ISIS Neutron training course.

6th March 2014

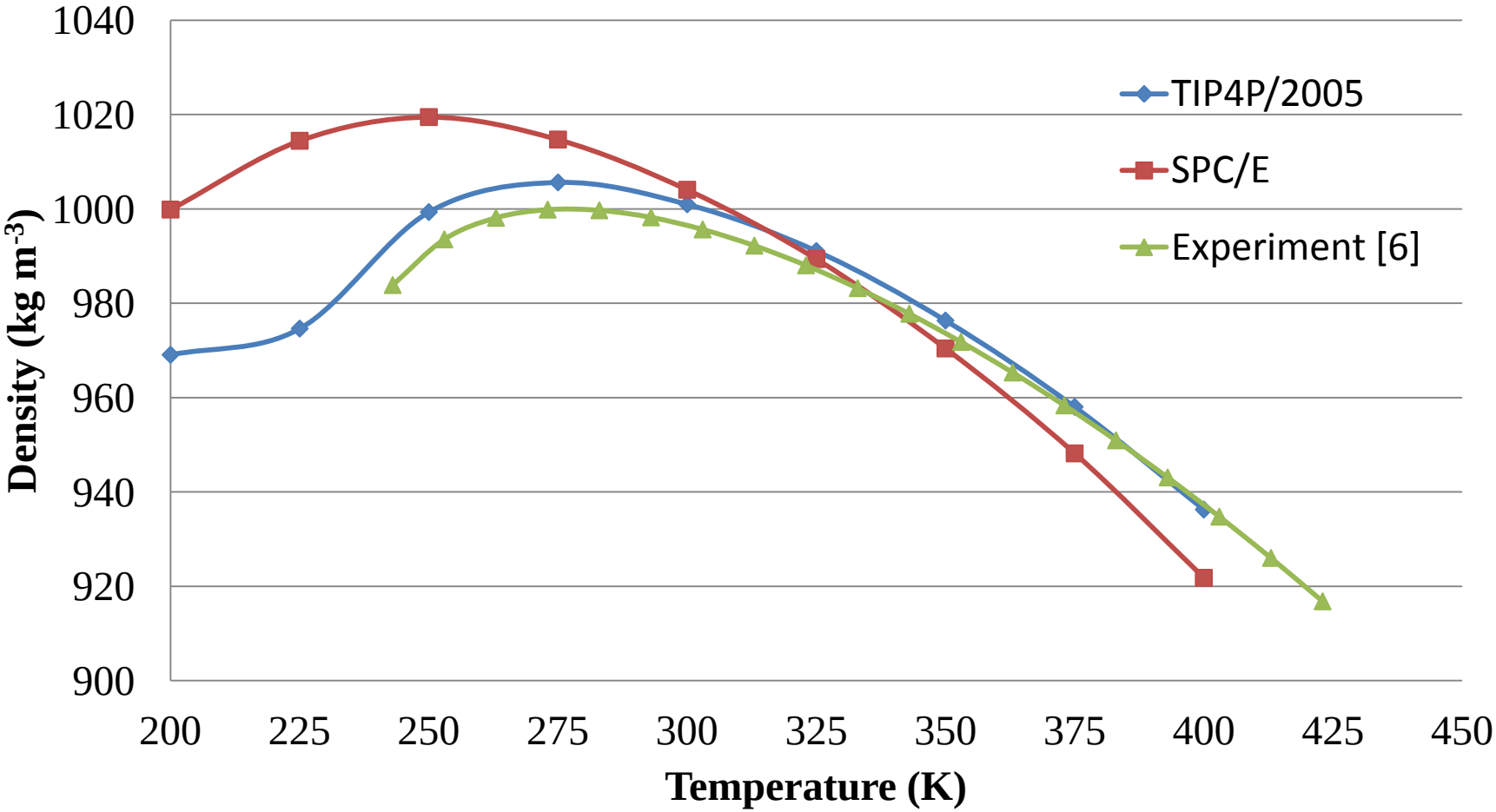
Molecular Dynamics

Lecture 3: Analysis of the results, some examples.

David J. Willock

Cardiff University, U.K.

