Molecular Dynamics

$$F = ma$$

What is Molecular Dynamics?

The solution of the <u>classical</u> equations of motion for atoms and molecules to obtain the <u>time evolution</u> of the system.

MD Features

Applied to many-particle systems - a general analytical solution not possible. 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 (r_i^0, v_i^0)

$$\vec{v}_{i}^{n+1} = \vec{v}_{i}^{n} + \frac{\Delta t}{2m_i}\left(\vec{F}_{i}^{n} + \vec{F}_{i}^{n+1}\right) + \vartheta\left(\Delta t^3\right)$$

$$\vec{r}_{i}^{n+1} = \vec{r}_{i}^{n} + \Delta t \quad \vec{v}_{i}^{n} + \frac{\Delta t^2}{2m_i}\vec{F}_{i}^{n} + \vartheta\left(\Delta t^4\right)$$

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 ?

Density functional theory

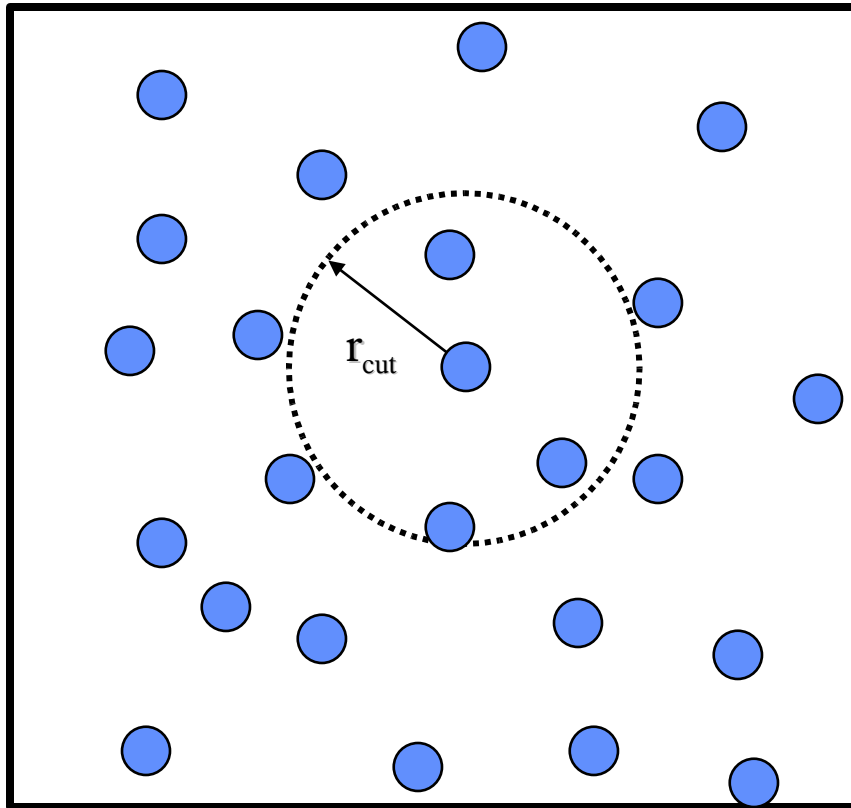$$\vec{F}_i = \frac{\partial E[\rho]}{\partial \vec{r}_i}$$

