

CARDIFF
UNIVERSITY

PRIFYSGOL
CAERDYDD

ISIS Neutron training course.

6th March 2014

Molecular Dynamics

Lecture 2: Ideas on analysis.

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Analysing the results : radial distribution function

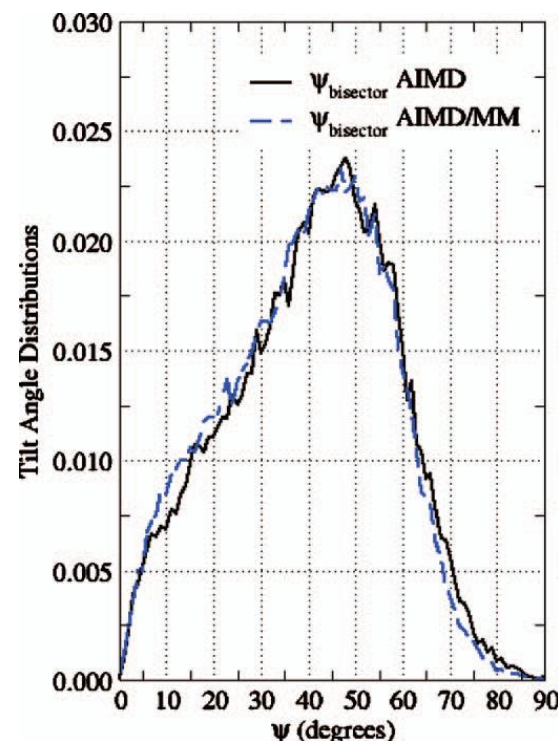
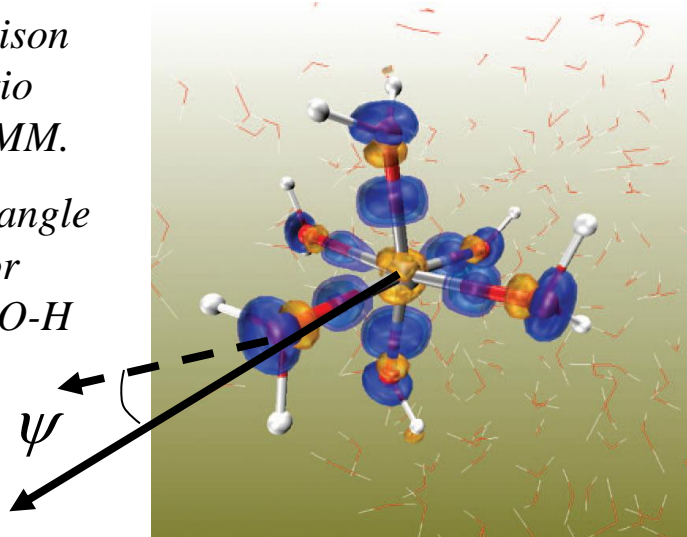
Molecular dynamics provides a trajectory for the entire system as a set of structures, or *frames, f*, rather than a single optimised geometry.

Structural features and properties can be averaged over this data.

Some features are straightforward, e.g. the tilt angle of waters in a Zn^{2+} solvation shell shown below.

This simulation was a comparison of fully ab initio MD and QM/MM.

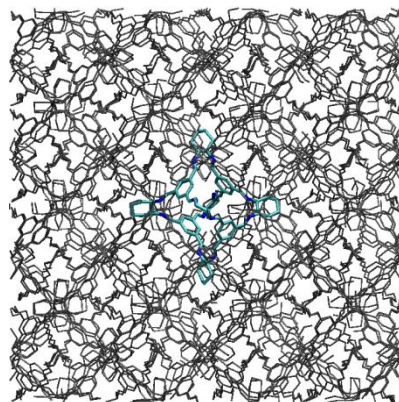
Graph shows angle distribution for bisector of H-O-H with O-Zn.