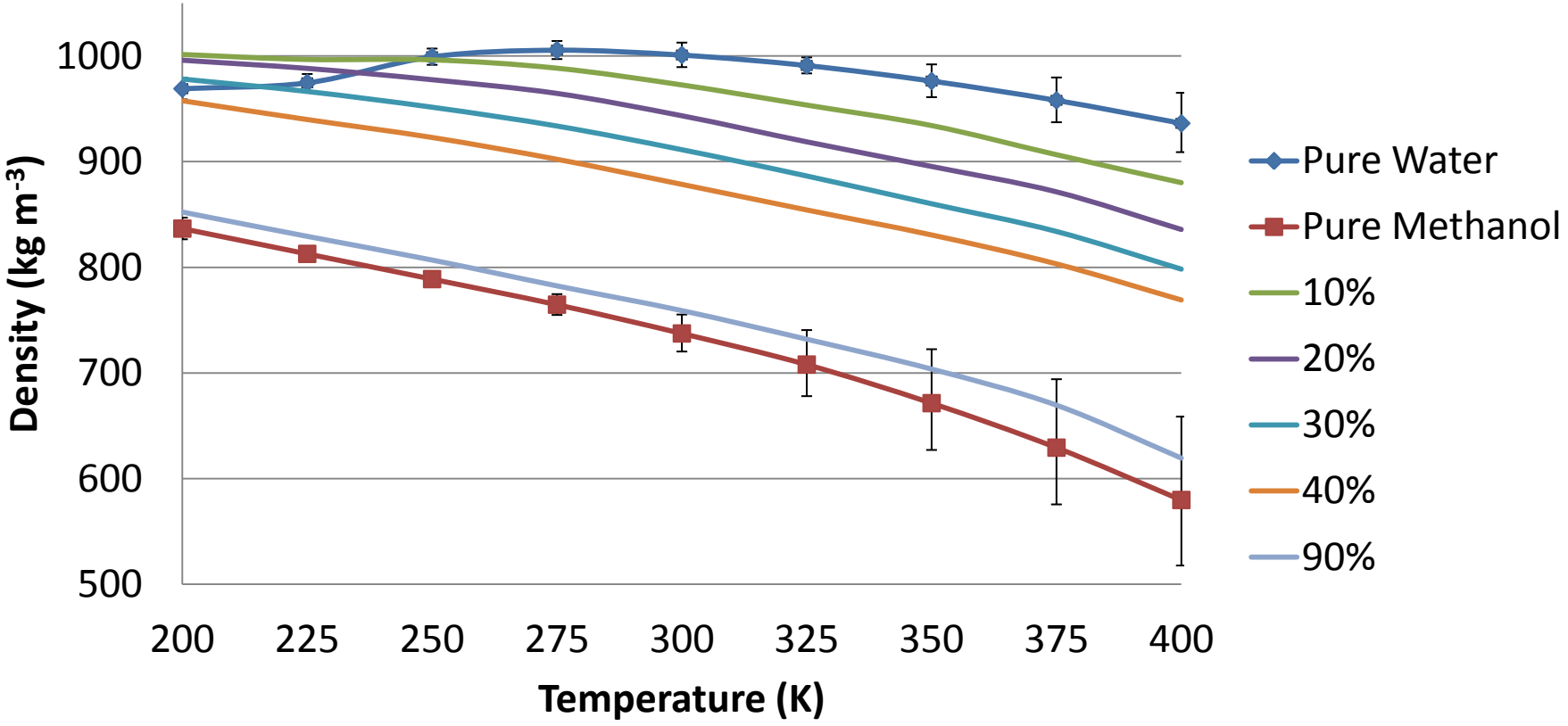
Water Models



- TIP4P/2005 provides a much more accurate description of liquid water than SPC/E
- SPC/E underestimates the temperature at which the density of water has its maximum, so the water structure will be affected.

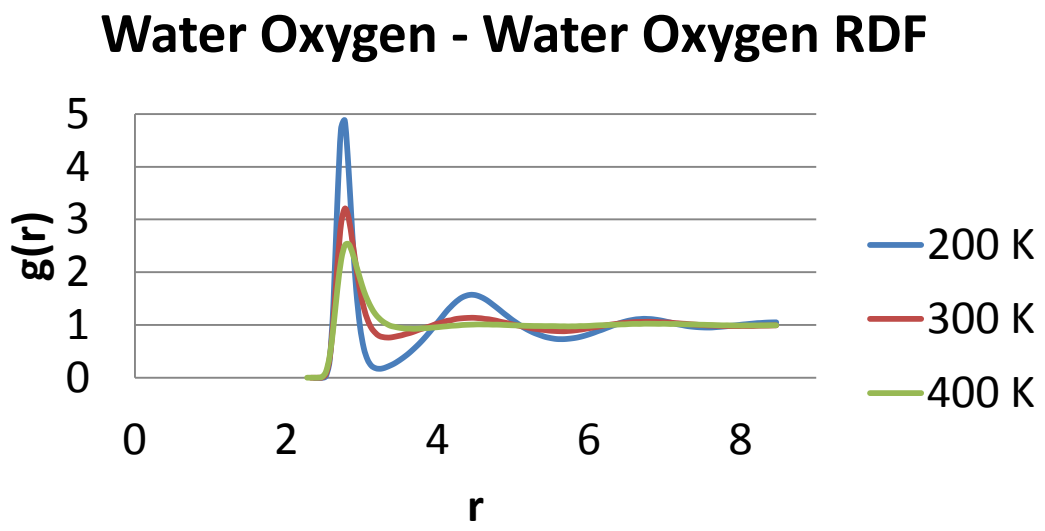
[6] G. S. Kell, *J. Chem. Eng. Data*, **20**, 97, (1975)

