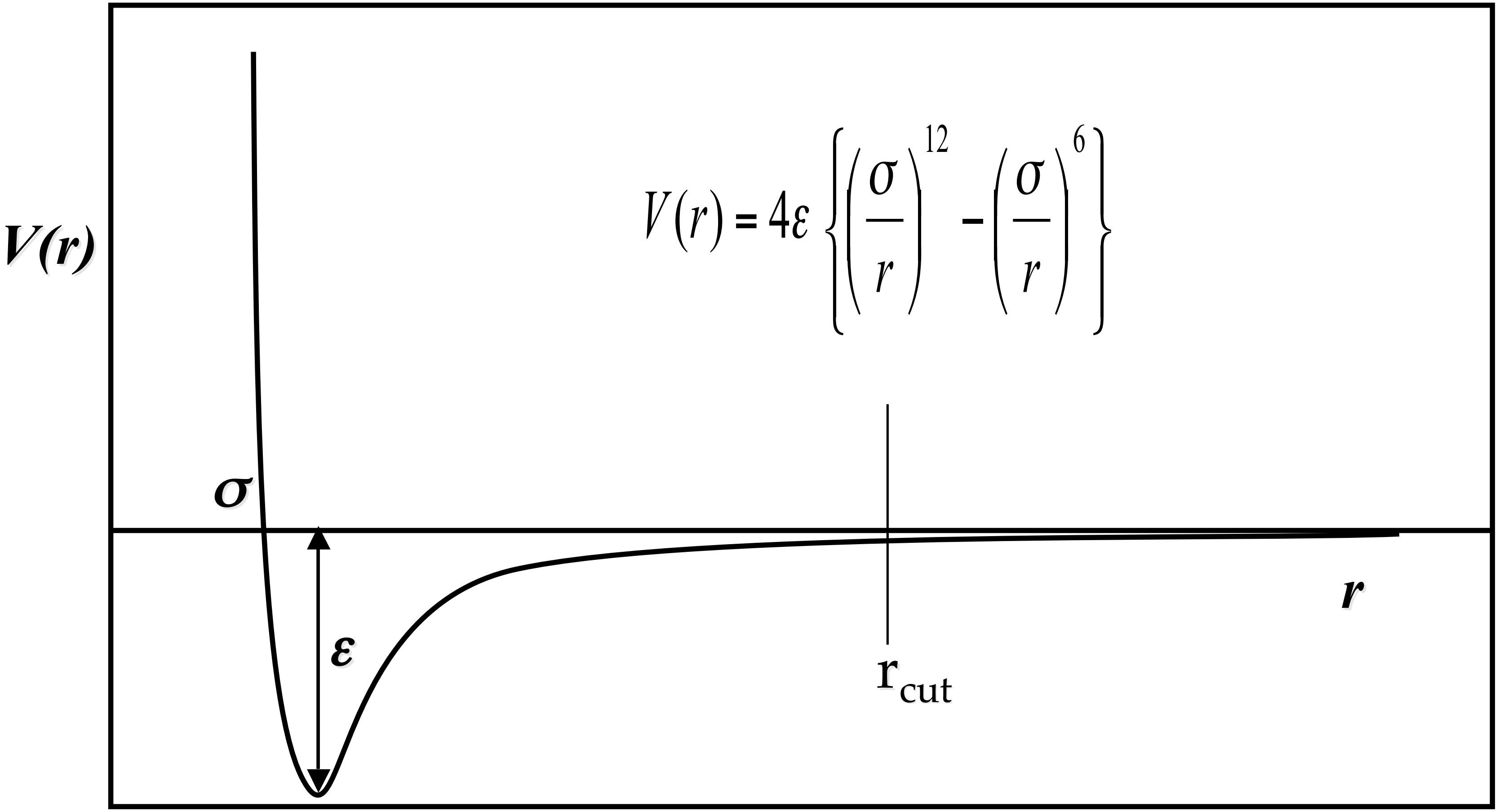
Simulation of Argon



Pair Potential:

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

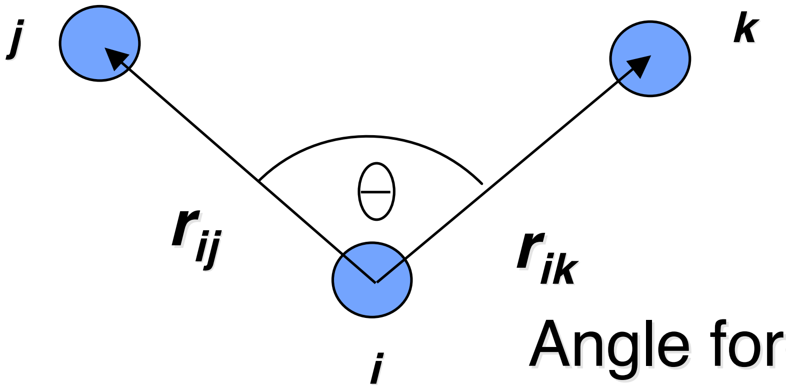
The Lennard-Jones Potential



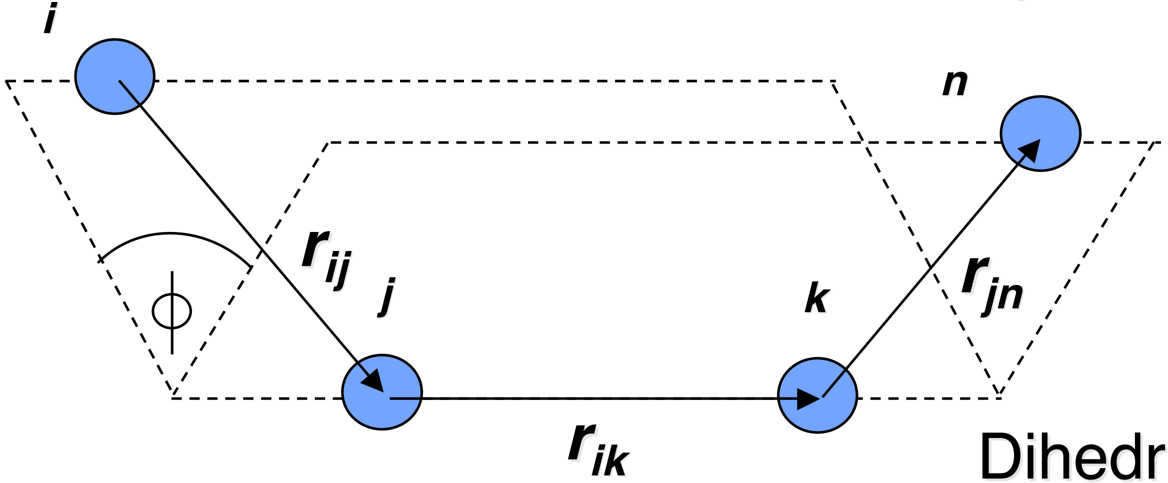
$$V(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\}$$

Covalent Bonds

Pair force

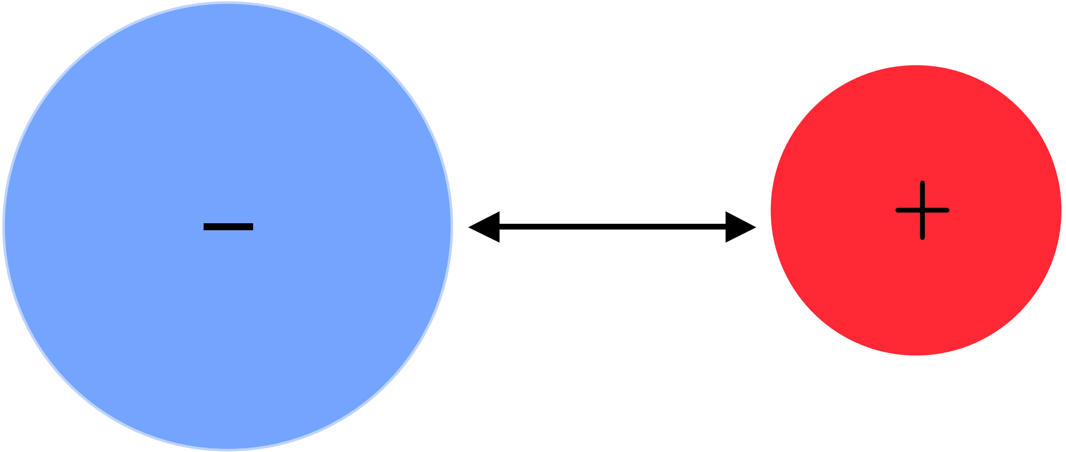


Angle force



Dihedral force

Ionic Interactions



$$E = \frac{q_i q_j}{4\pi\varepsilon_o r^2}$$

$$F = -\frac{dE}{dr} = -2\frac{q_i q_j}{4\pi\varepsilon_o r}$$

Force Fields

Force fields are plentiful, **but accurate in limited domains** !

Most simulations use force fields from literature but some systems demand the derivation of new ones.