E. Cauët *et al.*, *J. Chem. Phys.* **132**, 194502, (2010)

CC3 RESEARCH, DAN HOLDEN & ABBIE TREWIN, LIVERPOOL

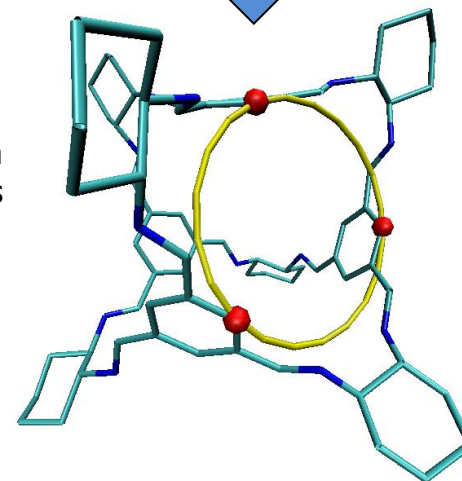
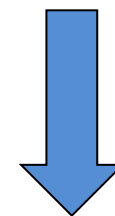
The first thing is to locate the PLD within **CC3**.



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

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

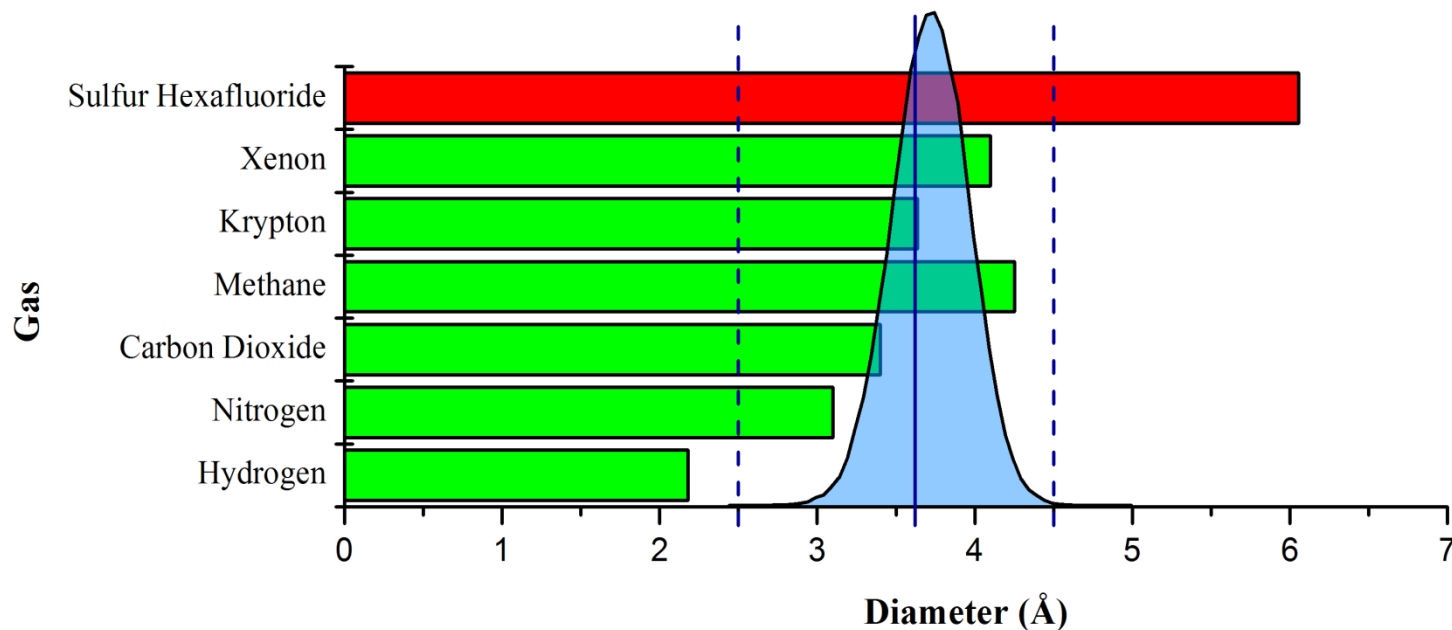
This cage was examined and the atoms involved in creating the narrow neck in the pore topology identified; the circumference of this circle was 3.62 Å – this is the PLD.