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 or, more often now, determined from DFT studies of model systems….
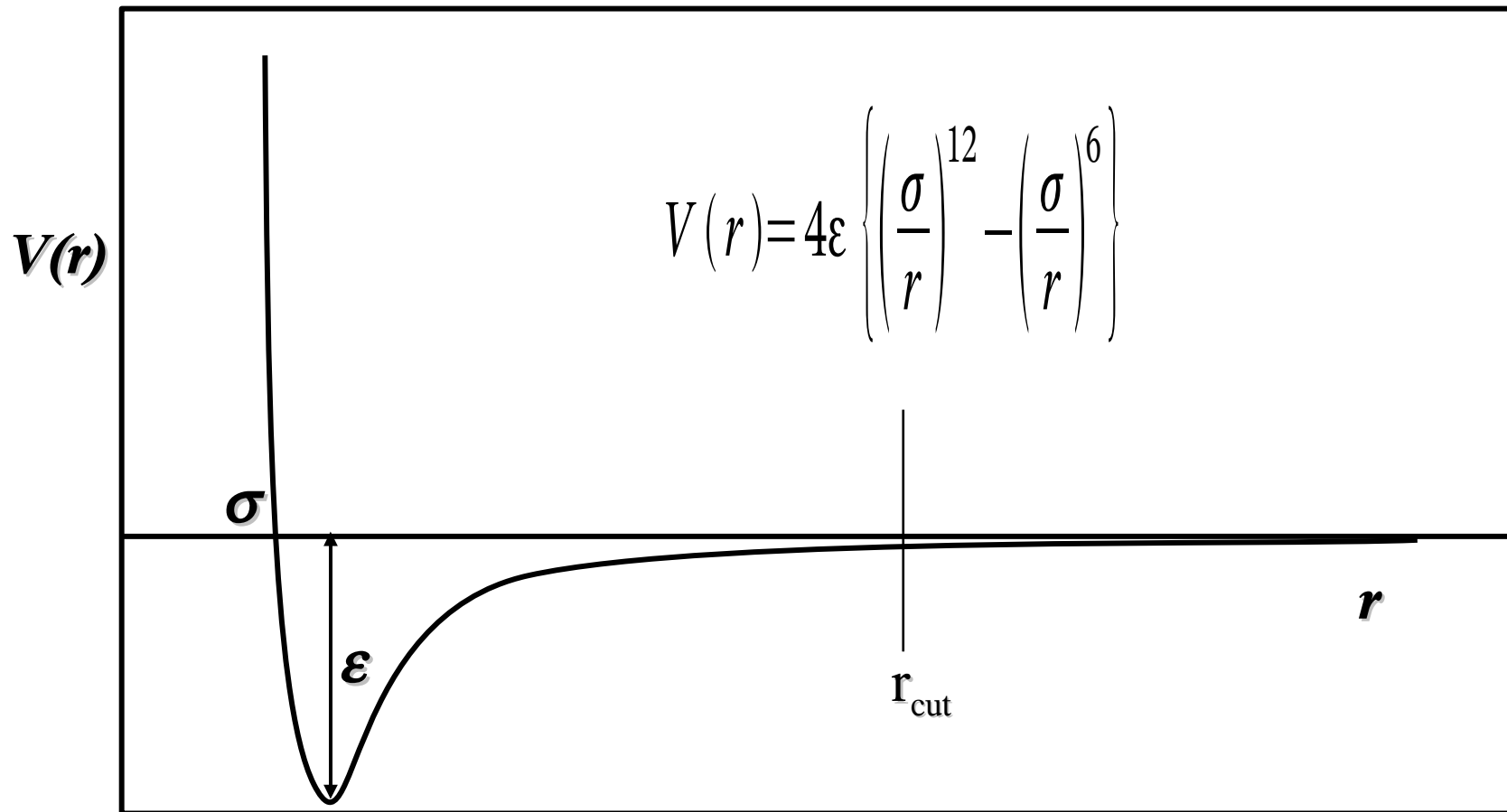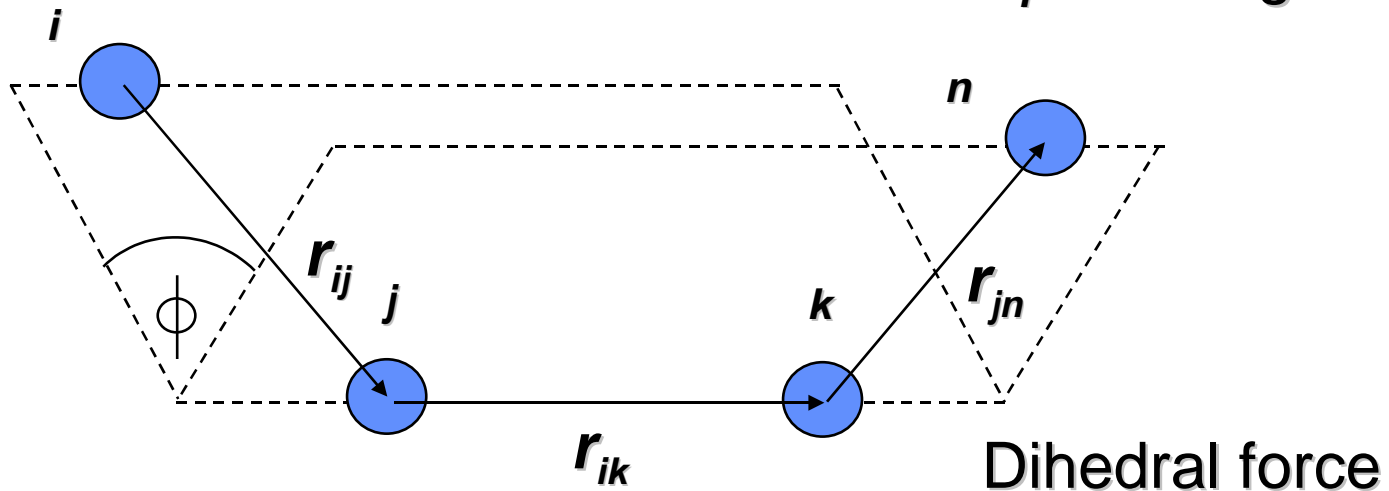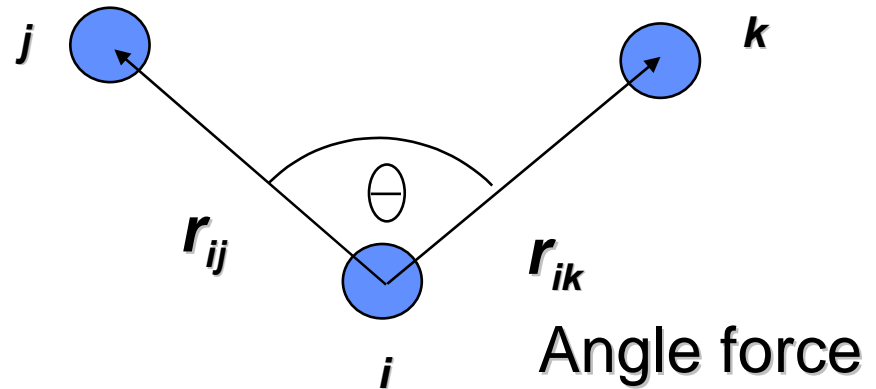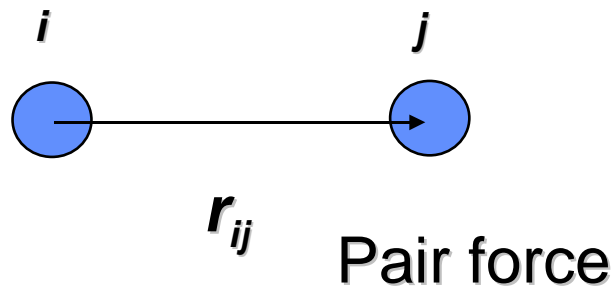
For Example