For biological systems use GROMOS, AMBER, CHARMM

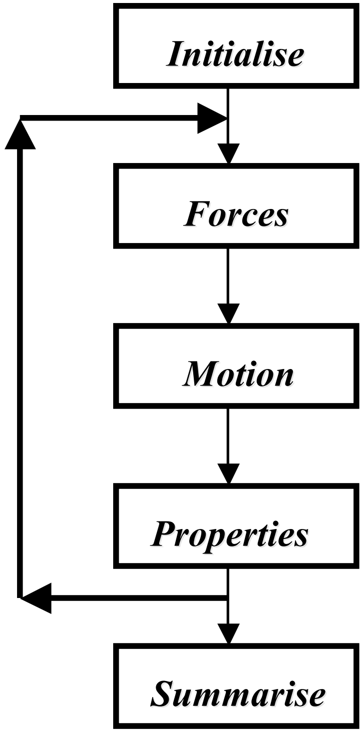
For metals use density dependent form e.g. **Finnis-Sinclair**.

Ionic systems – charges, polarisabilities … the **shell model**

Three-body (angle) potentials are required for glasses, zeolites etc.

Recently reactive force fields developed (eg: **Brener**)

An MD Simulation



Initialise

Forces

Motion

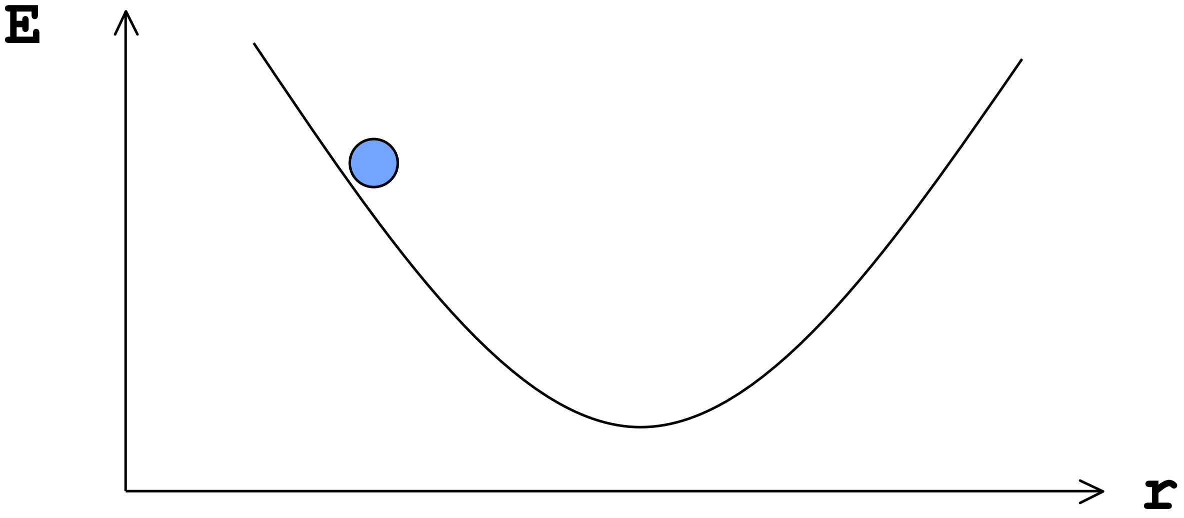
Properties

Summarise

Key stages in MD simulation:

- ***Set up initial system***
- ***Calculate atomic forces***
- ***Calculate atomic motion***
- ***Calculate physical properties***
- ***Repeat !***
- ***Produce final summary***

Time Scales - Oscillating in a Potential Well



On what time scales do atoms move ?