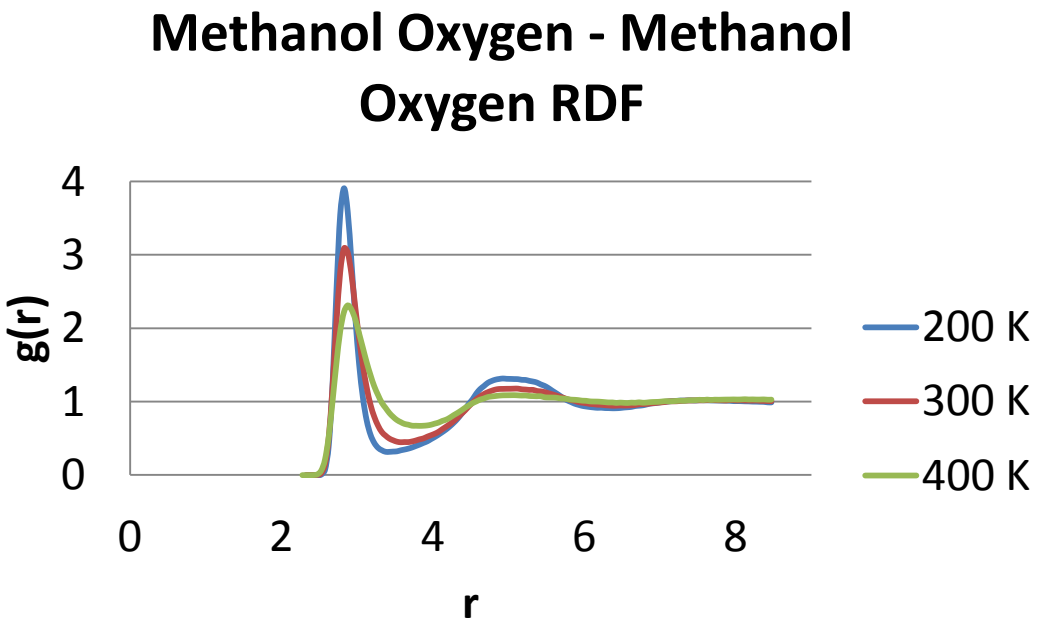
Water/Methanol mixtures.



- Even a small amount of methanol alters the properties of the solution by disrupting the hydrogen bonding network.

Radial Distribution Functions



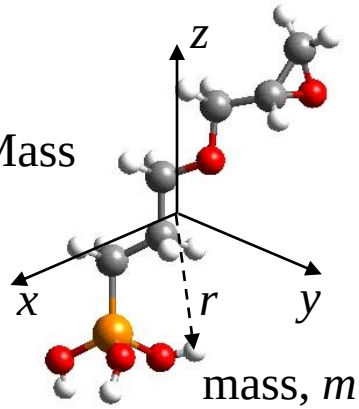


- Peaks show the distances of the first, second etc. neighbours
- Narrow peaks indicate that the system is more ordered
- Integrating the radial distribution functions to their first minima allow us to calculate the average number of hydrogen bonds formed by each molecule.

Moment of Inertia of molecules

The moment of inertia of a molecule is a matrix which pays the role of mass in rotational motion. It is defined as:

Origin :
Centre of Mass

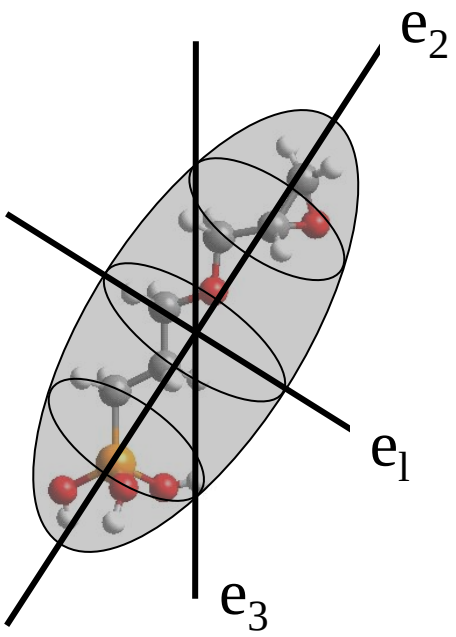


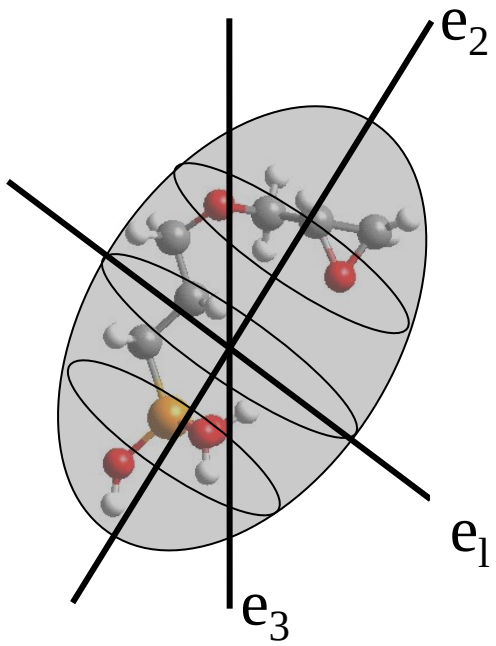
$$I = \begin{pmatrix} \sum_{atoms} m\left(|r|^2 - r_x^2\right) & \sum_{atoms} m r_x r_y & \sum_{atoms} m r_x r_z \\ \sum_{atoms} m r_x r_y & \sum_{atoms} m\left(|r|^2 - r_y^2\right) & \sum_{atoms} m r_y r_z \\ \sum_{atoms} m r_x r_z & \sum_{atoms} m r_y r_z & \sum_{atoms} m\left(|r|^2 - r_z^2\right) \end{pmatrix}$$

If we diagonalise this matrix we get the three principle axes of rotation. Which give a frame of reference in which I is diagonal.

By comparing these we can see how elongated the molecule is.