Simulation of Argon

Pair Potential:

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

The Lennard-Jones Potential

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

$V(r)$

σ

ε

r_{cut}

r

Typical Force Fields – Covalent Bonds

Pair force

Angle force

Dihedral force

Force Fields

Force fields are plentiful, **but not all are accurate**!

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

Some "universal" force fields exist e.g. Dreiding. !!
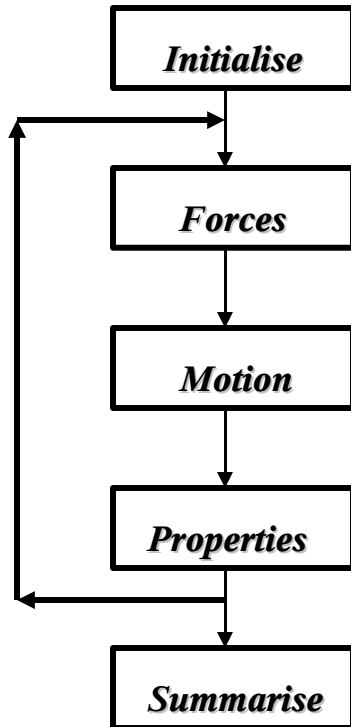
For biosystems use GROMOS, AMBER, CHARMM

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

Ionic systems – need charges, polarisabilities etc.