Vibrational frequency for an X-H bond ~3500 cm^{-1} = 10^{14} Hz

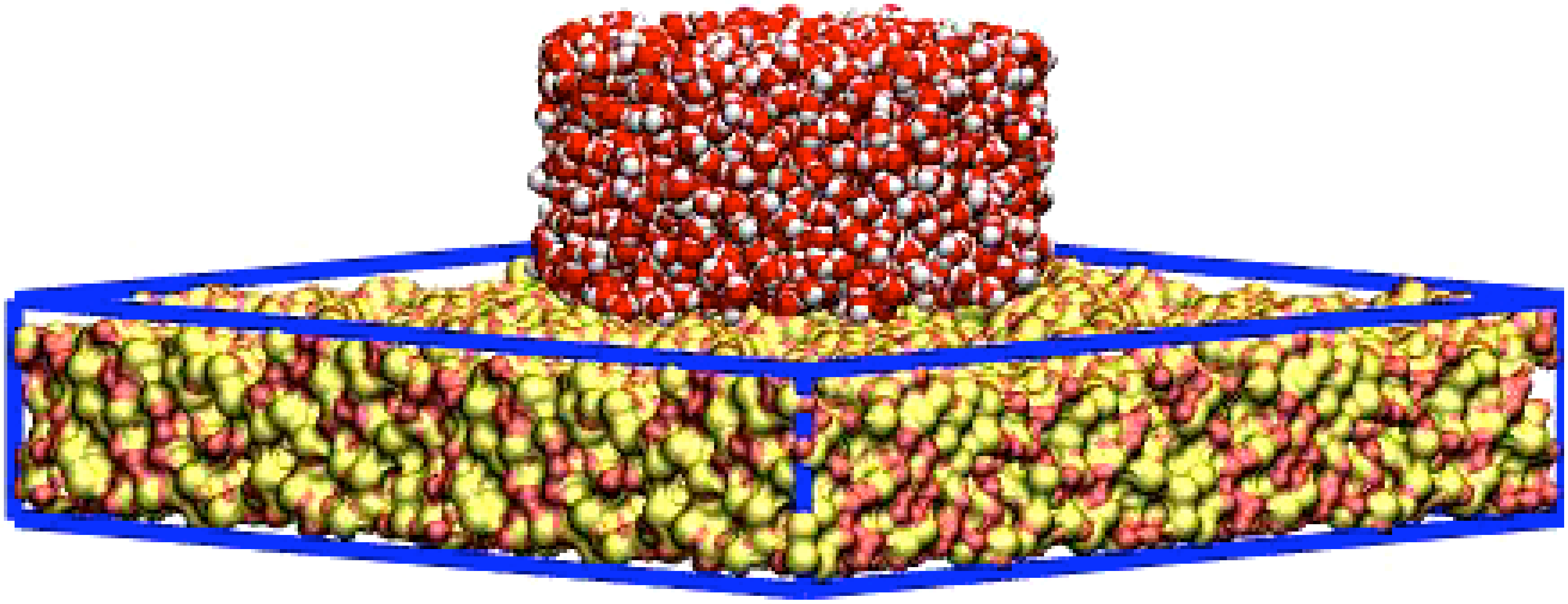
A cycle of oscillation takes 10^{-14} seconds

A time step must be a small fraction of a cycle ~ 1 femtosecond

Why ?

