Disordered Materials:

Lecture I

Concepts of disorder:

How we quantify it

and

How we measure it

Alan Soper

Disordered Materials Group

ISIS

Disordered Materials:

Lecture II

Finding and refining a structural model

Alan Soper

Disordered Materials Group

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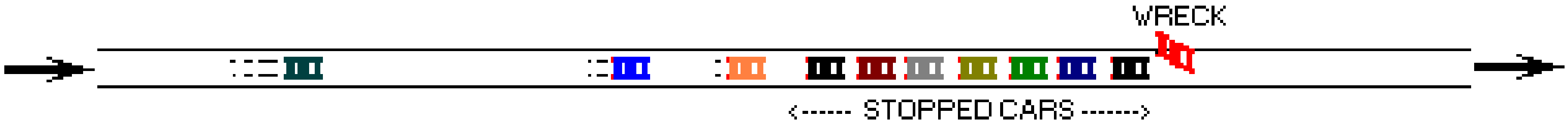
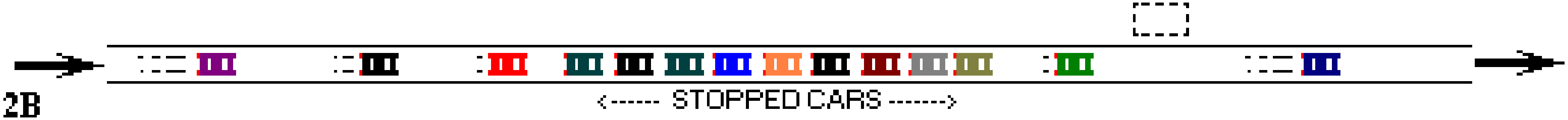
A well known example of disorder…



(Courtesy of http://www.amasci.com/amateur/traffic/traffic1.html)


WRECK IS
REMOVED
<------ STOPPED CARS ------->

2A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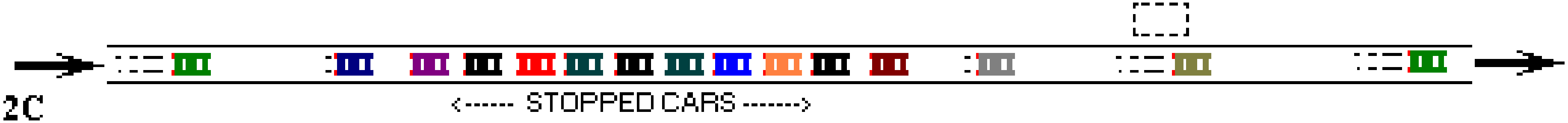
2B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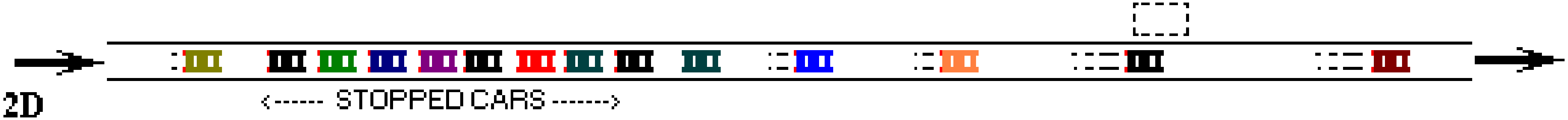
2C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2D

How to avoid traffic congestion...


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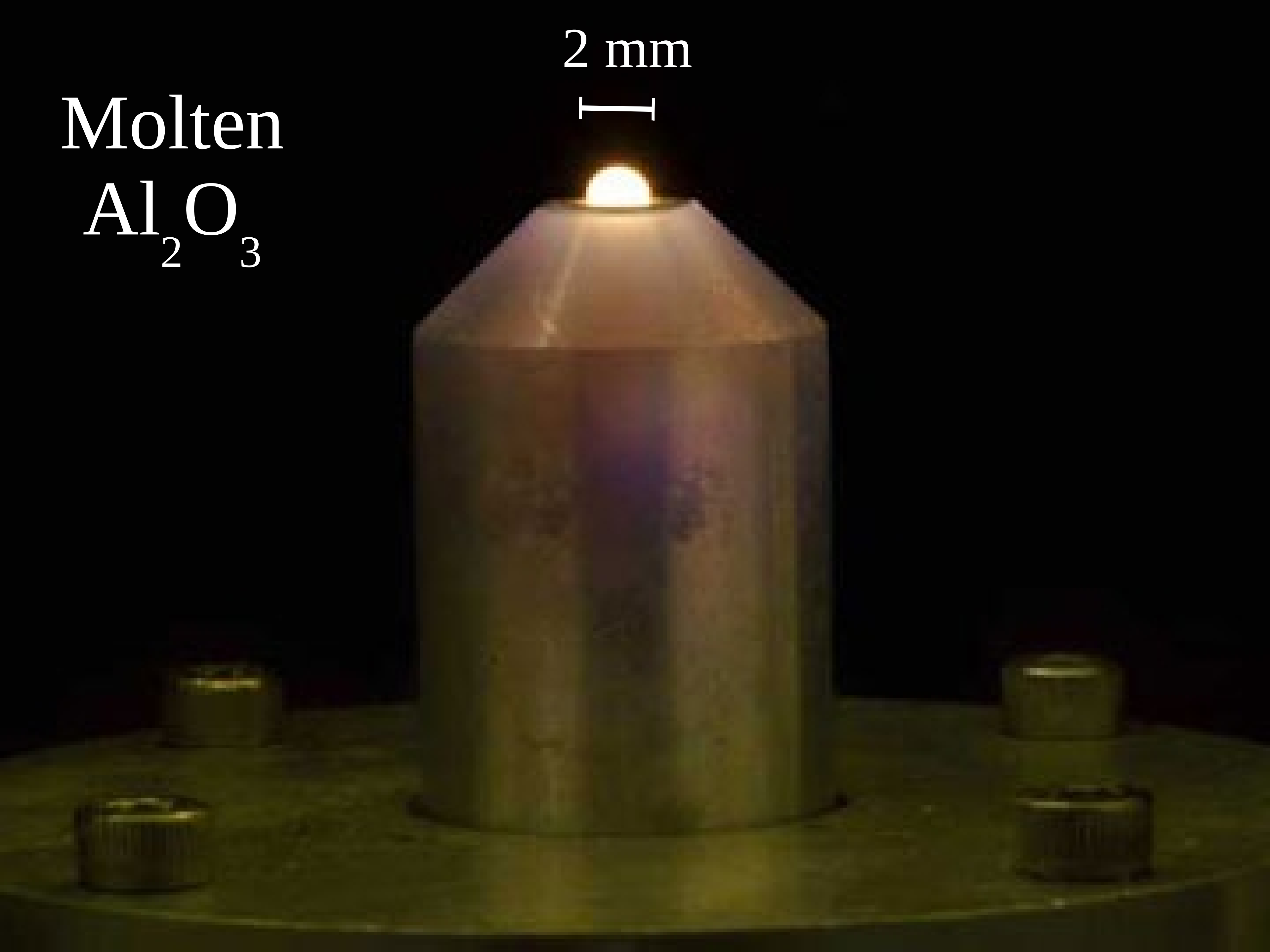
An interesting fact about water:

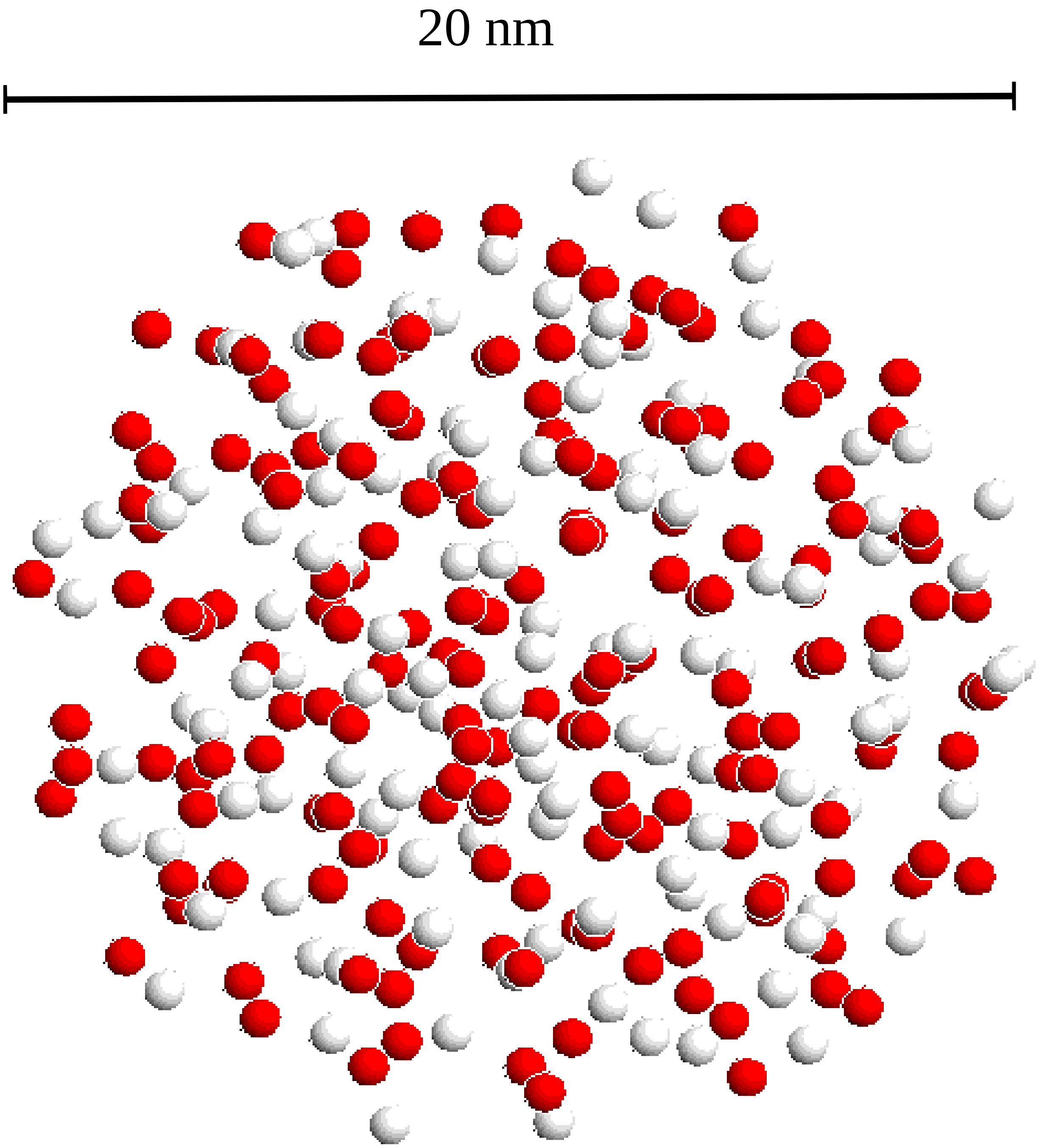
- *It takes about 41.5 kJ per mole (i.e. 18 gm) to bind a water molecule in the liquid.*
- *This means for every second that it rains, 41.5 kJ of heat energy is released for every 18gm of water deposited on the ground.*
- *A heavy rain shower producing 2.5mm of rain over 1km*^{2} *releases 5.764×10*^{12} *J (=1 cycle of ISIS!).*


FRESH STEPS
Let By
Chicken Village
INTERNET & CHEAP PHONE CALLS
CORAL



Molten Al_2O_3

Molten Al_2O_3



Disorder affects us in many different ways…

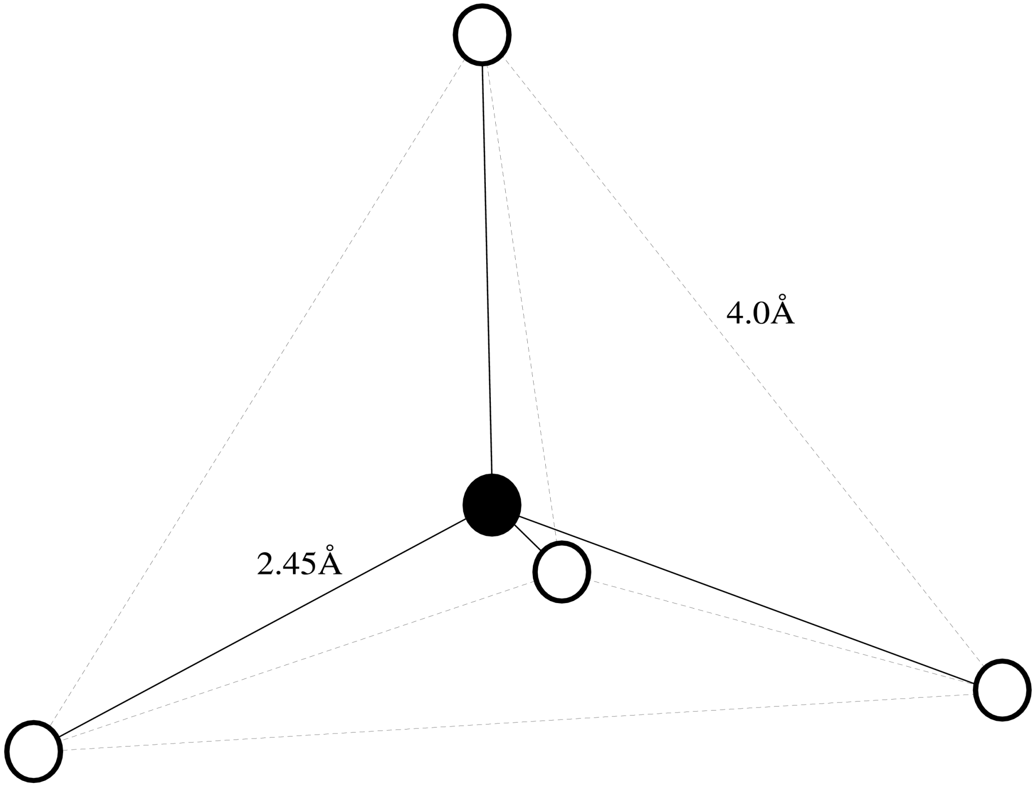
- Avalanches
- Sand, shingle and earth piles
- Congestion in shopping centres, etc.
- Football crowds
- Blood clots
- …
- Gases, liquids and glasses

What is common to all these examples?