D. Holden, K. E. Jelfs, A. I. Cooper, A. Trewin, and D. J. Willock, *J. Phys. Chem. C*, **116** (31), 16639–16651, (2012).

CC3 RESEARCH

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



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

D. Holden, K. E. Jelfs, A. I. Cooper, A. Trewin, and D. J. Willock,
J. Phys. Chem. C, **116** (31), 16639–16651, (2012).

System Properties: Dynamic (1)

The bulk of these are in the form of *Correlation Functions* :

$$C(t) = \frac{1}{T_\infty} \int_0^{T_\infty} (f(t + \tau) - f_{av})(f(\tau) - f_{av}) d\tau$$

Note : Multiple time origins implied.

or

$$C(t) = \langle f(t) f(0) \rangle - \langle f_{av} \rangle^2$$

Example: Velocity autocorrelation function.

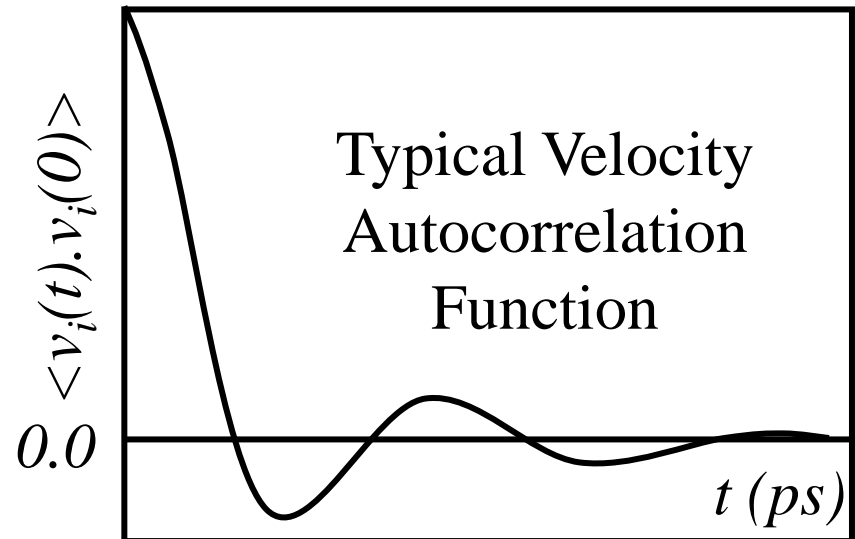
Range up to 1.0, all velocities identical to time zero.

For velocity the average overall must be zero.

Decays as velocities lose correlation through randomising collisions.

Related to self diffusion coefficient:

$$D = \frac{1}{3} \int_0^\infty \langle v(t) \cdot v(0) \rangle dt$$



Fick's law

Fick's law states that the flux, J , of the diffusing species is proportional to the negative gradient in the concentration of that species:

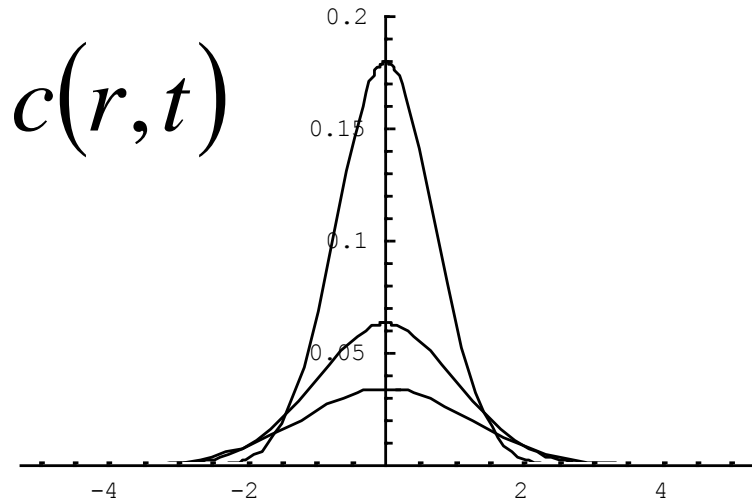
$$J = -D\nabla c$$

The constant of proportionality, D , is the diffusion coefficient.