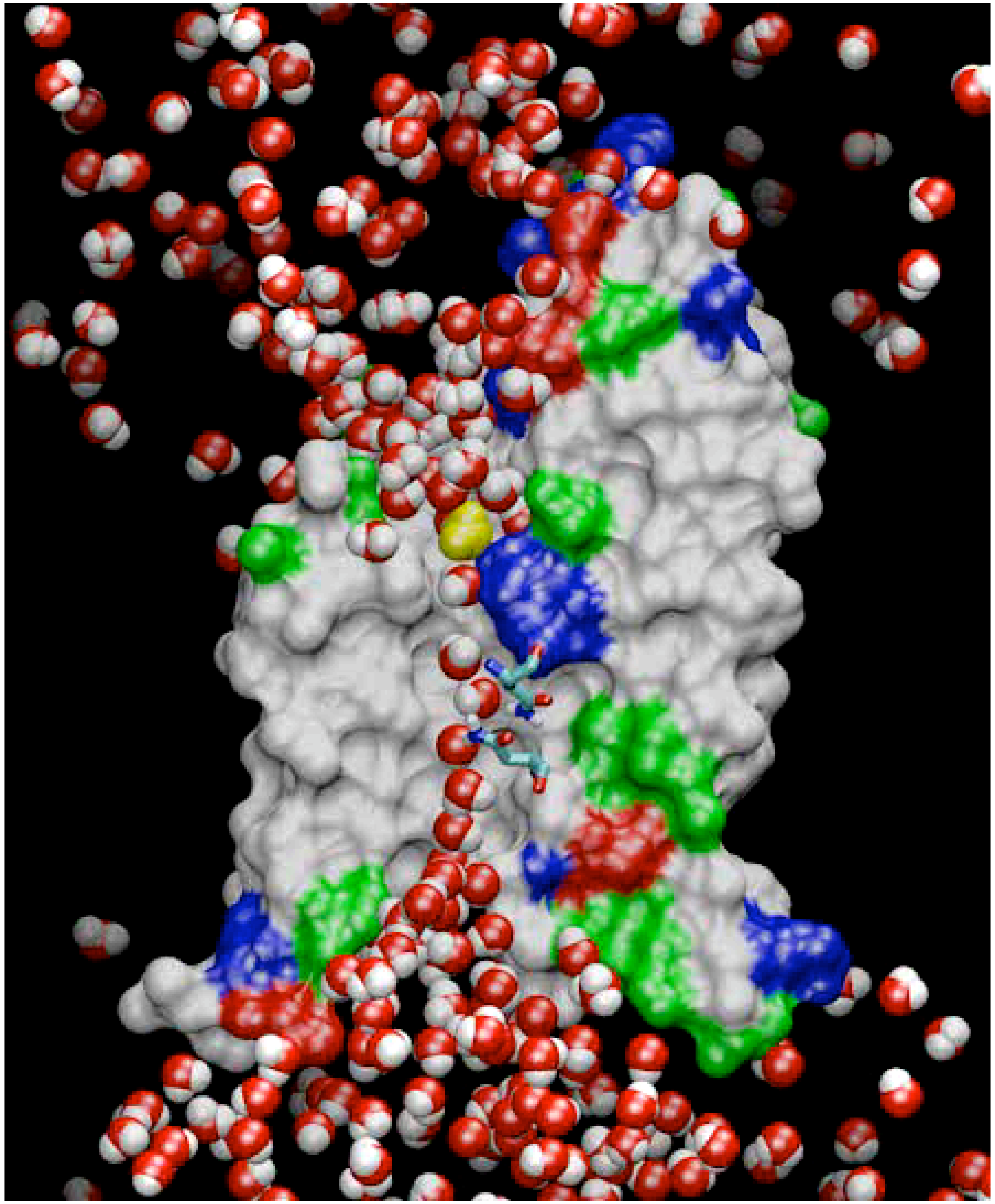
Example 1

A water droplet on a hydrophobic surface



http://www.ks.uiuc.edu/Gallery/Movies

Example 2 : Water Channel in a Cell Membrane



Equilibration

All simulations must be equilibrated!

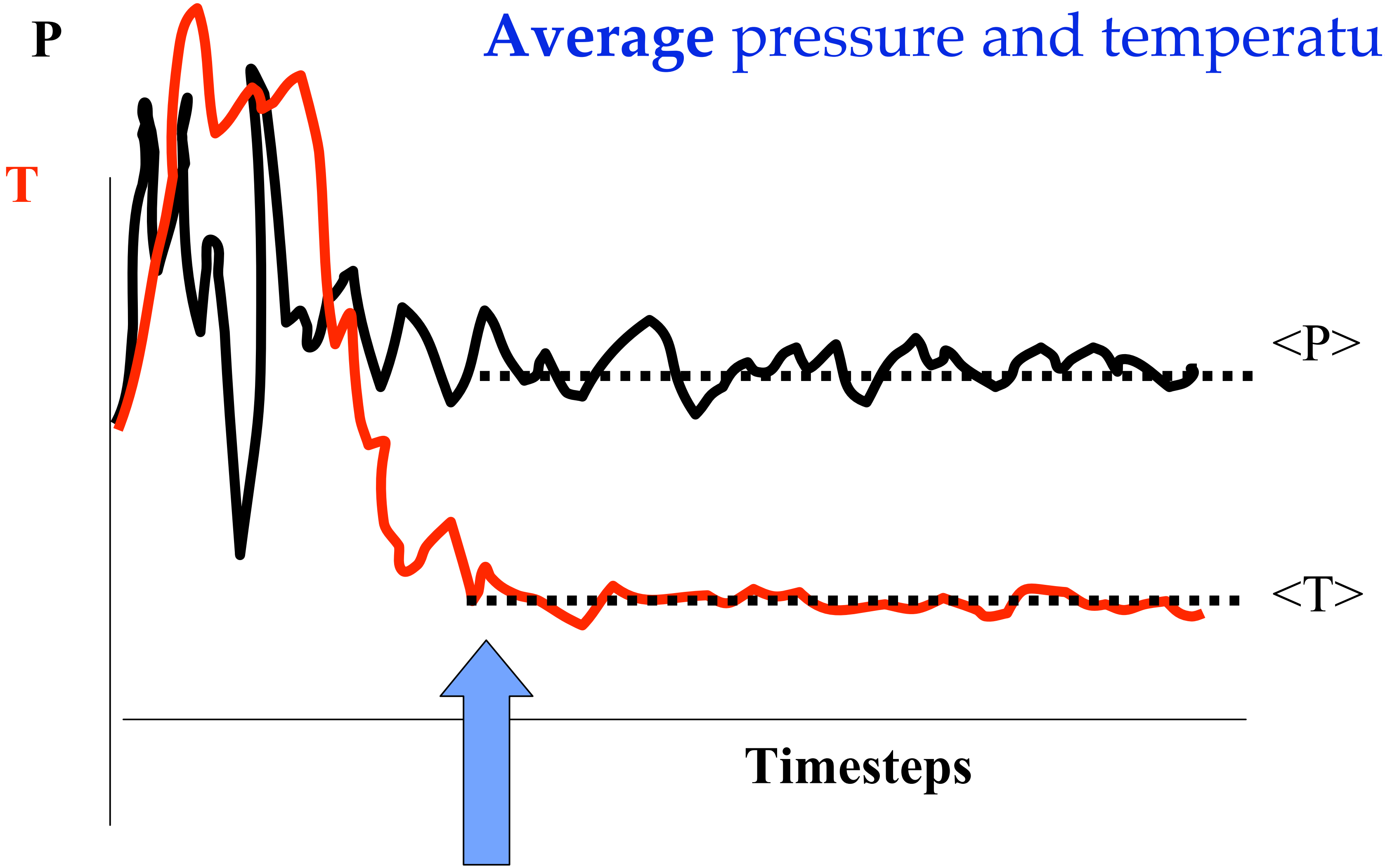
Monitor system temperature, configuration energy, volume (for NPT) to indicate approach to equilibration.