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

In Summary

Key stages in MD simulation:

- **Set up initial system**
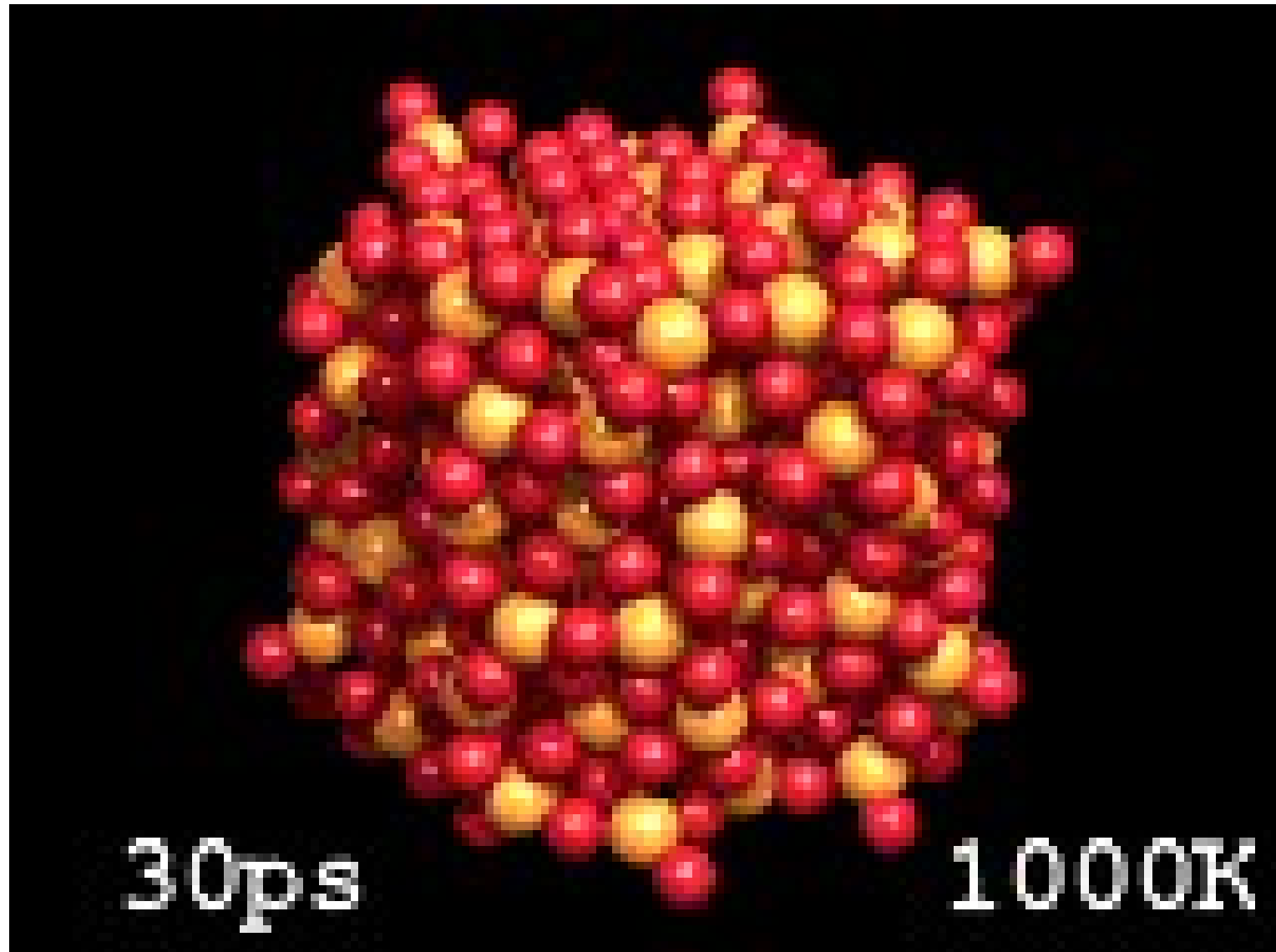
- **Calculate atomic forces**