Answer…

- No two objects can occupy the same space.
- Nonetheless, (usually) there is overall attraction between objects, some force which brings them closer together
- Only relative positions are correlated.
- No overall arrangement, therefore resort to *correlation functions* to describe arrangement.

In reality not quite so simple…



- Three- and many- body forces may be important.

What are the fundamental requirements for disordered correlation to occur?

- Some attractive forces…
- Some repulsive forces…
- High packing fractions.
- Random motions (for liquids).

Disordered materials can be classified as atom jams where marked correlation occurs.

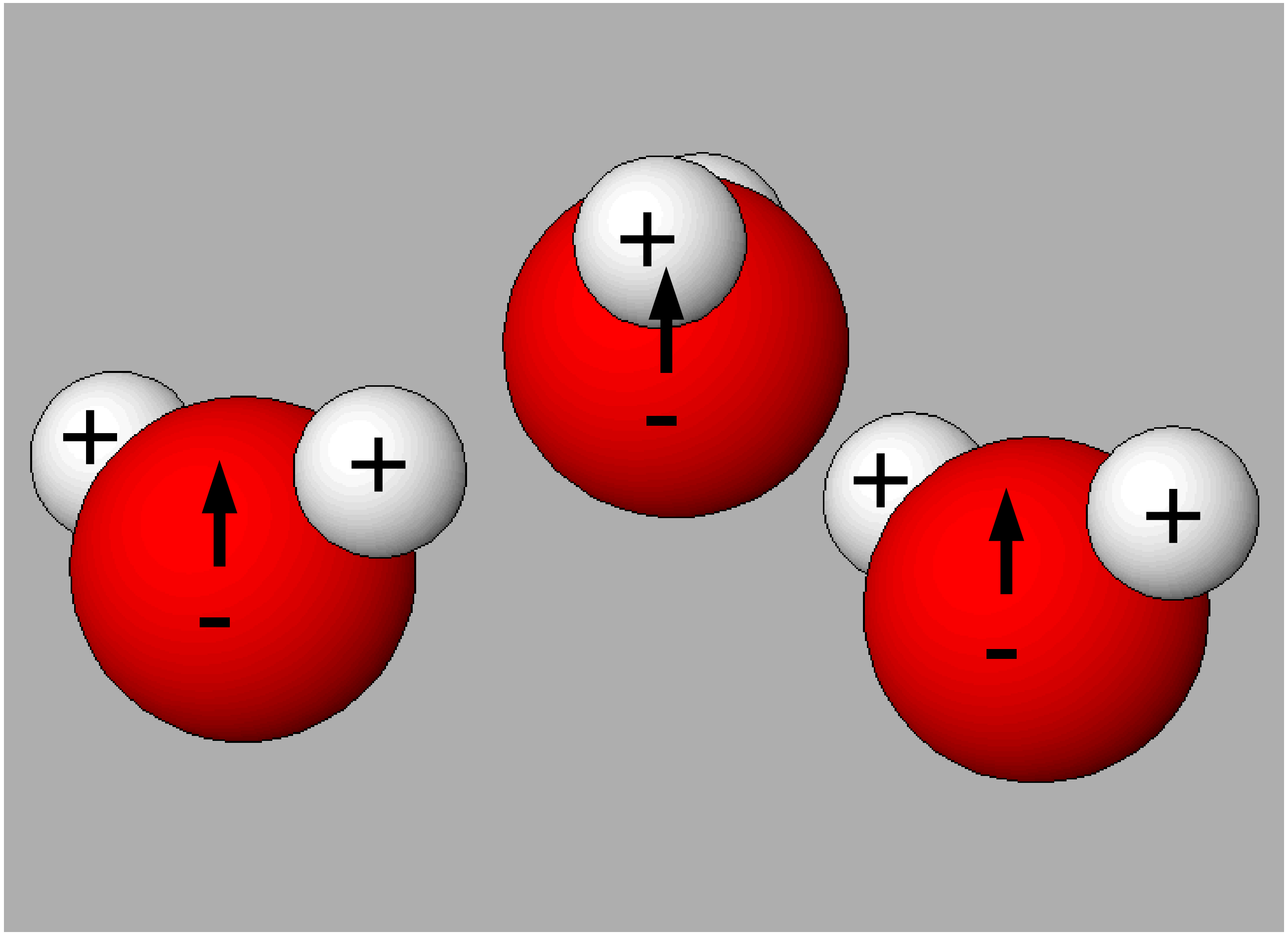
In a gas the atoms are free to move (almost) anywhere.

In a liquid the atoms and molecules are jammed but can still diffuse.

In a glass the atoms are highly jammed and are unable to diffuse.