But note this may not be sufficient if phenomenon of interest has a long time scale. e.g. water relaxation around a protein substituent may be relatively fast but the protein structural relaxation may be very slow. Keep the time scale issue in mind always.

Make good use of statistical methods to ensure convergence has occurred. e.g. blocking method

Typical Output

Average pressure and temperature



Thermodynamic Properties (time averages)

Kinetic Energy:

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

Temperature:

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

And...

Configuration Energy:

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

Pressure:

$$PV = Nk_BT - \frac{1}{3}\left\langle \sum_i^N \vec{r}_i \cdot \vec{f}_i \right\rangle$$

Specific Heat
(from fluctuations)

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

Average Structural Properties

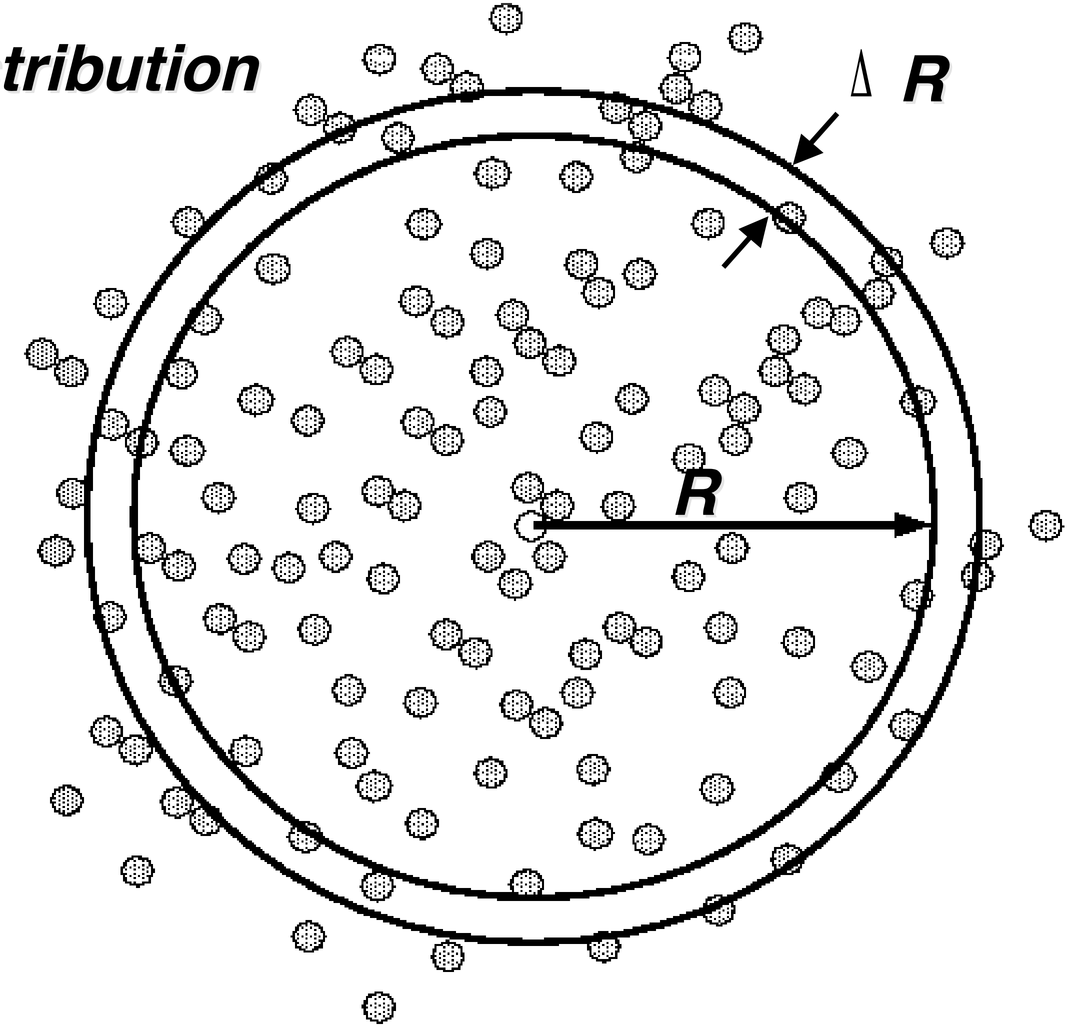
Pair correlation (Radial Distribution Function):