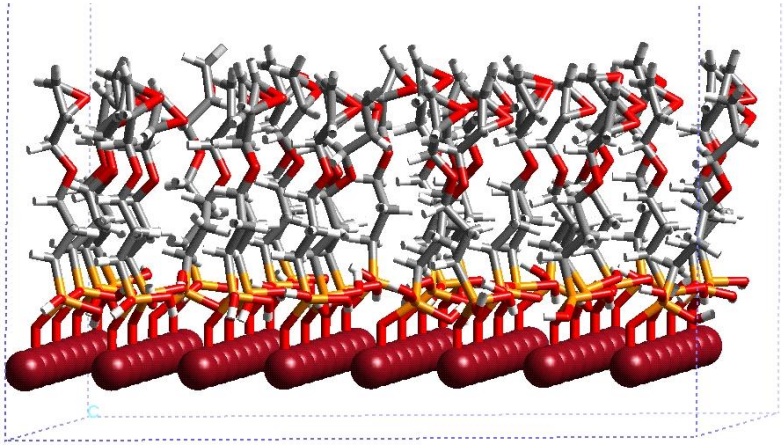
3 similar values tells us the molecule is near spherical.

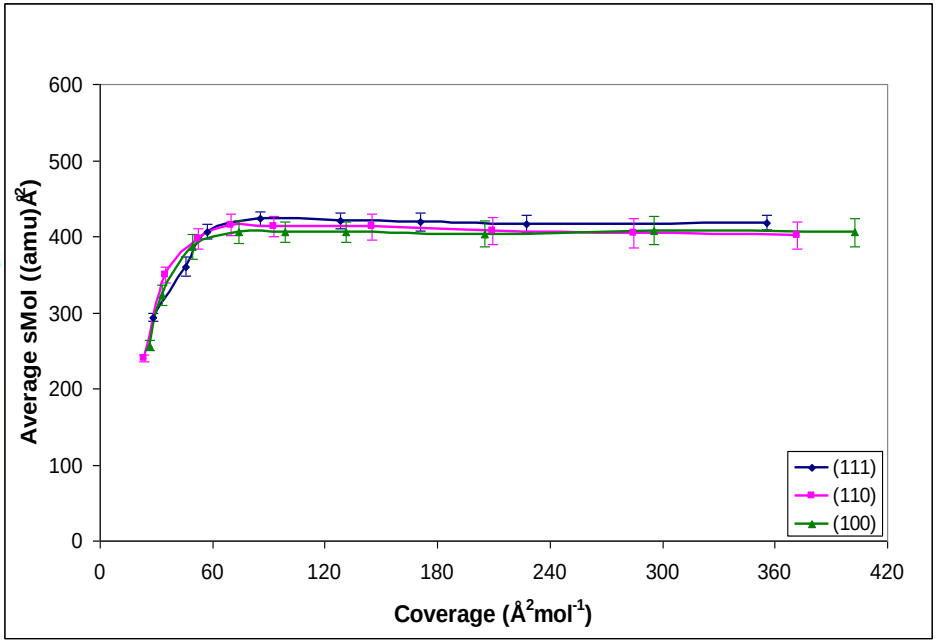




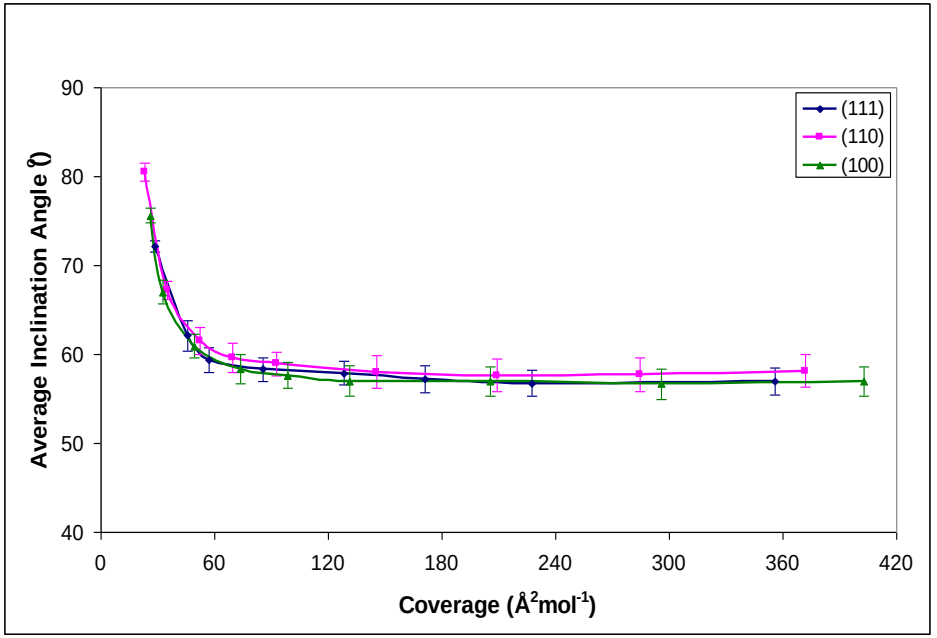
MoI in Analysis of Results

Average sMoI against coverage for 3-GPMS on the (111), (110) and (100) surfaces of iron (with torsion angles).



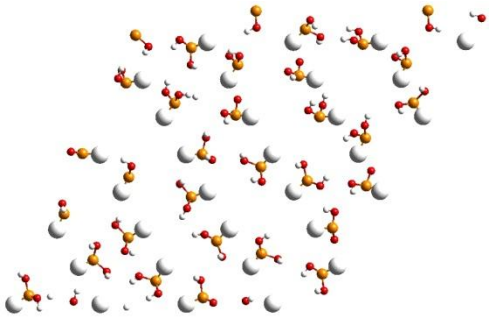


Average inclination angle against coverage for 3-GPMS on the (111), (110) and (100) surfaces of iron (with torsion angles).