- **Calculate atomic motion**

- **Calculate physical properties**

- **Repeat !**

- **Produce final summary**

Initialise → Forces → Motion → Properties → Summarise

Gratuitous Video

30ps   1000K

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

P

T

<P>

<T>

Timesteps
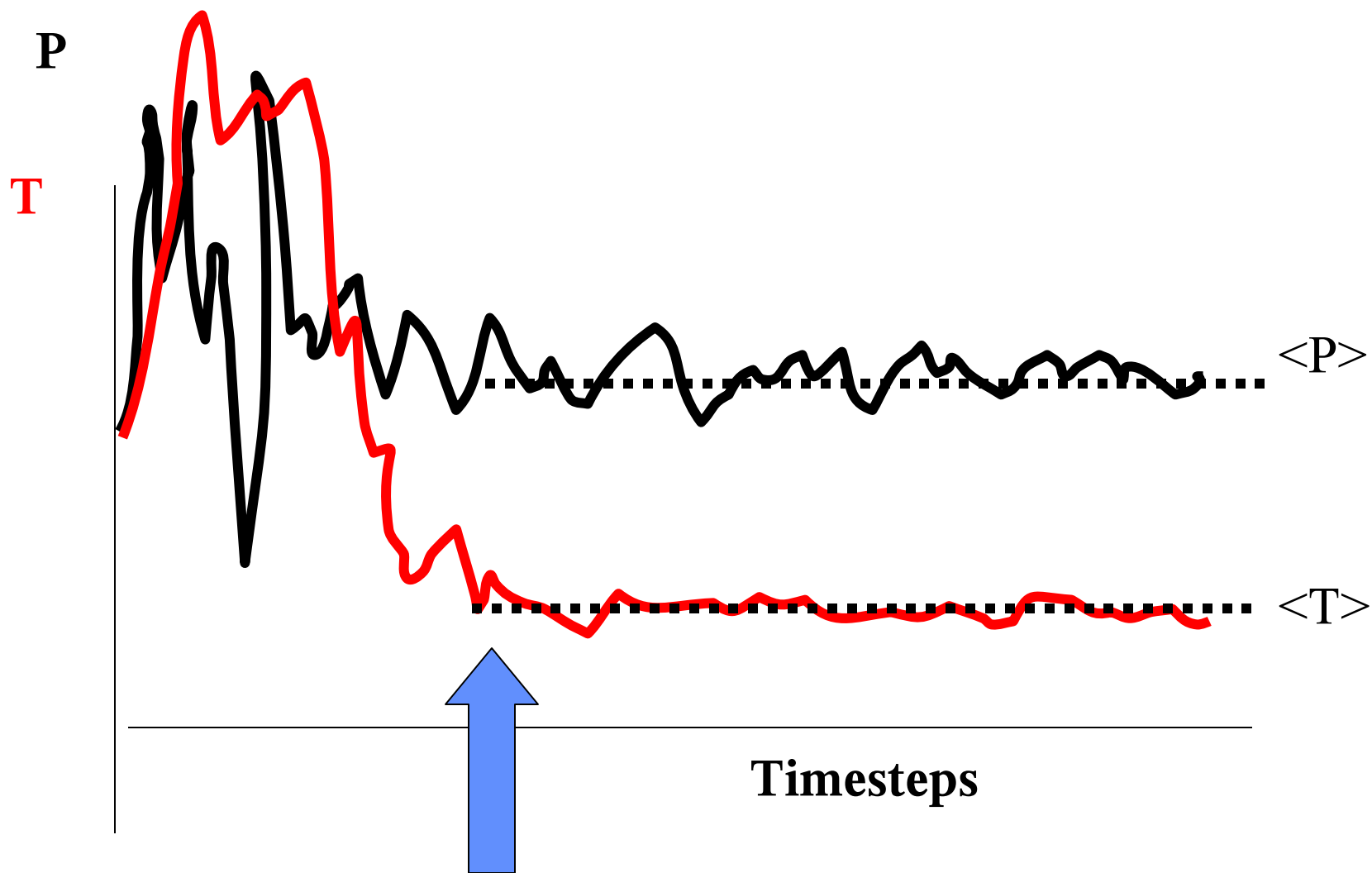
Thermodynamic Properties (time averages)

Kinetic Energy:

$$\langle K.E.\rangle = \langle \frac{1}{2}\sum_i^N m_i v_i^2 \rangle$$

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:

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

Specific Heat
(from fluctuations)