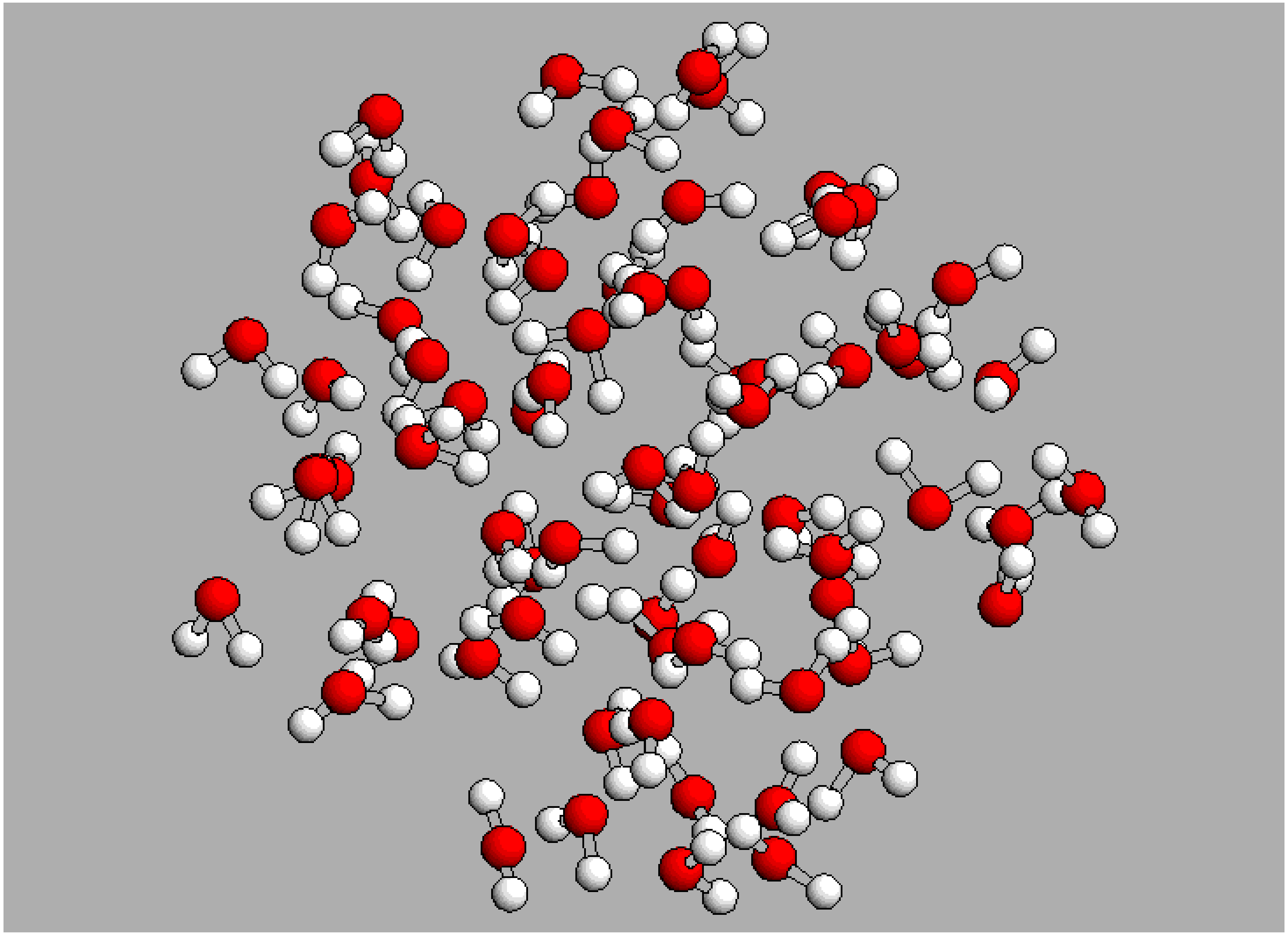
A "typical" liquid, water…

The water molecule



This results in a material which looks like this:-

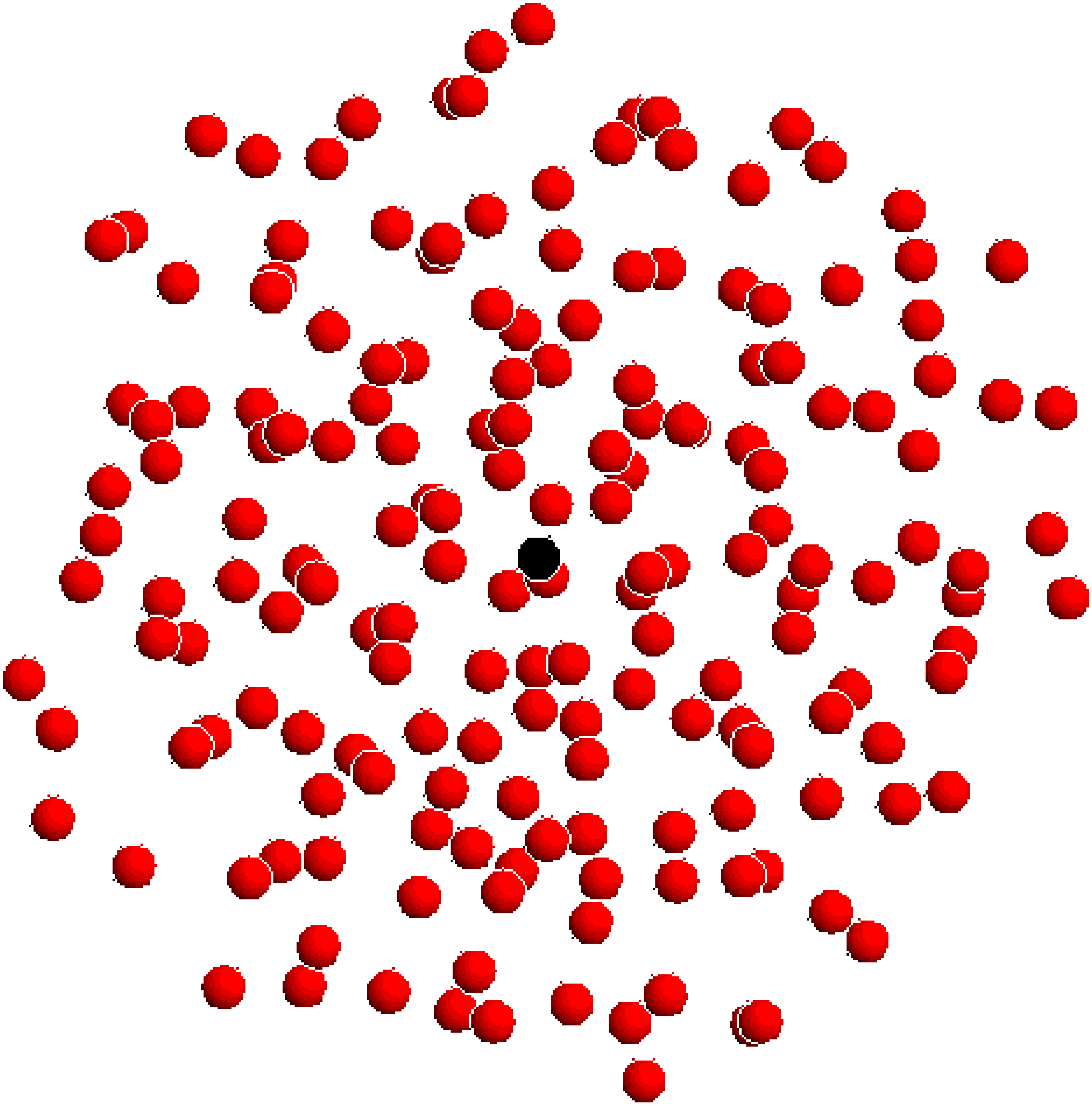
and this:-



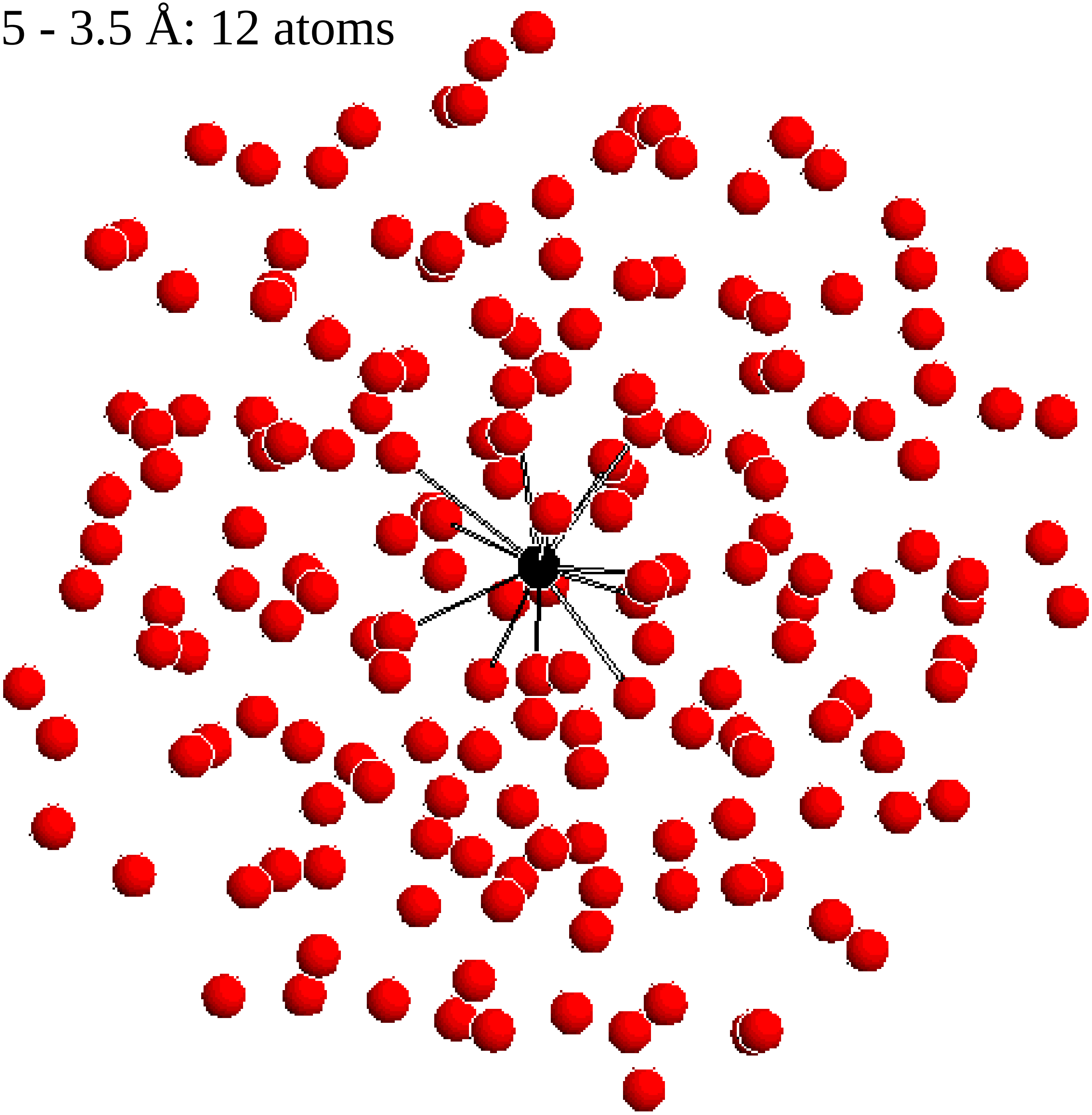
So how do you characterise structure in a disordered system?

By counting.

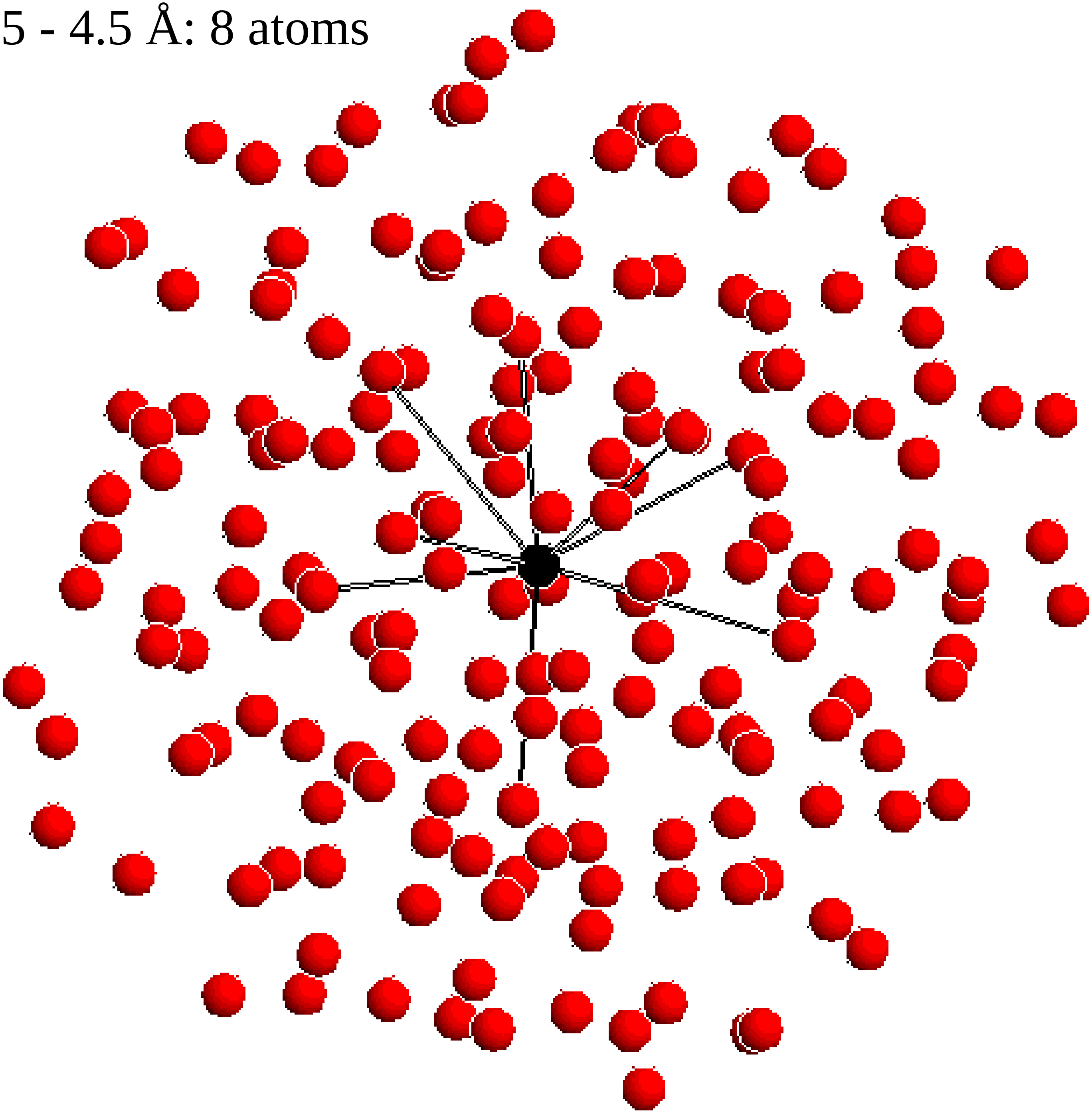
This gives the “radial distribution function ”, $g(r)$:



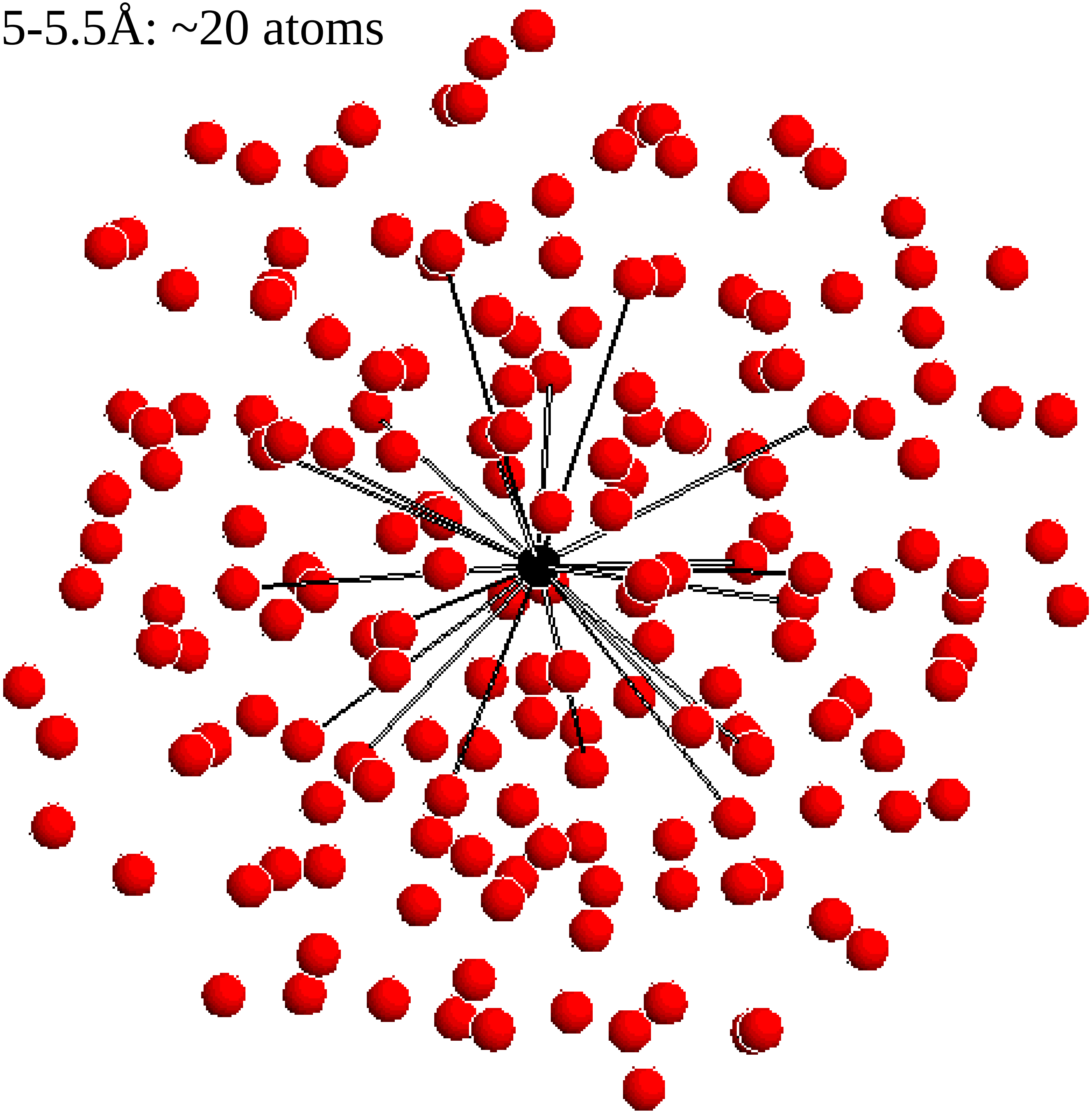
2.5 - 3.5 Å: 12 atoms



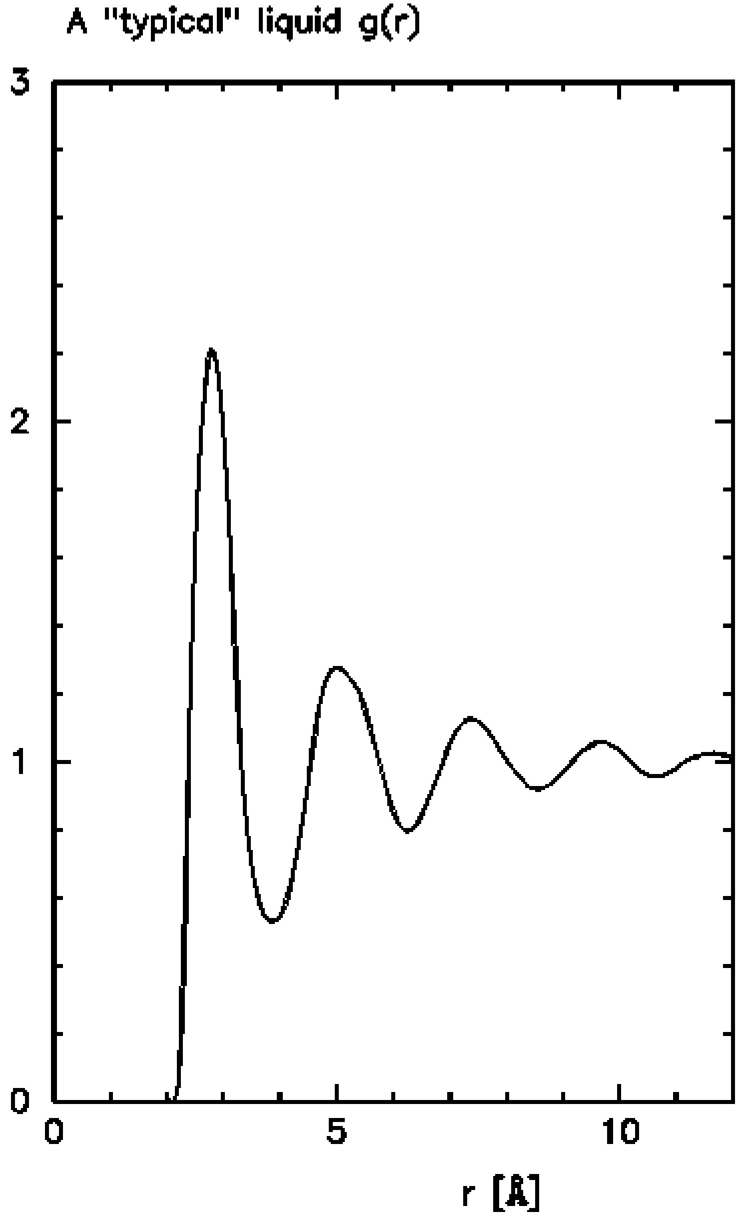
3.5 - 4.5 Å: 8 atoms



4.5-5.5Å: ~20 atoms



Average over every site in the liquid ~ 10^{23} sites...

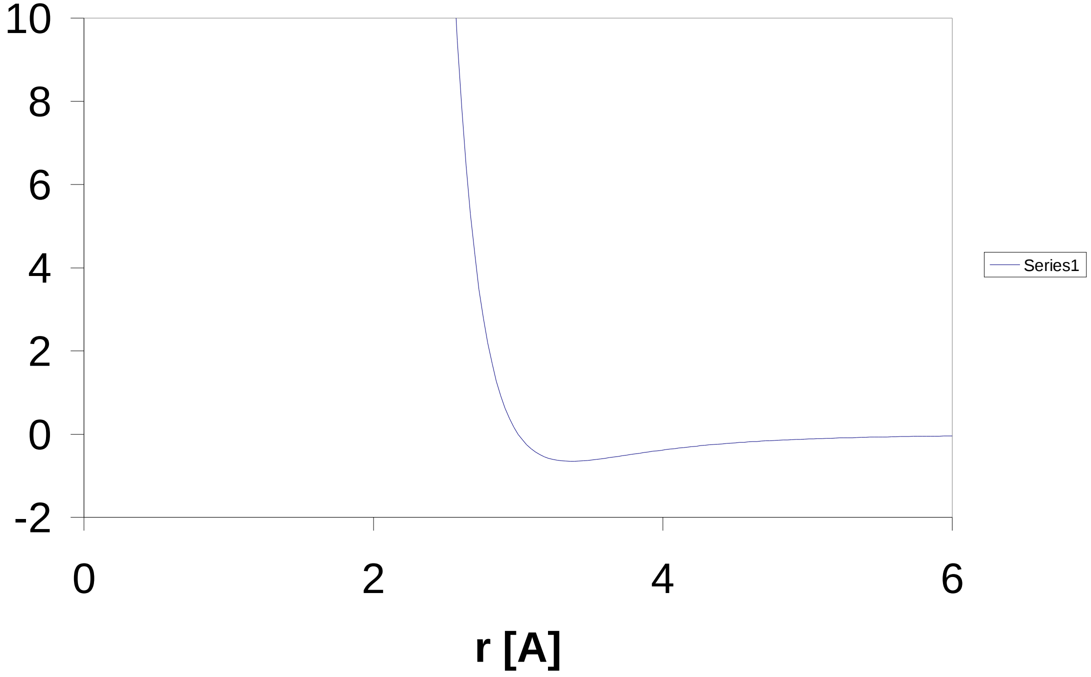


What is this radial distribution function, g(r), telling us?

- It tells us about the nearest-neighbour numbers and distances;
- It tells us about the hardness of the atomic core repulsion;
- It tells us about the attractiveness each atom has for its neighbours;
- In other words it tells us about the local potential energy environment of an atom in the material.

There is a complication however…

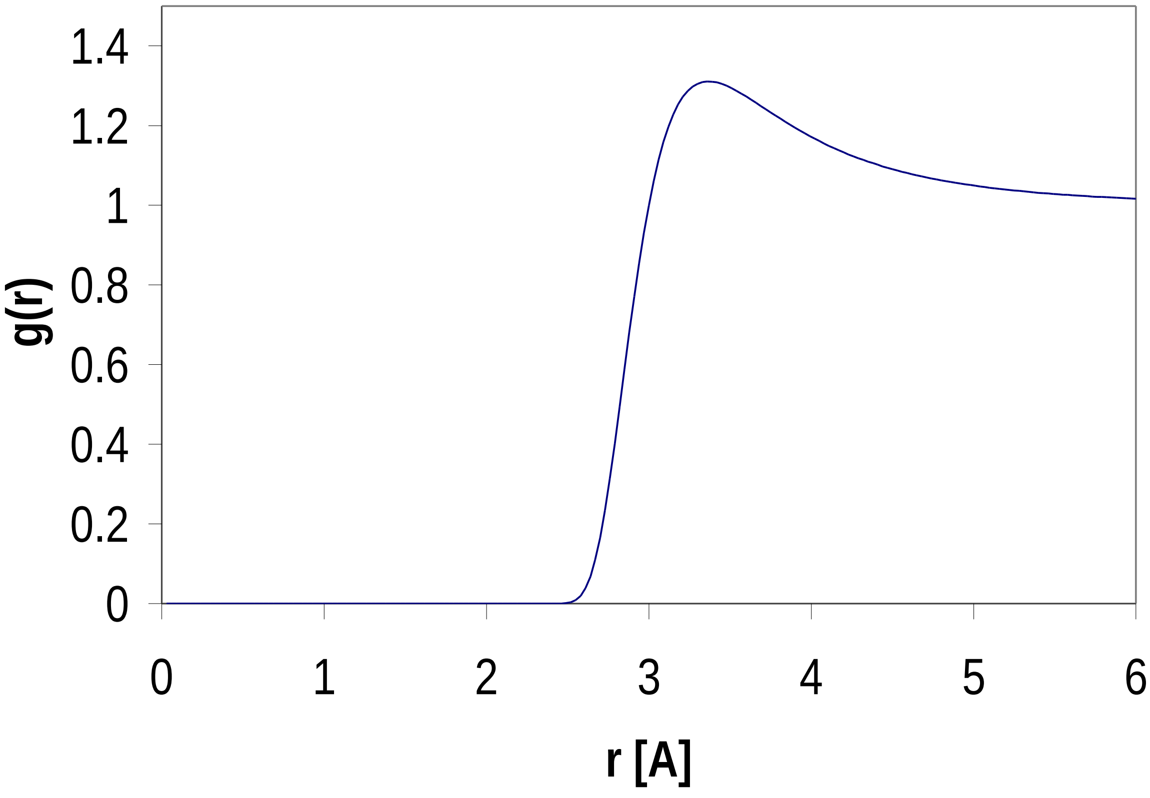
- Typical interatomic potentials are not oscillatory – they have a repulsive core and are attractive beyond the core – van der Waals forces.



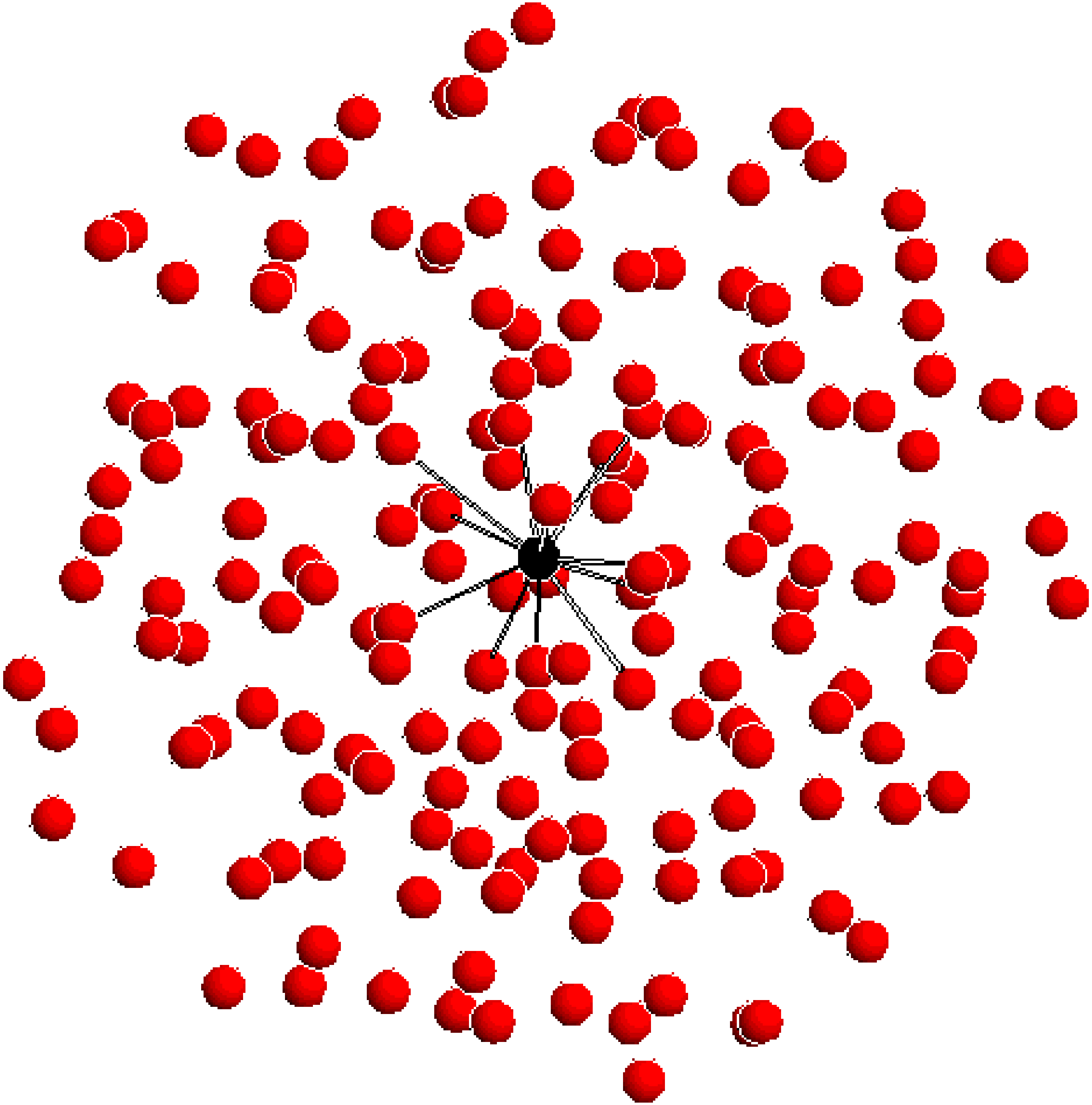
Corresponding g(r):