This is a macroscopic model of diffusion and relates the flux of particles to a concentration gradient.

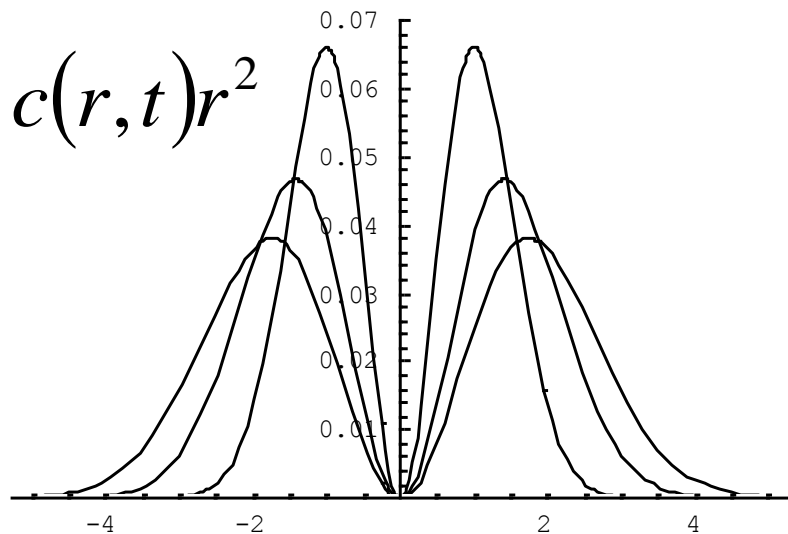
Diffusion of a labelled species among otherwise identical particles is called self diffusion.

We can label particles experimentally by altering nuclear spin and then following the labelled species with time, (pFG-NMR).



In a sample of fluid, if we marked some of the molecules and then monitored their distribution as a function of time.

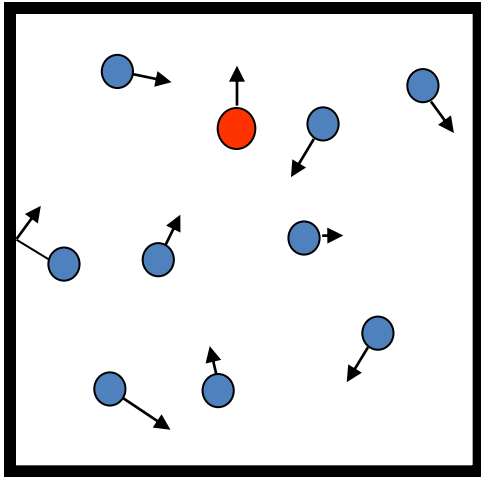
$$\frac{\partial c(r, t)}{\partial t} - D\nabla^2 c(r, t) = 0$$



The concentration itself decays symmetrically about the origin, however its second moment moves away from the origin with time.

In 3-dimensions can be shown that:

$$\frac{\partial}{\partial t} \int c(r, t)r^2 dr = 6D$$



In a simulation we are ideally positioned to work out the self diffusion coefficient, since we can follow any particle we choose.