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

Structural Properties
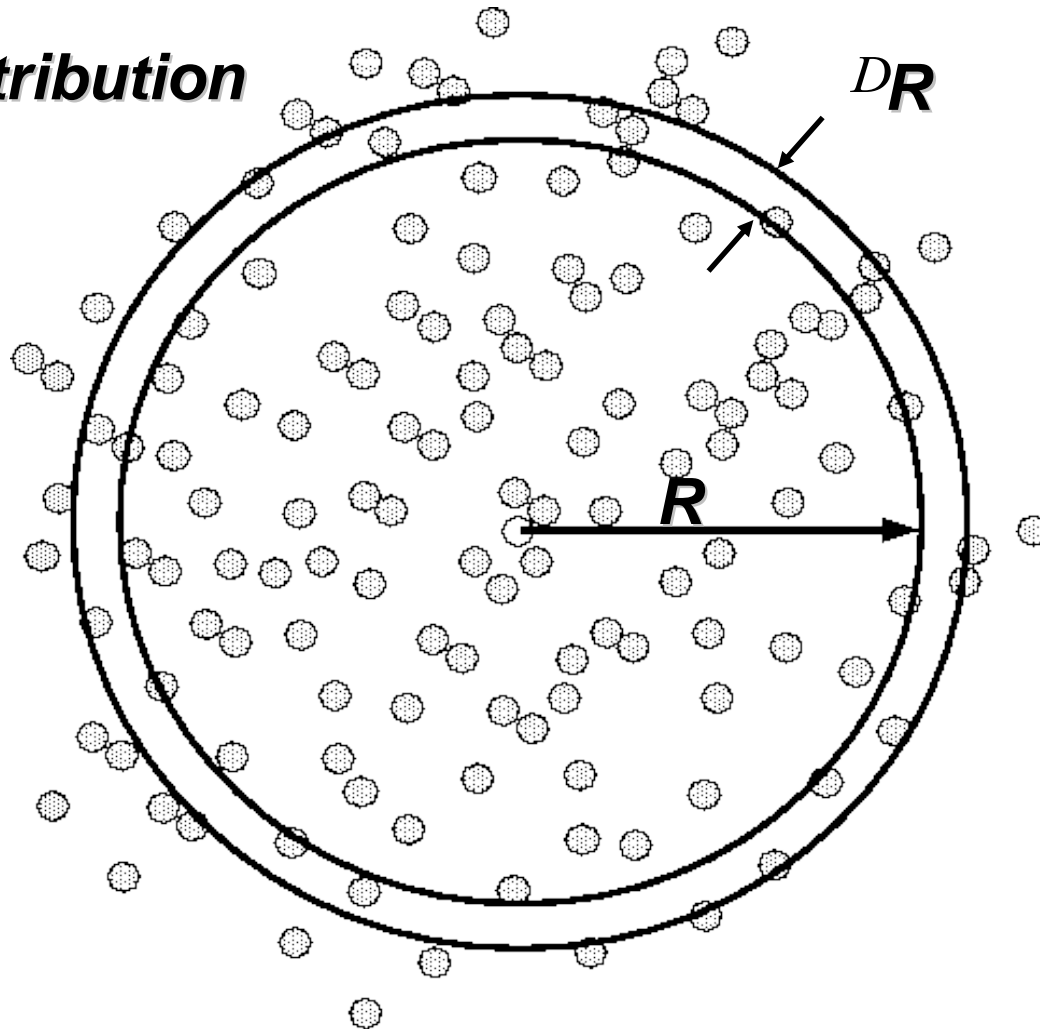
Pair correlation (Radial Distribution Function):