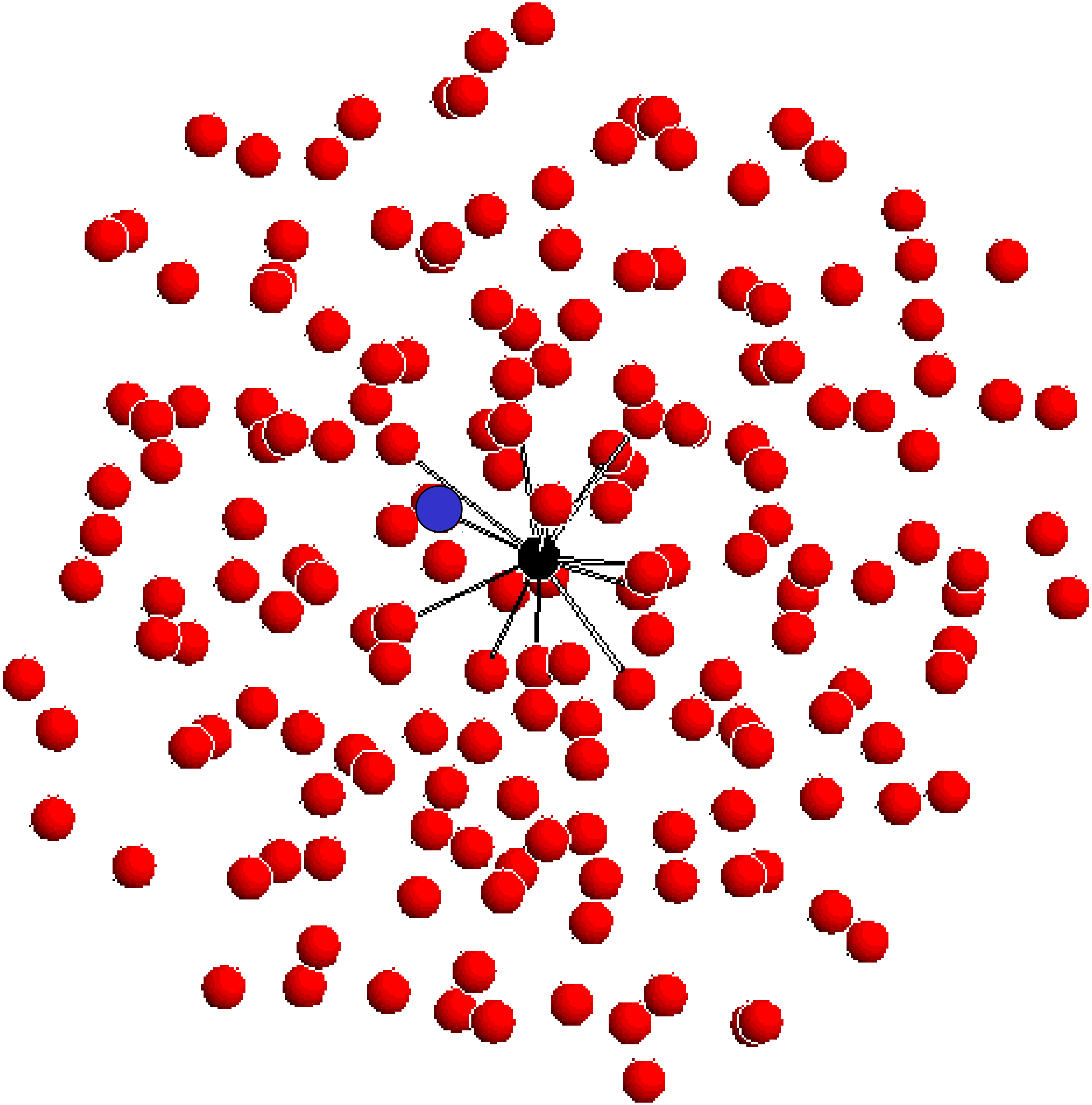
- At zero density, formally exact result:

$$g(r)=\exp\left[-\frac{U(r)}{kT}\right]$$



- So why does g(r) oscillate?
- Many body effects…

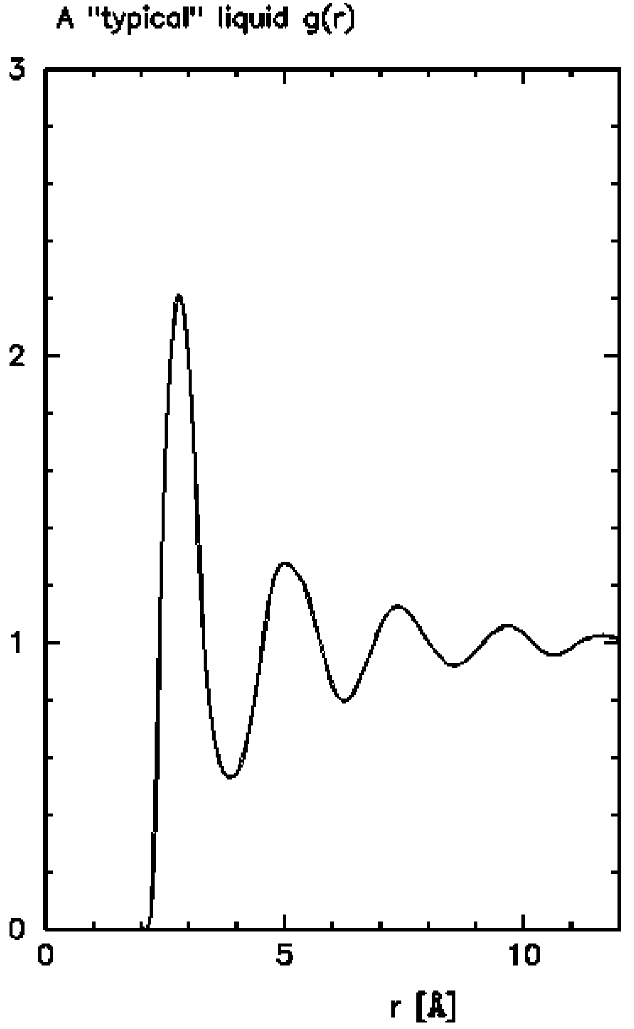




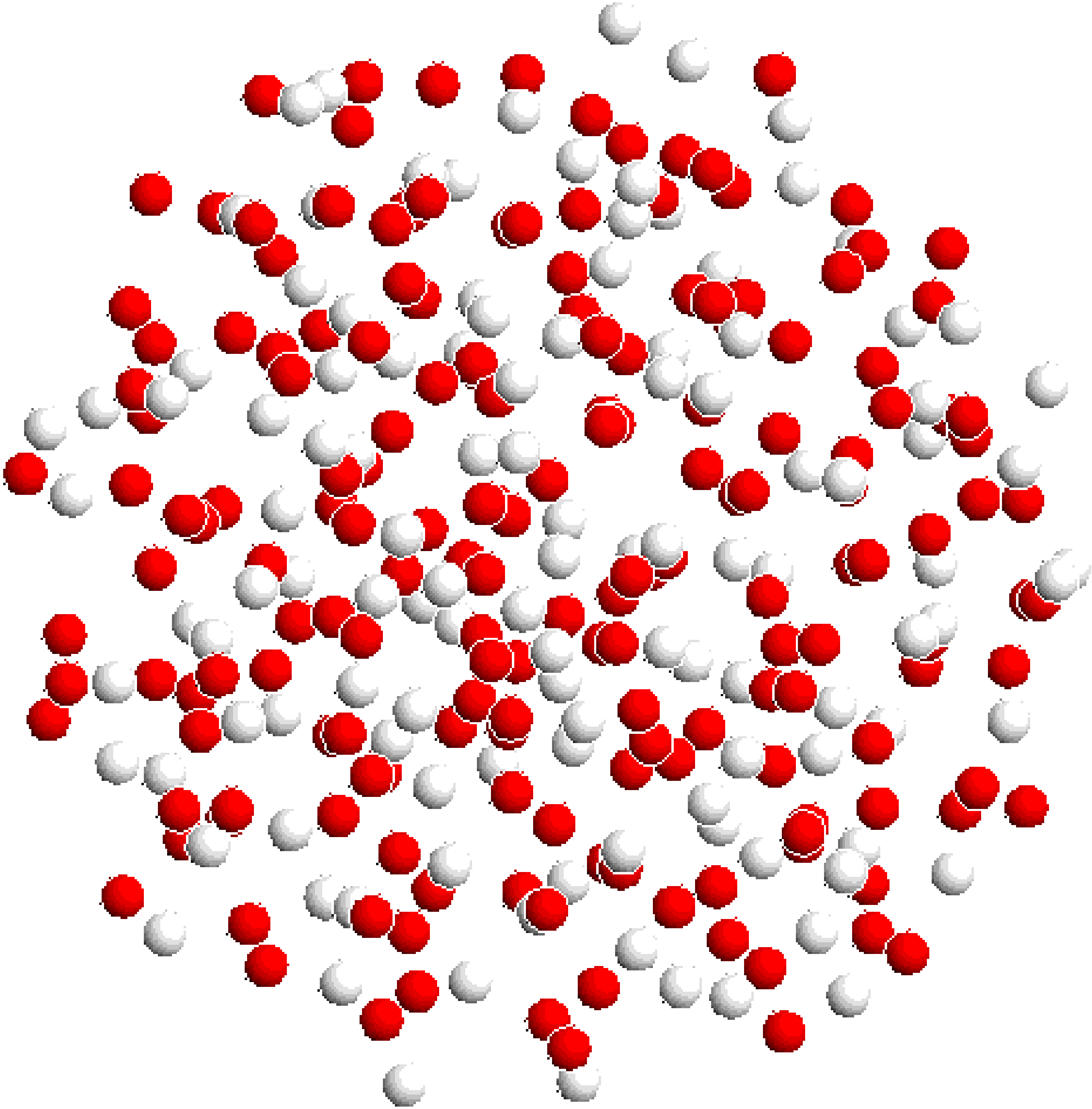
Effect of many body correlations

Many body correlations give rise to the oscillations...

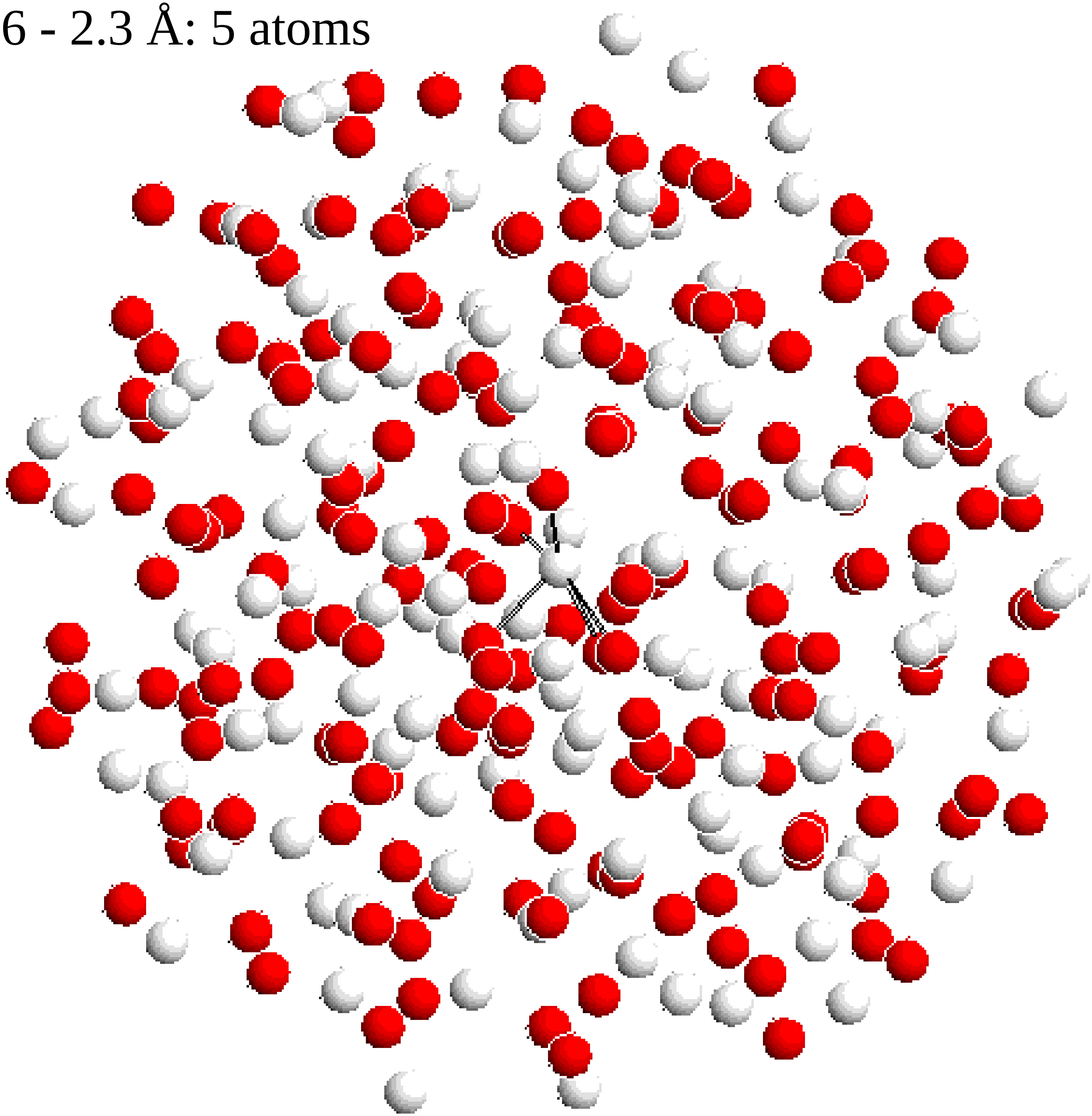
BUT we can’t estimate them without the aid of computer simulation