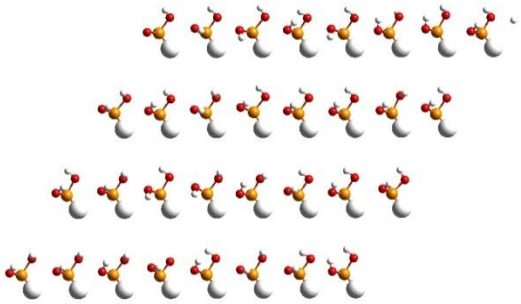


RDF for $O_{epoxide}$-$O_{epoxide}$ at ½ AA and ½ AB surface coverages.

a) ½ AA starting structure;

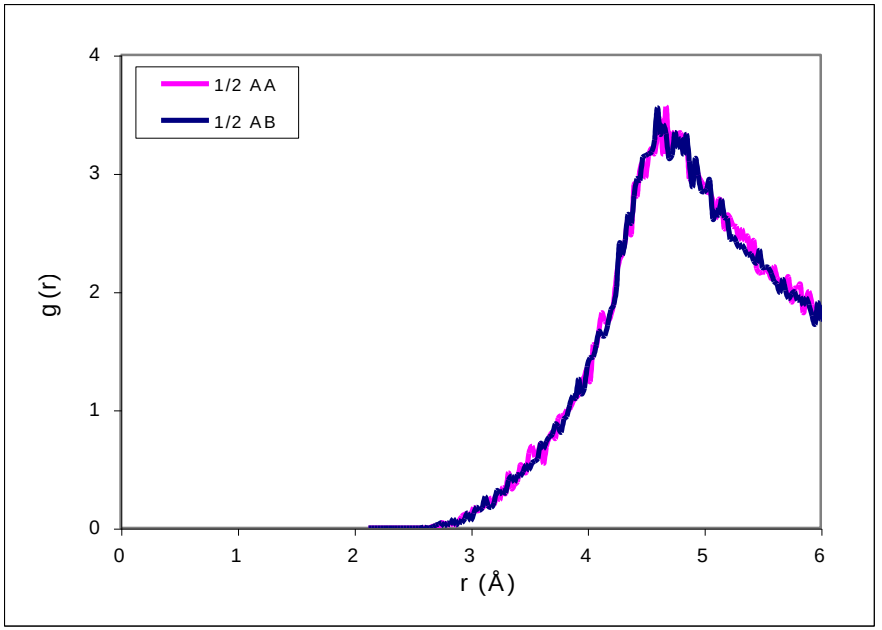


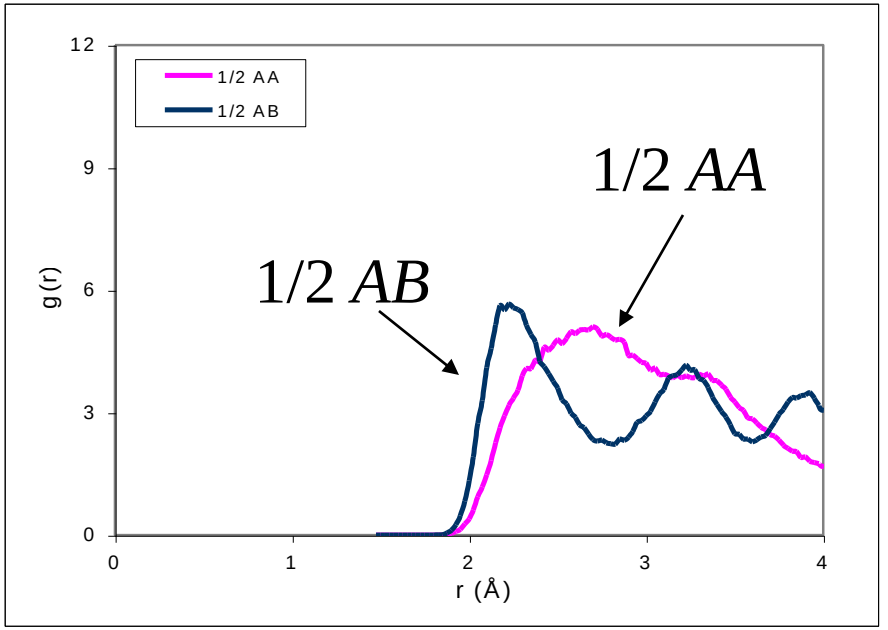
b) ½ AB starting structure.



½ AB is trapped: none ergodic.

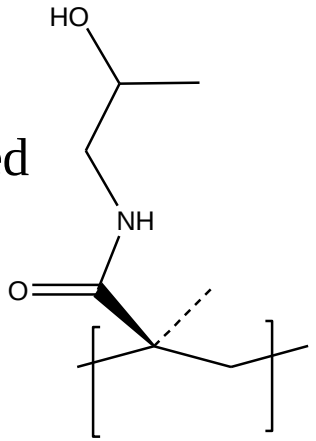
RDF for $H_{alcohol}$-$H_{alcohol}$ at ½ AA and ½ AB surface coverages.