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

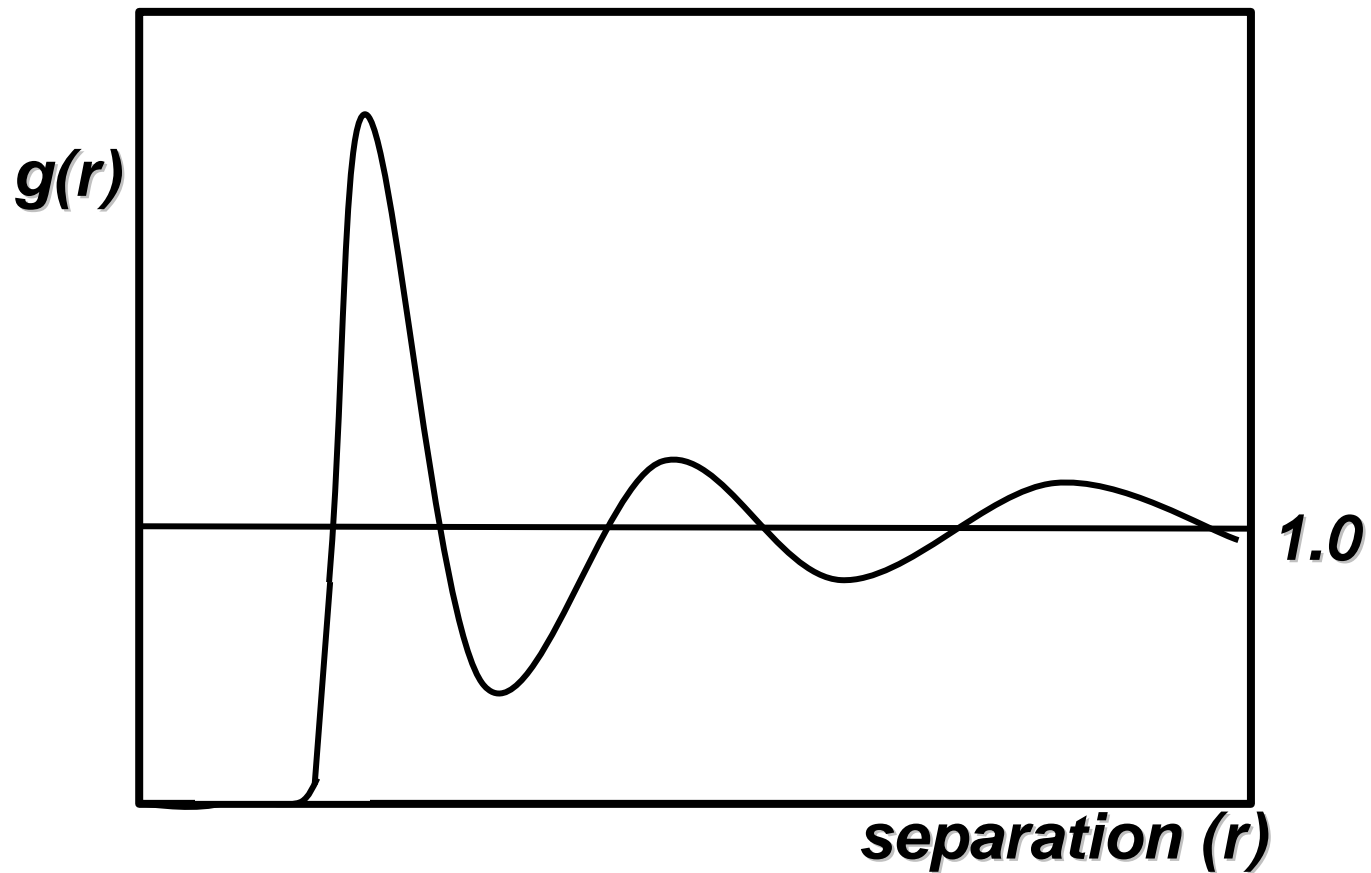Structure Factor (Measured by X-ray or Neutron scattering)

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

Radial Distribution Function

$D\mathbf{R}$

$\mathbf{R}$

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

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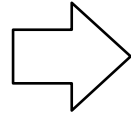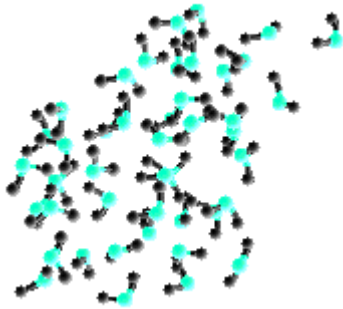
is the Partition Function.

But you can calculate a **free energy difference**!
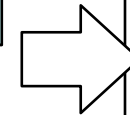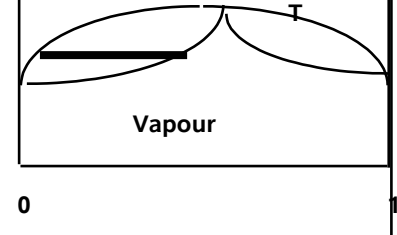
This is Explicit Statistical Mechanics

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

**Statistical Mechanics
Time and Ensemble
Averages**

Macroscopic
(~s, mm)

Liquid

Vapour

0   1

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 (Rough Guide)