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

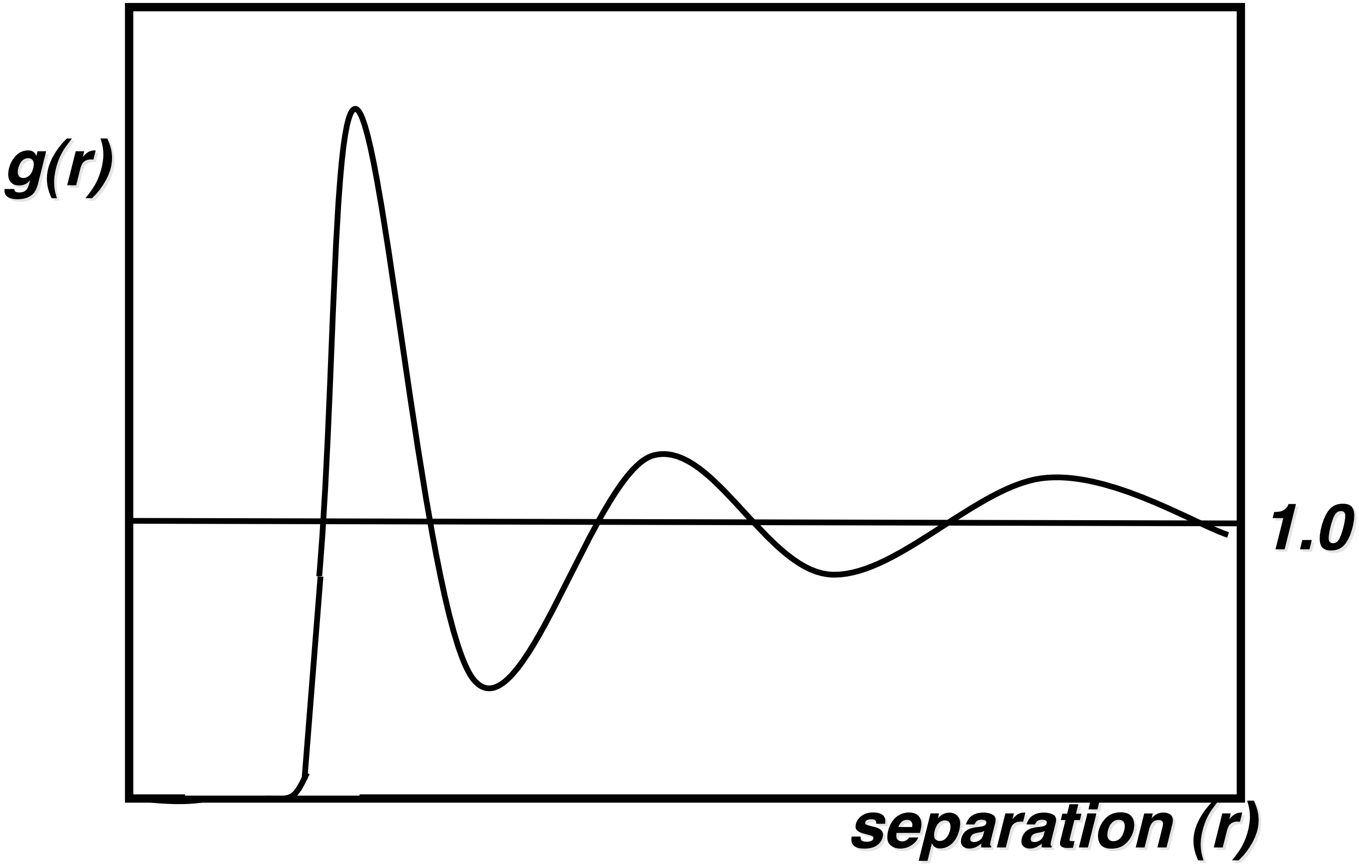
Structure Factor (Measured by X-ray or Neutron scattering)

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

Radial Distribution Function



Radial Distribution Function



The Free Energy ?

All above calculable by molecular dynamics or Monte Carlo simulation.