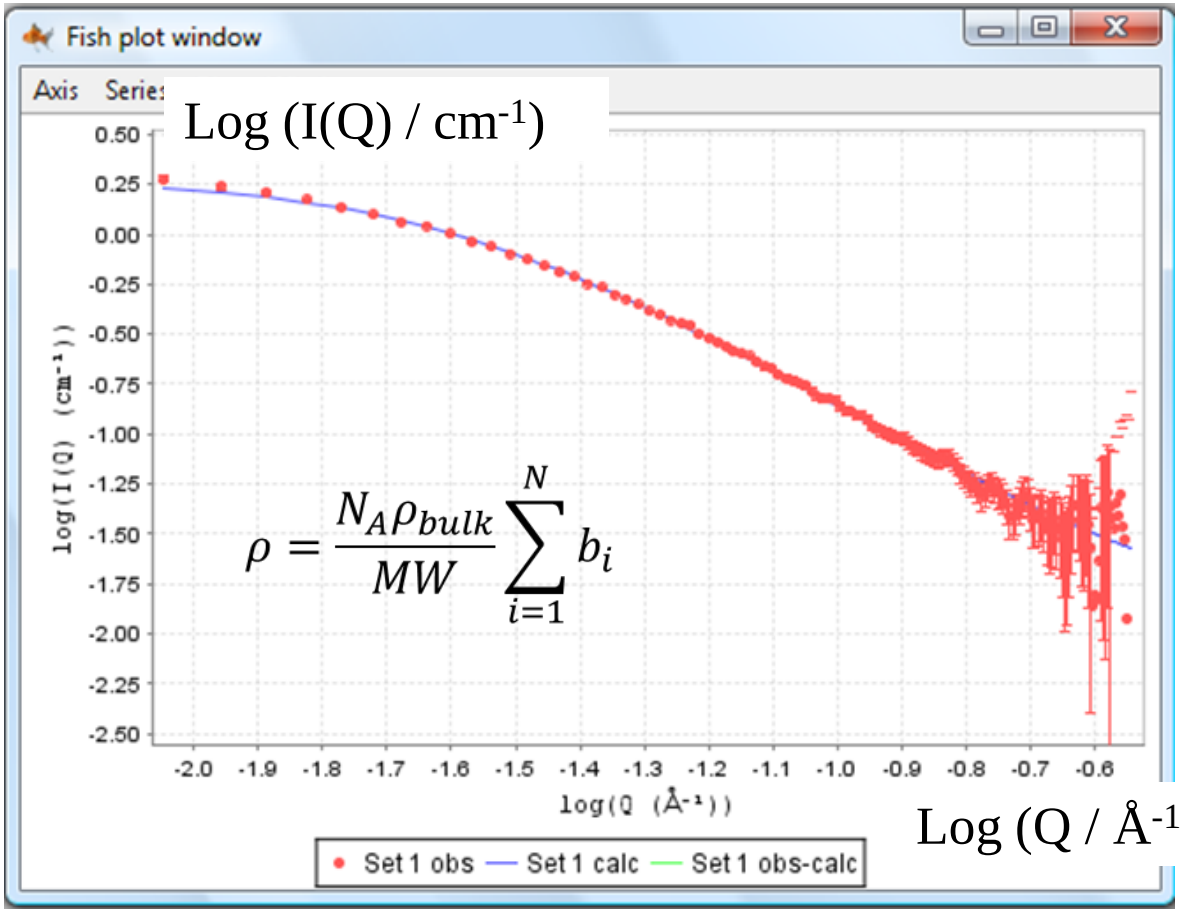




SANS data

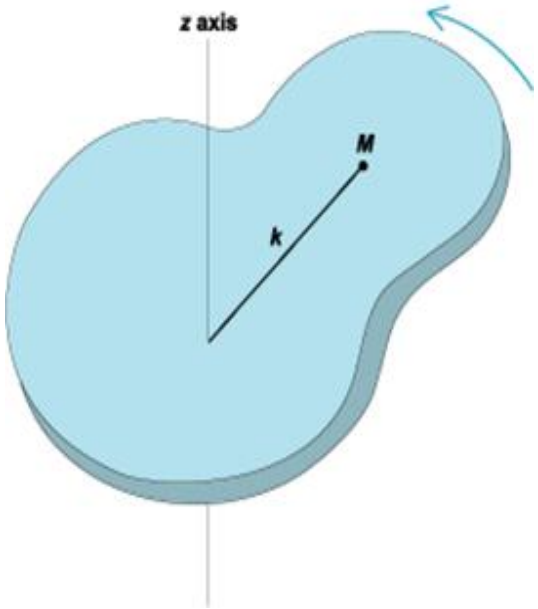
- N-(2-hydroxypropil) methacryleamide (HPMA) is a polymer used as carrier in drug delivery systems.
- MD compared with small angle neutron scattering (SANS) data.