$$\frac{\partial}{\partial t} \int c(r, t) r^2 dr = 6D$$

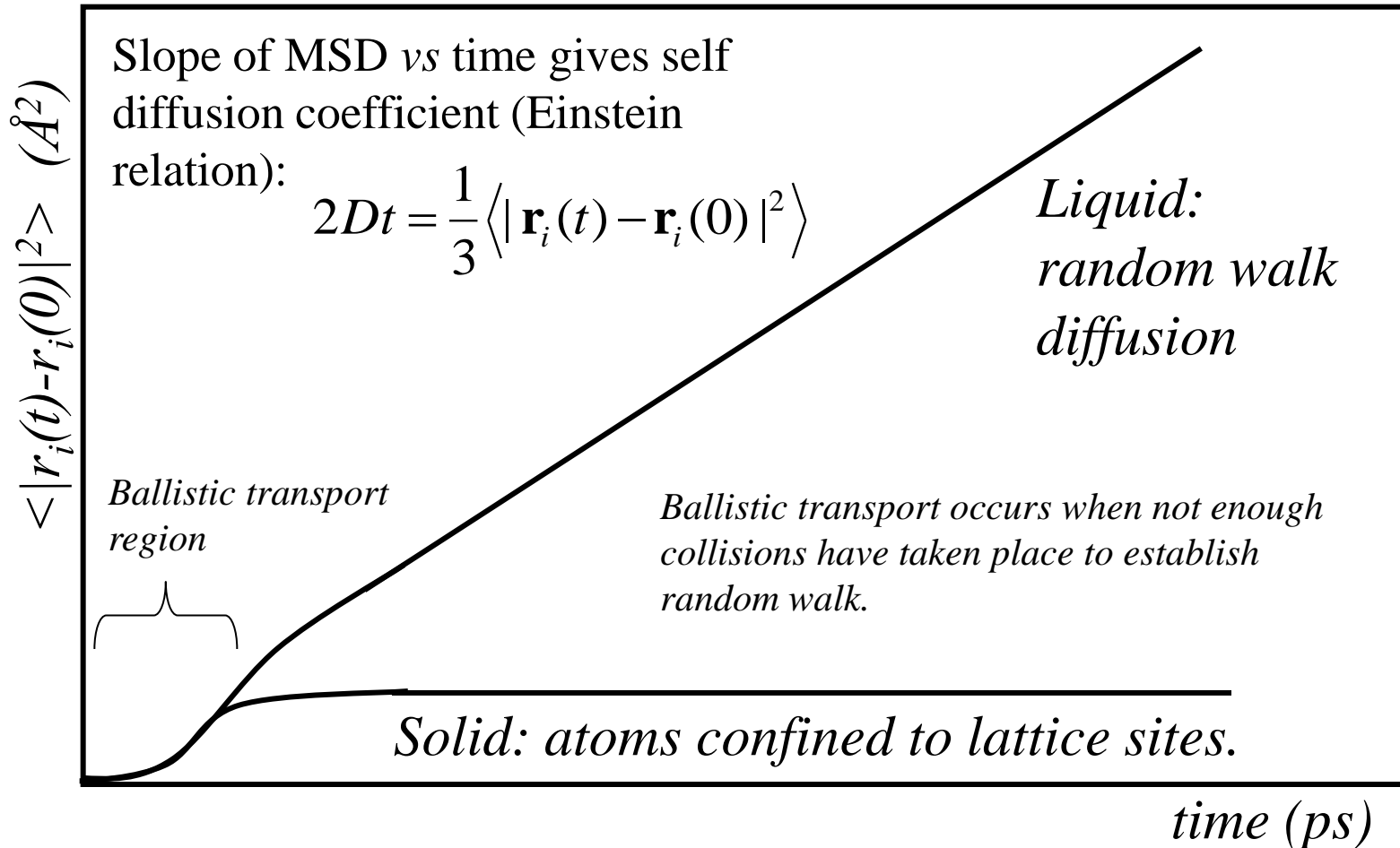
Taking the concentration as a measure of probability we can take the integral of the left hand side as the mean square displacement for a molecule:

$$\langle \Delta x^2 \rangle_t = \frac{1}{N_{mols}} \sum^{mols} [x(t) - x(0)]^2$$

$$D_s = \frac{1}{6} \frac{d \langle \Delta x^2 \rangle}{dt}$$

System Properties: Dynamic (2)

Mean Square Displacement, MSD.