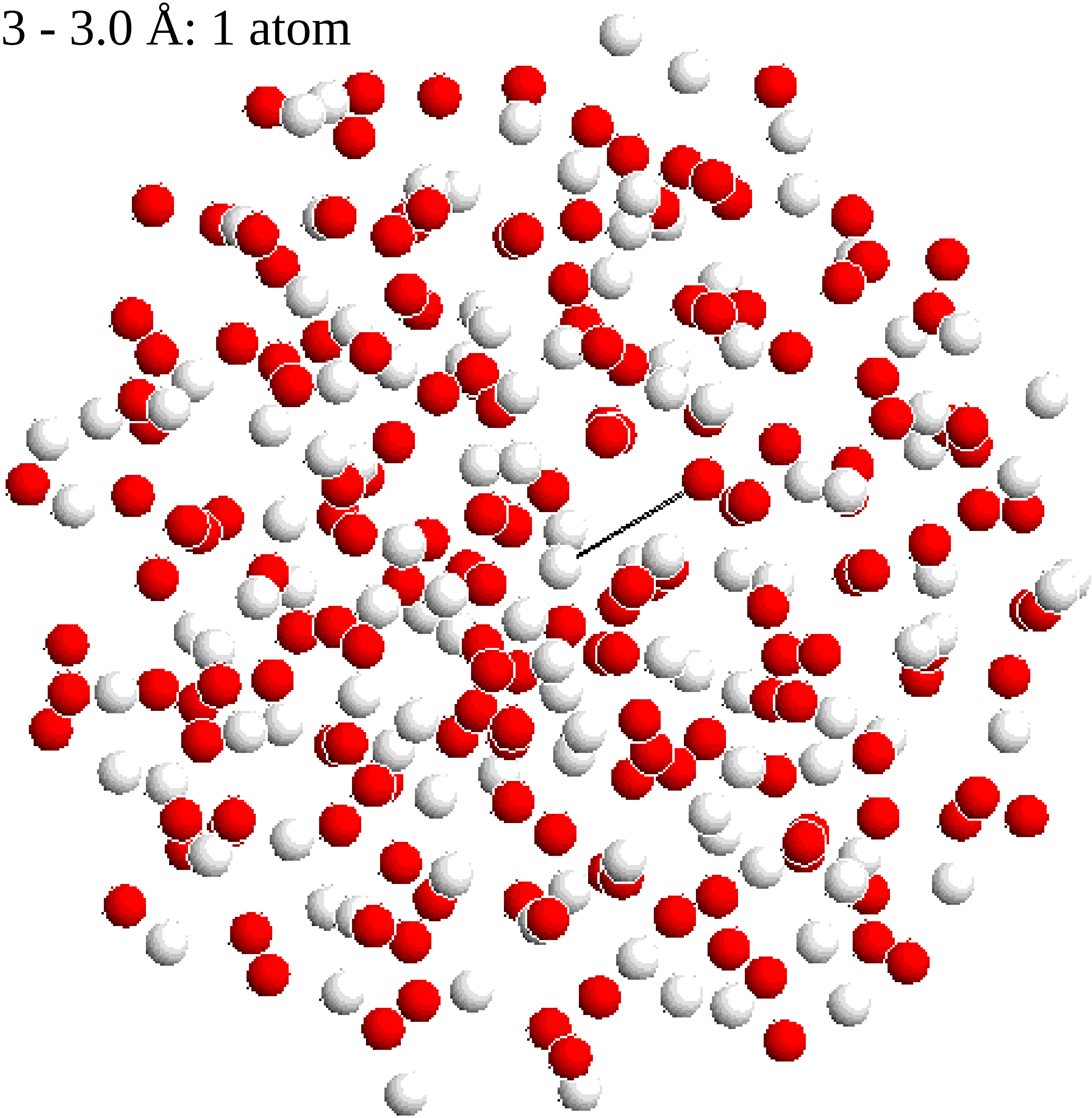
Now consider a 2-component system:



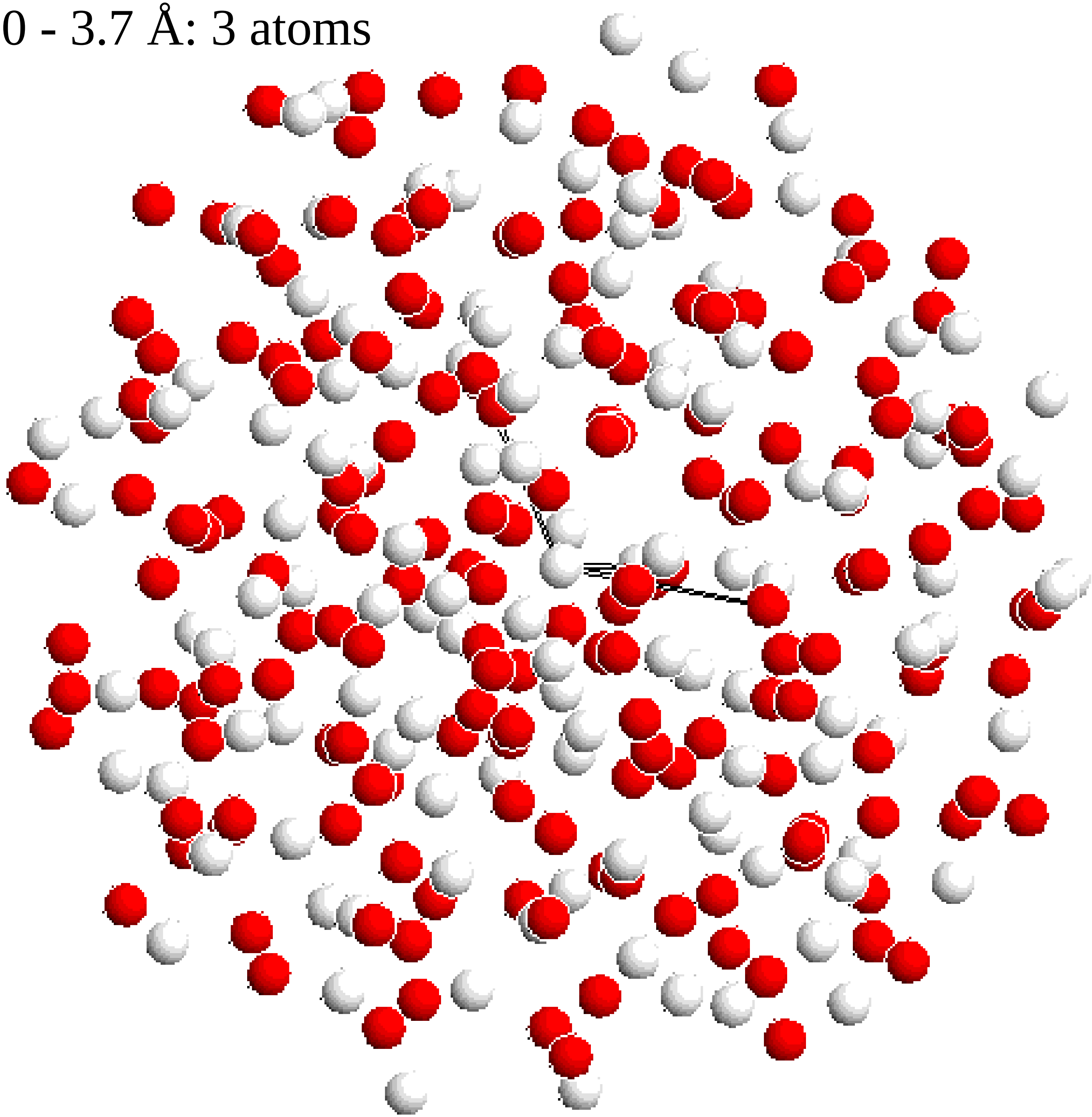
1.6 - 2.3 Å: 5 atoms



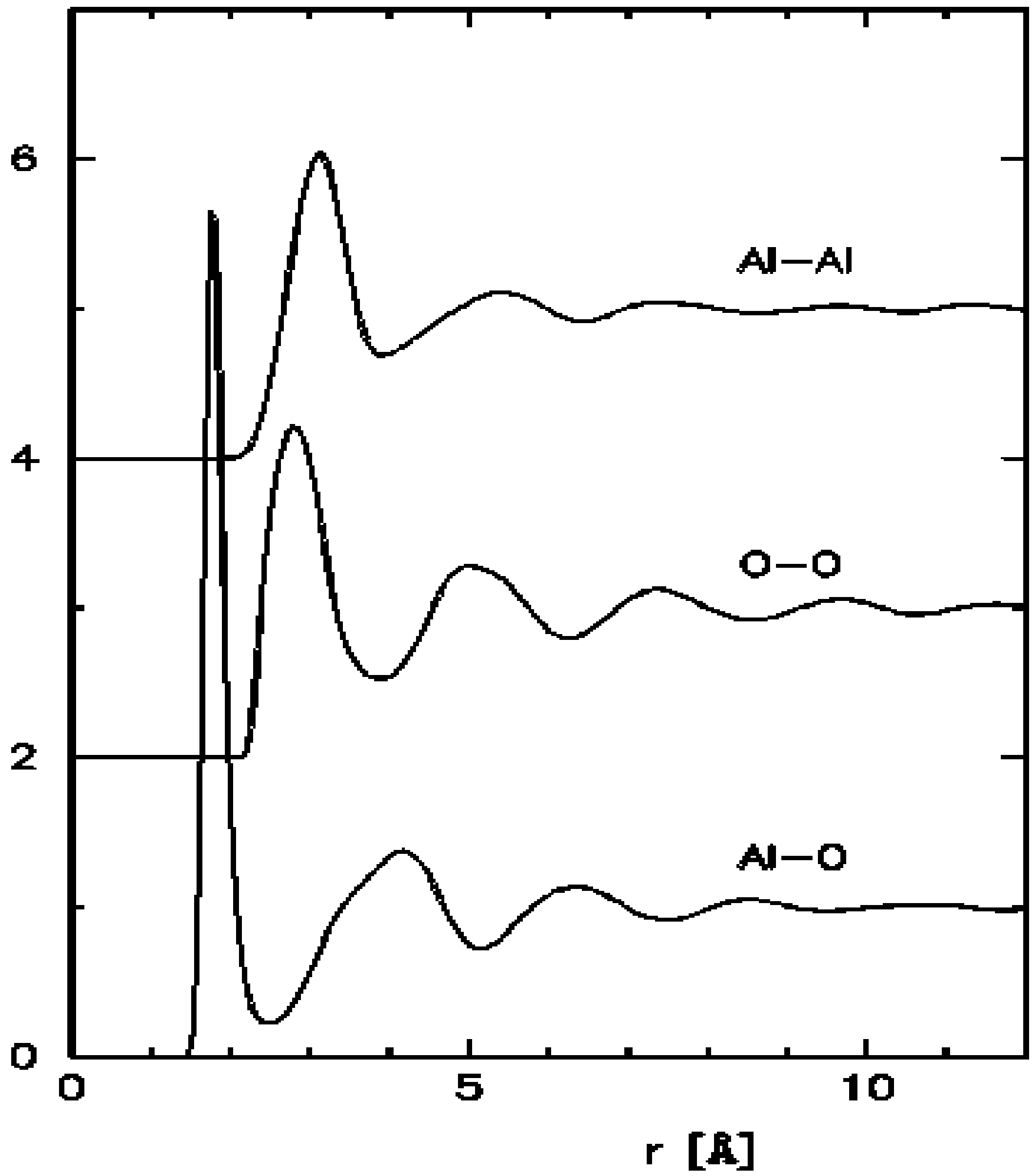
2.3 - 3.0 Å: 1 atom



3.0 - 3.7 Å: 3 atoms



Partial *g(r)'s for Al_2O_3*



For “N” components there are N(N+1)/2 site-site radial distribution functions.

How do we measure these?