$$\rho = \frac{N_A \rho_{bulk}}{MW} \sum_{i=1}^{N} b_i$$

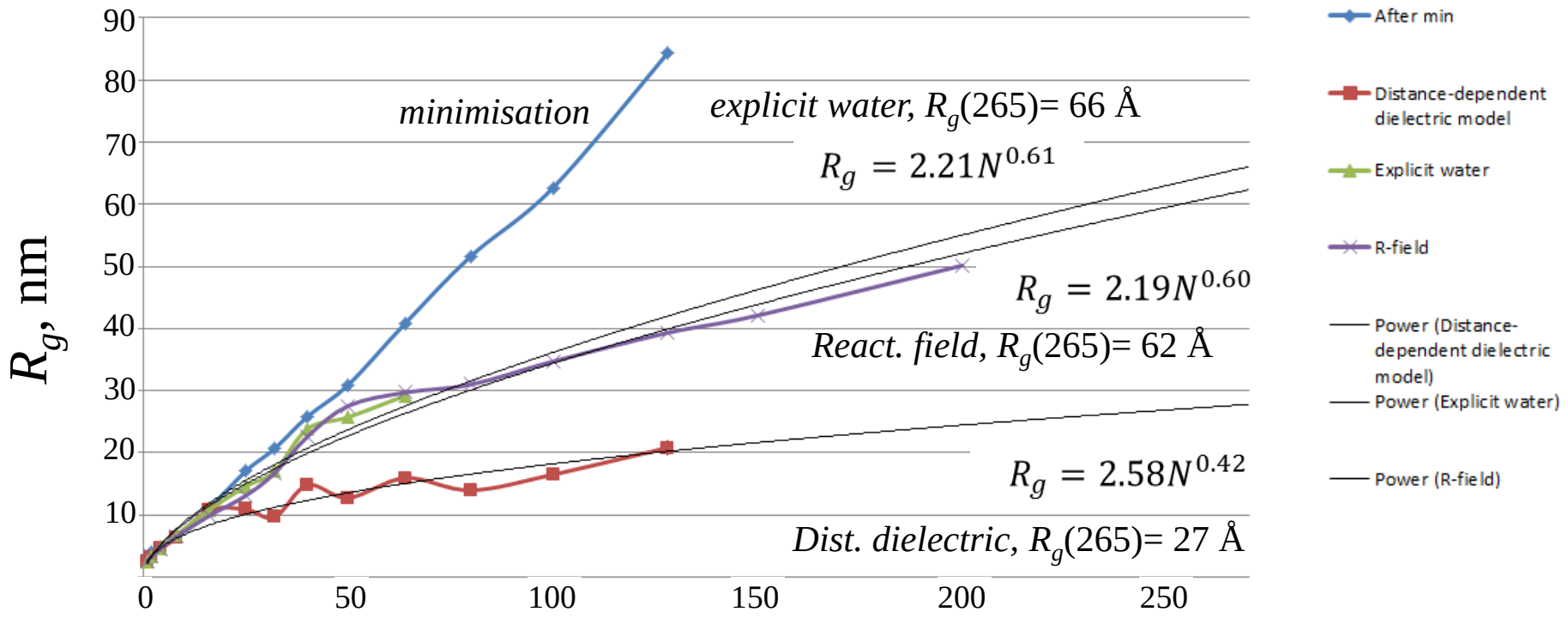
$$R_g = \left(\frac{\sum_i \|\mathbf{r}_i\|^2 m_i}{\sum_i m_i} \right)^{\frac{1}{2}}$$



Flory power law approximation

Flory used self avoiding random walks to show that a polymer conformation should be expected to lead to a radius of gyration that depends on monomer number via a power law:

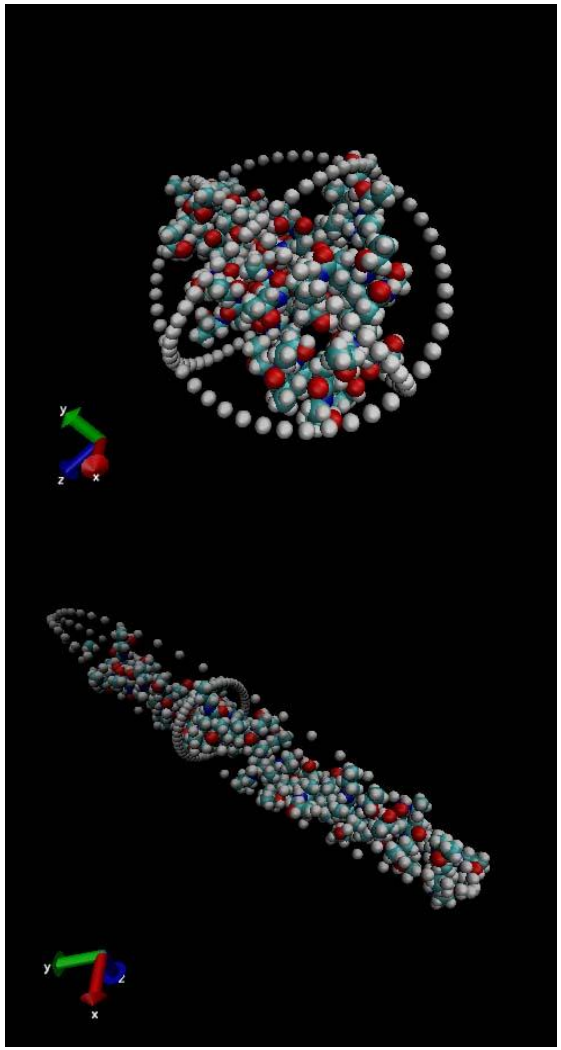
$$R_g = R_0 N^{\nu}$$ With $\nu = 0.6$ for a "good" solvent



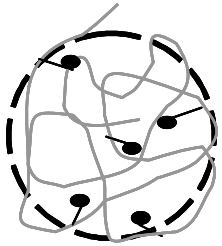
N (number of HPMA monomers)