Extended Systems

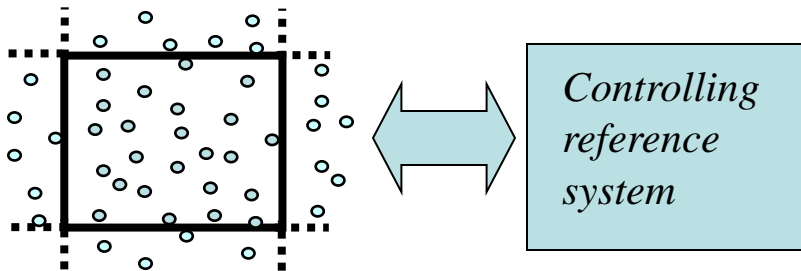
We have seen that Newton's Laws conserve energy and so the basic MD procedure samples the NVE ensemble.

Extended systems are required to handle:

The canonical ensemble (NVT)

The isotropic isothermal-isobaric ensemble (NPT)

To do this we will look at equations of motion for systems of particles coupled to thermal baths with which energy can be exchanged to maintain T (thermostat) and/or explicit introduction of degrees of freedom for the system volume to allow constant pressure (barostat).

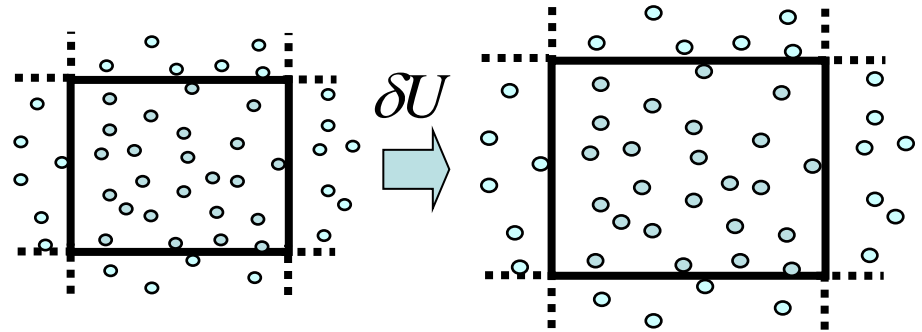


References:

- H.C.Andersen, *J. Chem.Phys.*, **72**(4), 2384, (1980).
- W. G. Hoover, *Phys. Rev. A*, **31**, 1695, (1985).
- S. Nosé, *Mol. Phys.*, **52**, 255, (1984).
- S. Nosé, *J. Chem. Phys.*, **81**, 511, (1984).
- M. Parrinello & co-workers, *J. Chem.Phys.*, **130**, 074101, (2009).

Constant Pressure MD

Suppose we want to run an MD simulation with the system subject to some external pressure, P .



We must adapt the equations of motion to allow fluctuations in the system volume in response to P .

$$r_i = V^{1/3} q_i$$

Bring cell volume into atom co-ordinates.

$$L(q, \dot{q}, V, \dot{V}) = \underbrace{\frac{1}{2} V^{2/3} \sum_i m_i \dot{q}_i^2 - \sum_{i,j>i} U_{ij}(V^{1/3}, q_{ij})}_{\text{KE and PE of particles}} + \underbrace{\frac{1}{2} M \dot{V}^2 - PV}_{\text{“KE and PE” of cell.}}$$

The cell mass, M , is the external mass generating the pressure, P , and has to be set.

Constant Temperature MD

In the constant pressure dynamics we introduced a scaling of the positional co-ordinates based on the volume of the system so that dynamical variables could be associated with the cell volume.

For constant temperature we scale the momenta so that the temperature of the system can be controlled by a new dynamical variable, s .

$$q_i = r_i \quad \dot{q}_i = \frac{\dot{r}_i}{s}$$

$$L(q, \dot{q}, s, \dot{s}) = \underbrace{\frac{s^2}{2} \sum_i m_i \dot{q}_i^2 - \sum_{i,j>i} U_{ij}(q_{ij})}_{\text{KE and PE of particles}} + \underbrace{\frac{1}{2} M_T \dot{s}^2 - gkT \ln s}_{\text{“KE and PE” of thermostat.}}$$

Where T is the set temperature and the mass, M_T , and constant g control the exchange of energy with the heat bath.