But the Free Energy is not:

$$A(V,T) = -k_B T \log_e\left(Q_N(V,T)\right)$$

where

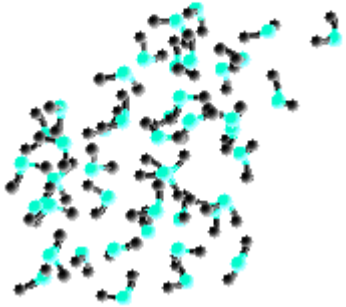
$$Q_N(V,T) = \frac{1}{N!h^{3N}} \iint \exp\left(-\beta H(\vec{r}^{\,N},\vec{p}^{\,N})\right) d\vec{r}^{\,N} d\vec{p}^{\,N}$$

is the Partition Function.

But you can calculate a **free energy difference**!

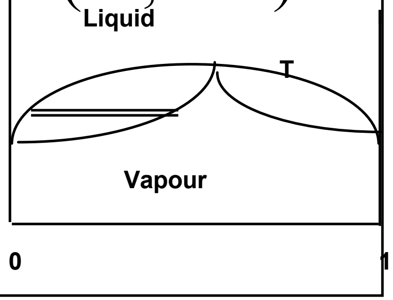
This is Explicit Statistical Mechanics

Microscopic
$V(r^N)$, ~ ps, nm



Statistical Mechanics Time and Ensemble Averages

Macroscopic
(~s, mm)



Connects force field with physical properties

Molecular Dynamics - Sampling

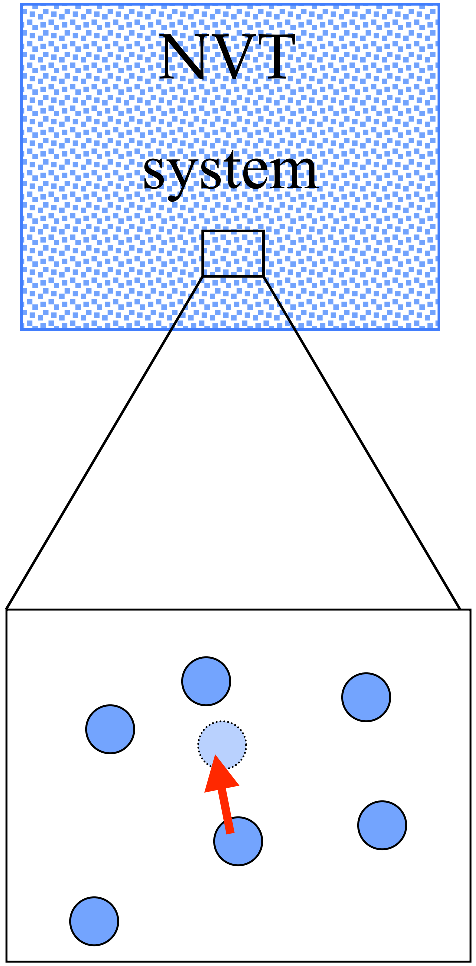
The macroscopic properties in MD are averages over the microstates of the system.

The accuracy of any such property depends on running the MD for long enough to sample configuration space.

In some cases MD is not an efficient way to explore configuration space.

Monte Carlo Simulations (in a slide !)

Alternative way to sample configuration space.



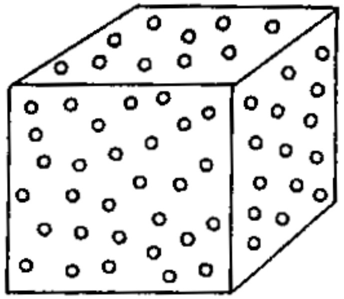
Generate new configs by moving an atom

Probability of the configuration - Bolztman

$$f_n = e^{-E_n/k_B T} / Z_N(V,T)$$

Average properties over configurations..

$$A = \langle \alpha \rangle^{ex} \approx \sum_n \alpha_n f_n$$



N ~ 100 - 10,000

Periodic Boundaries

Prescribed Intermolecular Potential

Monte Carlo

Specify, N, V, T

↓

Generate random moves

↓

Sample with $f = \exp\left[-\beta V_n\right]/Z_N(V,T)$

↓

Take averages

↓

Obtain equilibrium properties

Molecular Dynamics

Specify N, V, E

↓

Solve Newton's eq^n's
$F_i = m_i a_i$

↓

$r_i(t)$, $v_i(t)$, etc.

↓

Take averages

↓

Obtain equilibrium and nonequilibrium properties

Schematic description of the MC and MD methods.

MD and MC

Why would you ever use molecular dynamics ?

Explicit trajectories needed

Unknown configuration space (allow the system to explore it)

Process is known to be fast enough to be simulated within the MD time scale

Look out for new hot topics meta-dynamics, temperature accelerated dynamics etc….

Have a Play

There is an undergraduate exercise in vibrations and molecular dynamics of MgO crystals

http://www.ch.ic.ac.uk/harrison

Under the Teaching link.

The software is installed in the computer room.

You can use it to simulate a very wide variety of systems