SANS: HPMA-265, $R_g = 75 \pm 3$ Å

Shape Information: Moments of inertia



Ellipsoid dimensions:
$R_X / R_Z = 0.36$
$R_Y / R_Z = 0.43$
$R_Z / R_Z = 1.00$



$R_X / R_Z = 0.02$
$R_Y / R_Z = 0.02$
$R_Z / R_Z = 1.00$

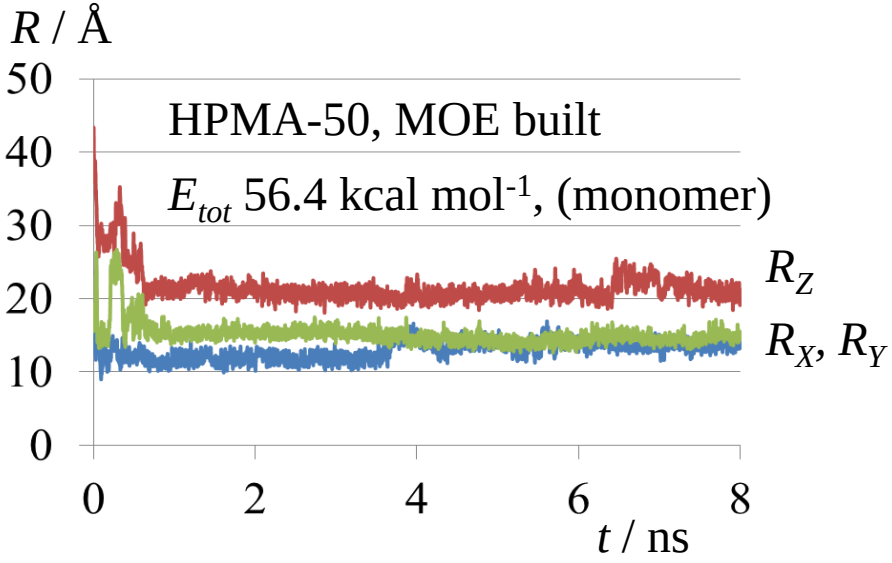
Neutron scattering is controlled by the scattering length density:

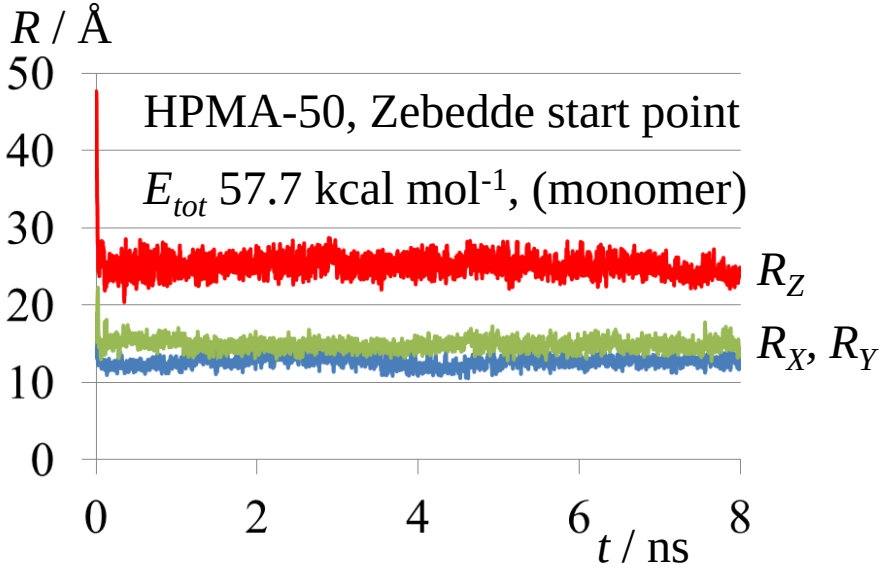
$$\rho = \frac{N_A \rho_{bulk}}{MW} \sum_{i=1}^{N} b_i$$

To describe the observed "shape" we can use the scattering factors, b_i, in place of mass in the moment of inertia matrix.

This allows us to define a set of axes and determine the dimensions of an ellipsoid that represents the shape using the furthest atom distance in each direction at each frame of the MD trajectory.

HPMA-50 comparison of starting points





MD runs comparing elongated (MOE) and Zebedde generated start points.

NVT ensemble, 310 K,
AMBER99 forcefield
Reaction field implicit water (ε = 80.1).

MOE start point eventually gives more spherical polymer shape.

Zebedde start point rapidly achieves constant shape parameters.

Comparison with SANS data

Conjugate	**Vol. Calc. / 10^5 Å^3**	**Vol. SANS / 10^5 Å^3**	**V_{calc}/V_{SANS}**	**Aspect ratio calc.**	**Aspect ratio SANS**
HPMA-C6-F-10	1.275	1.024	0.803	2.56	4.83
HPMA-C8-OH-10	1.232	1.024	0.831	1.95	4.83
HPMA-C6-OH-10	1.122	1.125	1.003	1.70	4.38
HPMA-C6-10	1.052	2.658	1.975	1.43	3.48
HPMA-C12-5	1.196	7.654	6.397	1.54	7.80

The volume from the MD ellipsoids and cylinders fitted to SANS measurements show reasonable agreement for first three cases.

For HPMA-C6-10 and HPMA-C12-5 cases data suggests that there is agglomeration of polymer in the experimental case.

Aspect ratios for single chains show more elongated structures than would be expected from the simulations.