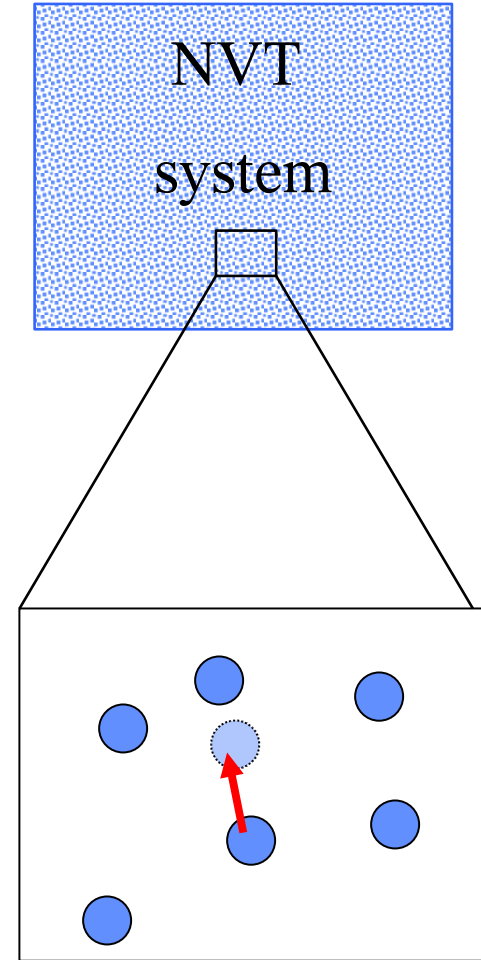Alternative way to sample configuration space.
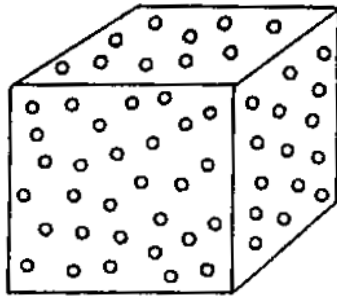
Generate new configs by moving an atom

Probability of the configuration - Bolztman

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

Average properties over configurations..

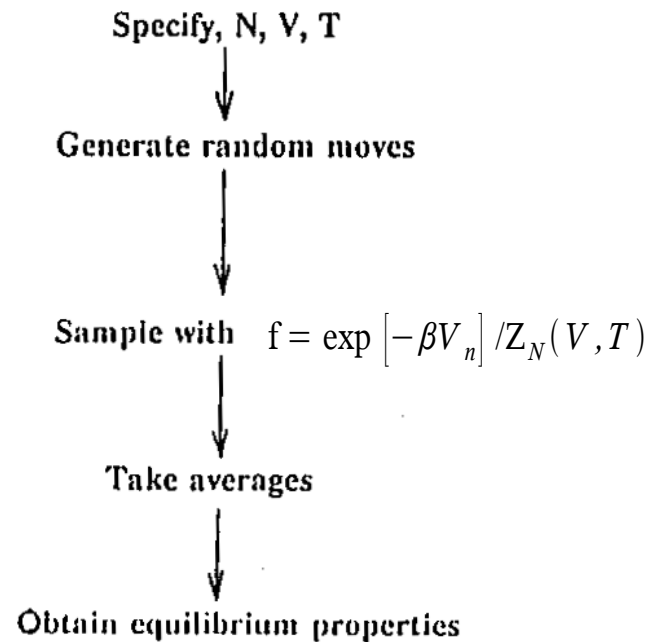$$A = \langle \alpha \rangle^{ex} \approx \sum_n \alpha_n f_n$$
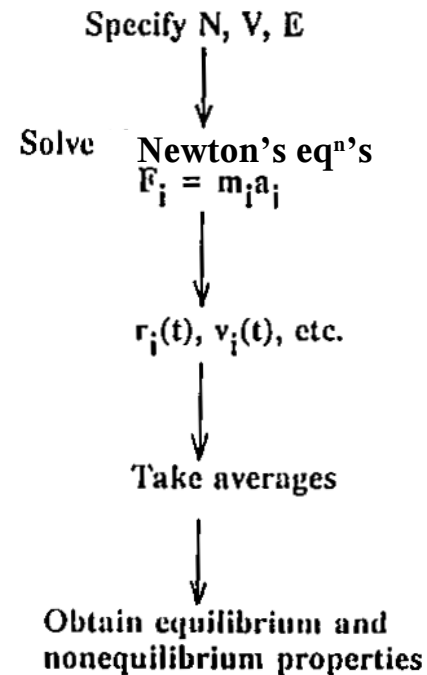
NVT system

$N \sim 100 - 10{,}000$

Periodic Boundaries

Prescribed Intermolecular Potential

Monte Carlo

Specify, N, V, T

↓

Generate random moves

↓

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

↓

Take averages

↓

Obtain equilibrium properties

Molecular Dynamics

Specify N, V, E

↓

Solve **Newton's eqⁿ'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 ?

Explict 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….