You can't measure *g(r)*

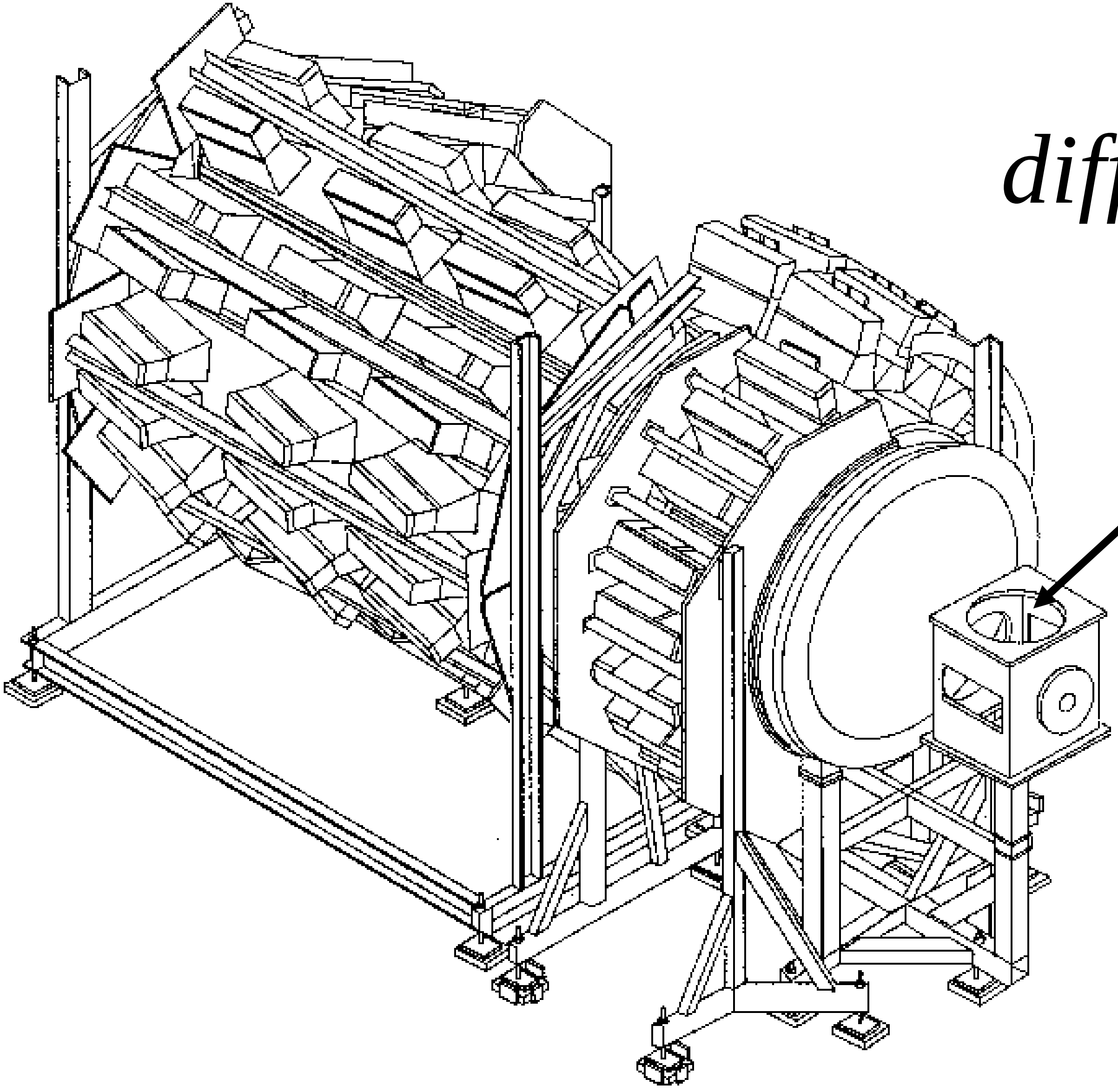
Instead you have to use a diffractometer to do the atom counting.

This produces a structure factor, *D(Q)*.

(Actually a differential scattering cross section)

Very different from the crystalline lattice structure factor as it has only a few peaks!

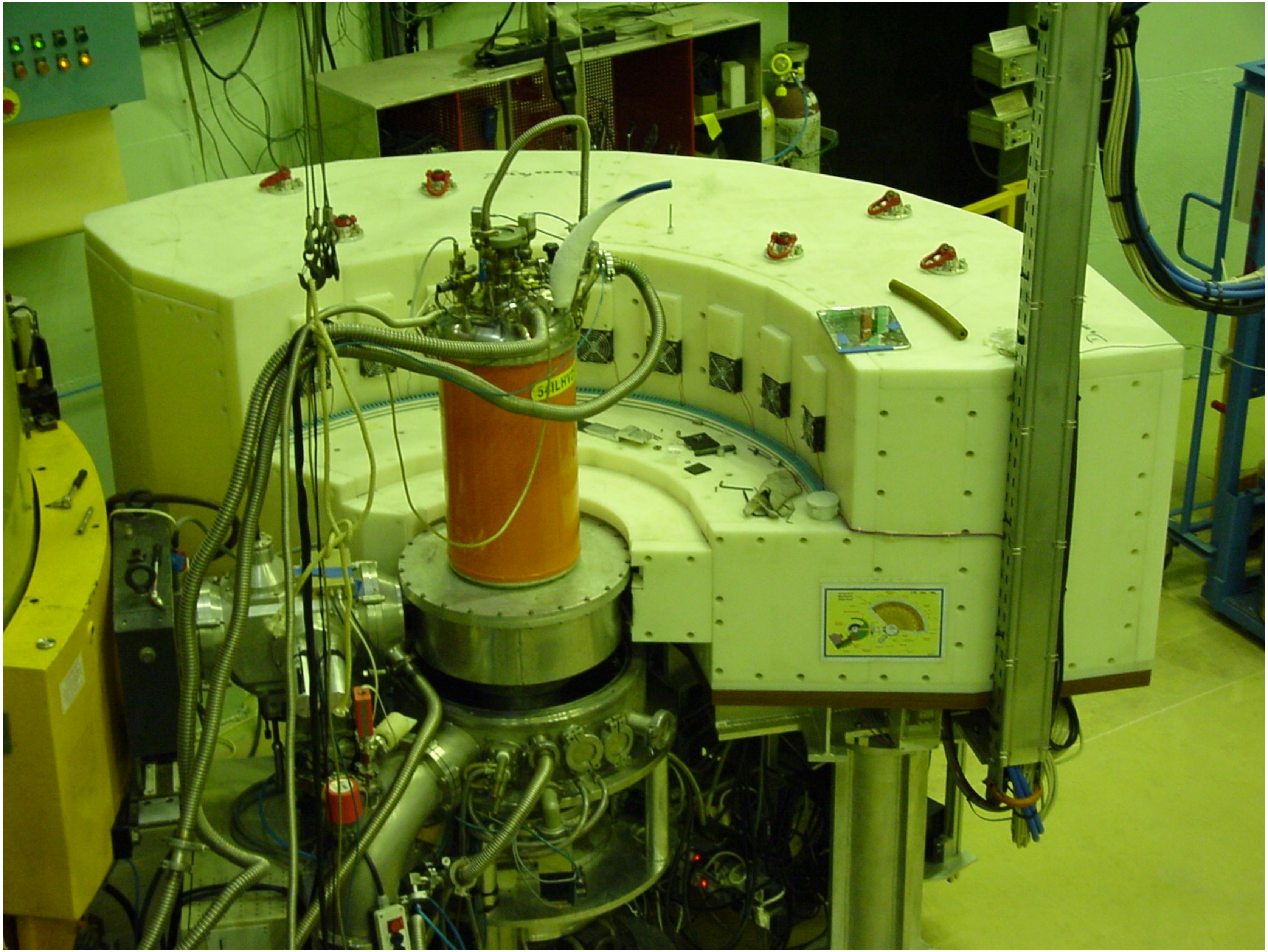
ISIS SANDALS (*liquids diffractometer*)



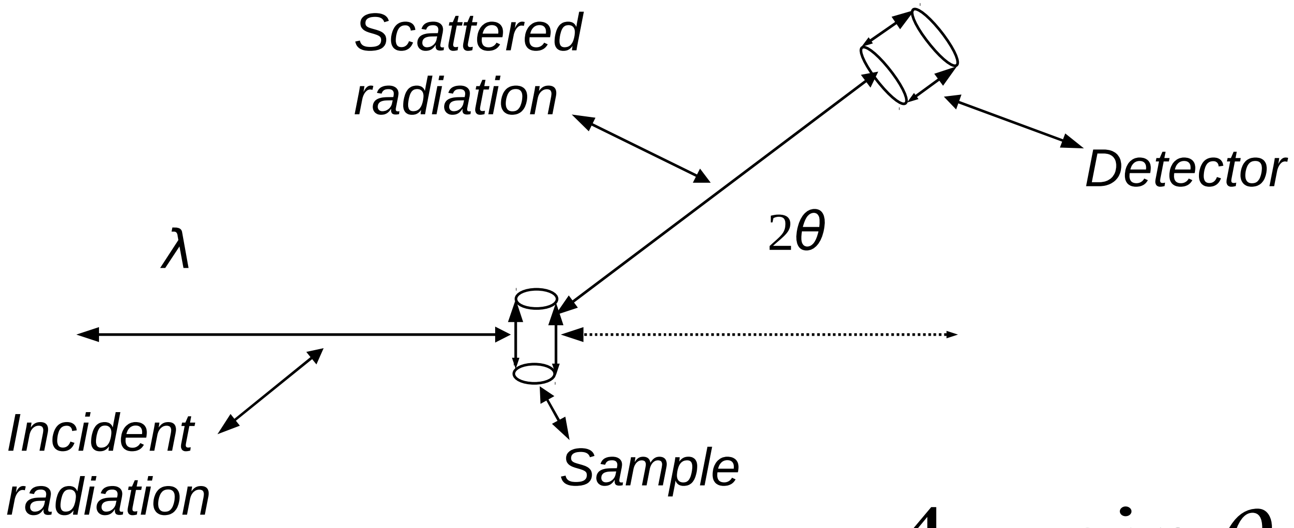
Sample position

Incident
neutron beam

ILL – D4C



Diffraction from disordered materials - a simple experiment in principle:



Scattered radiation

Detector

λ

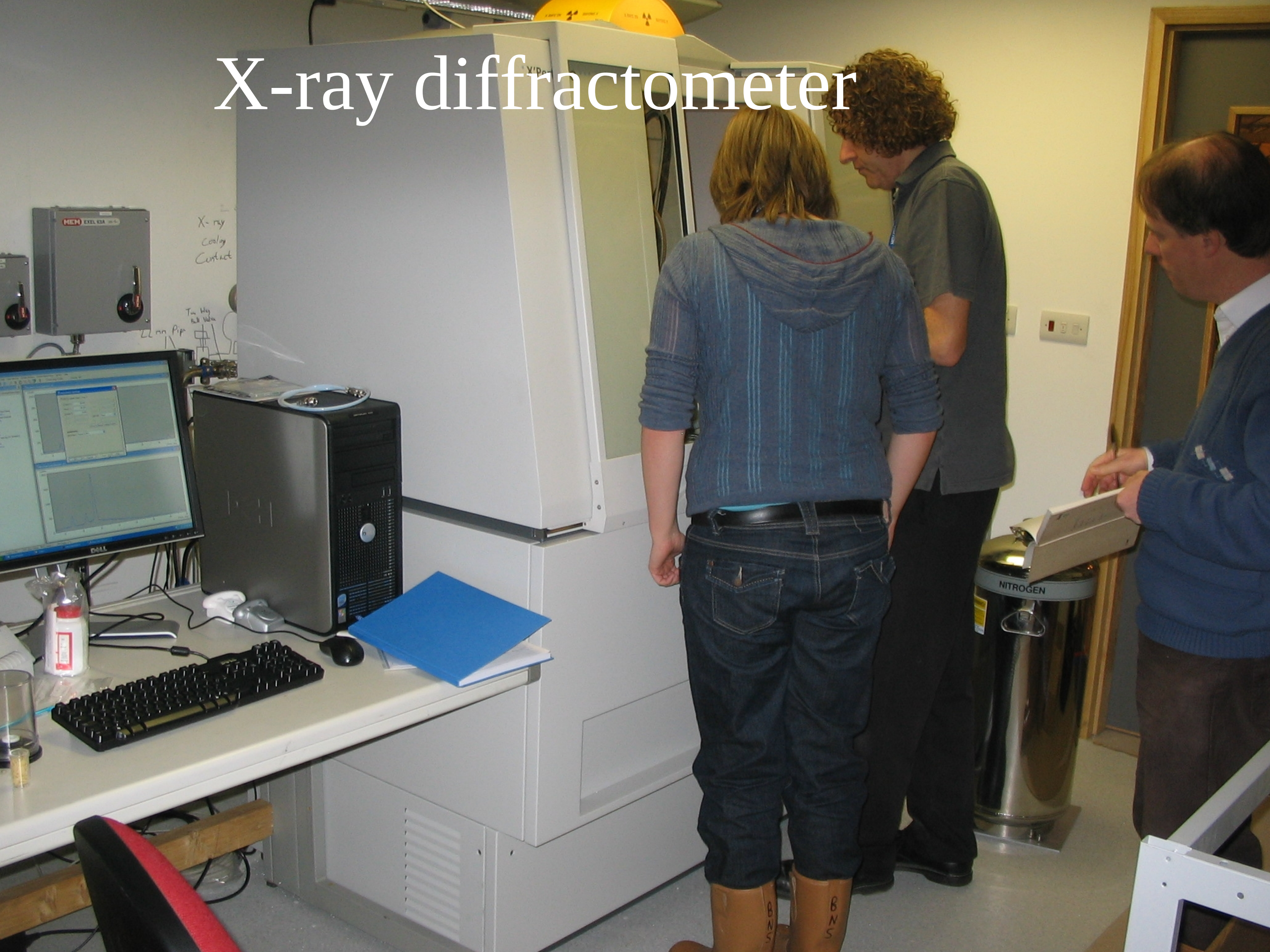
2θ

Incident radiation

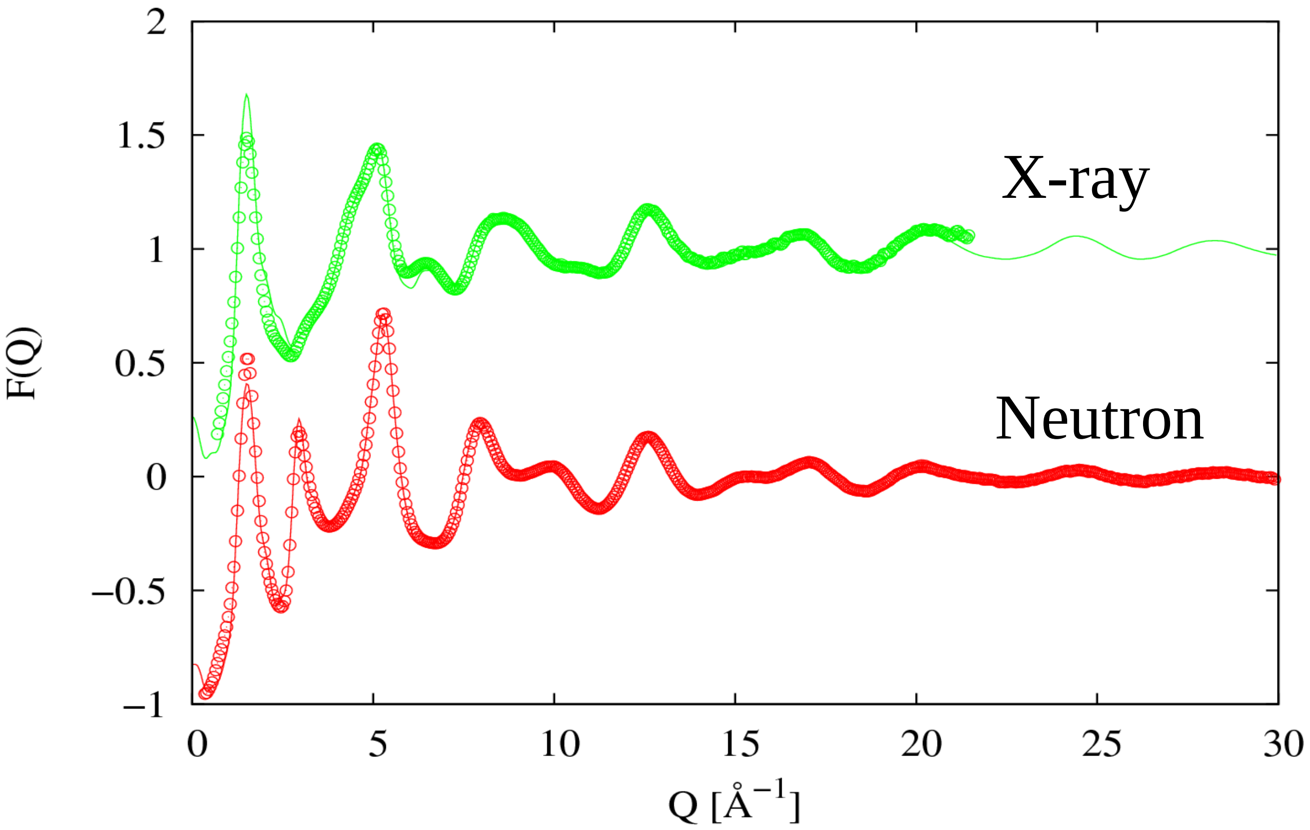
Sample

$$Q = \frac{4\pi \sin\theta}{\lambda}$$

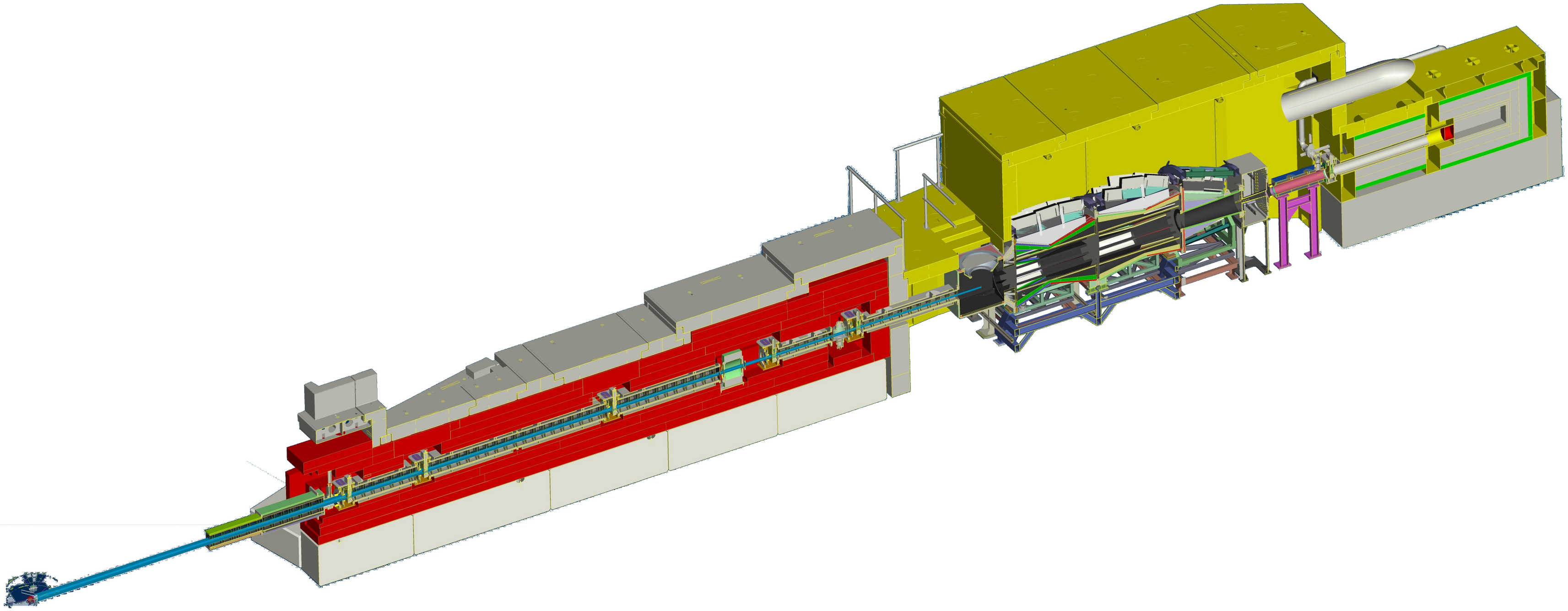
X-ray diffractometer



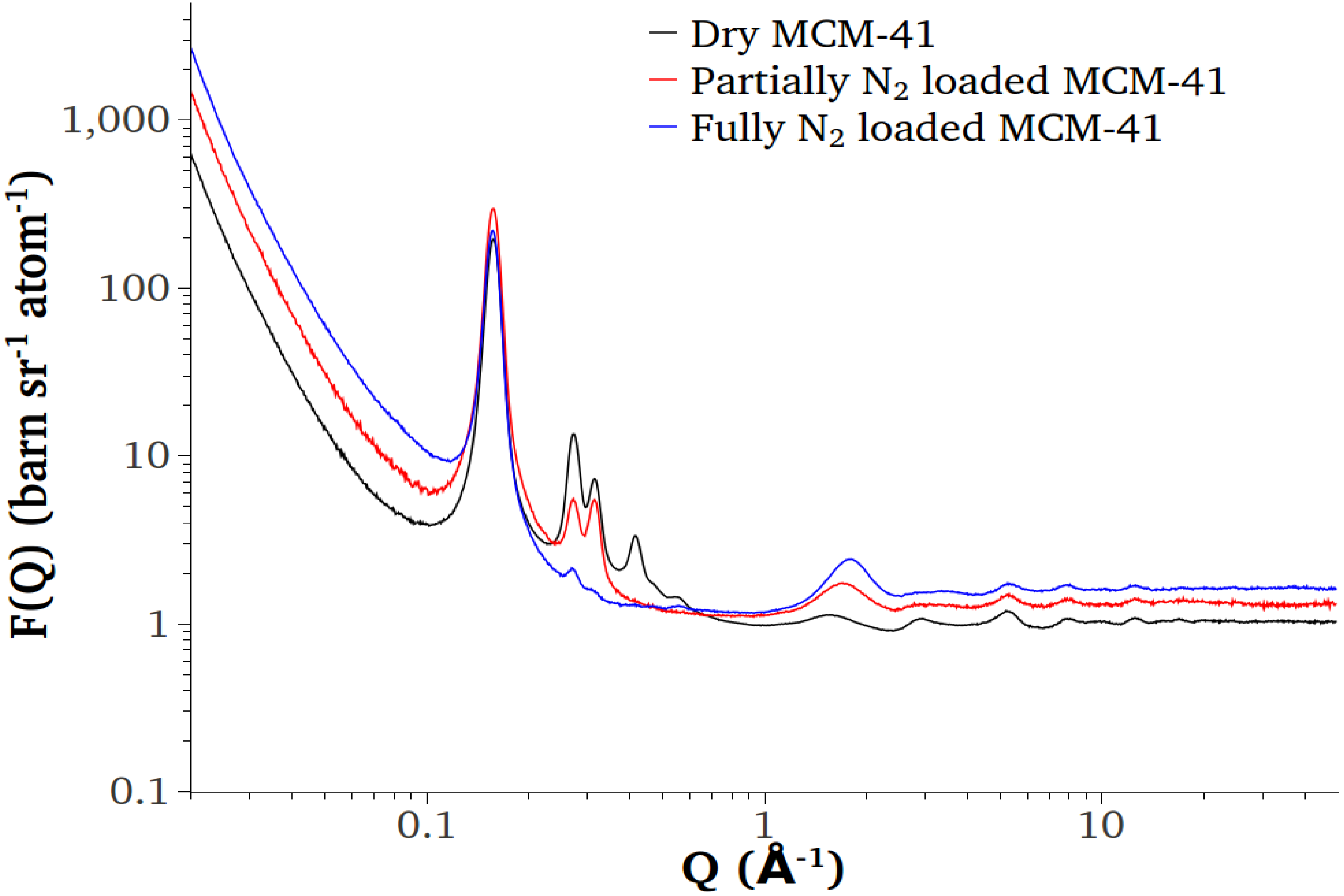
... gives some data:



Now… NIMROD



Wide length-scale data from NIMROD



Differential scattering cross section

- The differential scattering cross section is related to:-

$$\frac{d\sigma}{d\Omega}\left(Q_E,\theta\right)=F_s\left(Q_E,\theta\right)+F_d\left(Q_E\right)$$

- For neutrons the self term is subject to inelasticity corrections.
- For X-rays the self term is subject to Compton scattering corrections.

Properties of the neutron differential cross section – effect of inelastic scattering

- According to van Hove (1954) the dynamic structure factor, *S(Q,ε)*, splits into two terms:
  - The self term, $S_s(Q,\varepsilon)$, corresponds to atoms correlating with themselves.
  - The distinct term, $S_d(Q,\varepsilon)$, corresponds to atoms correlating with other atoms.
- The total scattering cross section is related to:-

$$\frac{d^2\sigma}{d\Omega\, d\varepsilon} \sim \frac{k_f}{k_i}\left\{ \langle b^2 \rangle S_s(Q,\varepsilon) + \langle b \rangle^2 S_d(Q,\varepsilon) \right\}$$

Sum rules: the "static" structure factor

- For distinct scattering :-

$$\int_Q S_d(Q,\varepsilon)\, d\varepsilon = S(Q,t=0) - 1 = \frac{4\pi\rho}{Q}\int r\left(g(r)-1\right)\sin Qr\ dr$$

[This must be carefully distinguished from the **elastic** structure factor, $S_d(Q,\varepsilon=0) \equiv S_d(Q,t=\infty)$]

- For self scattering:-

$$\int_Q S_s(Q,\varepsilon)\, d\varepsilon = 1$$

Effect of energy transfer

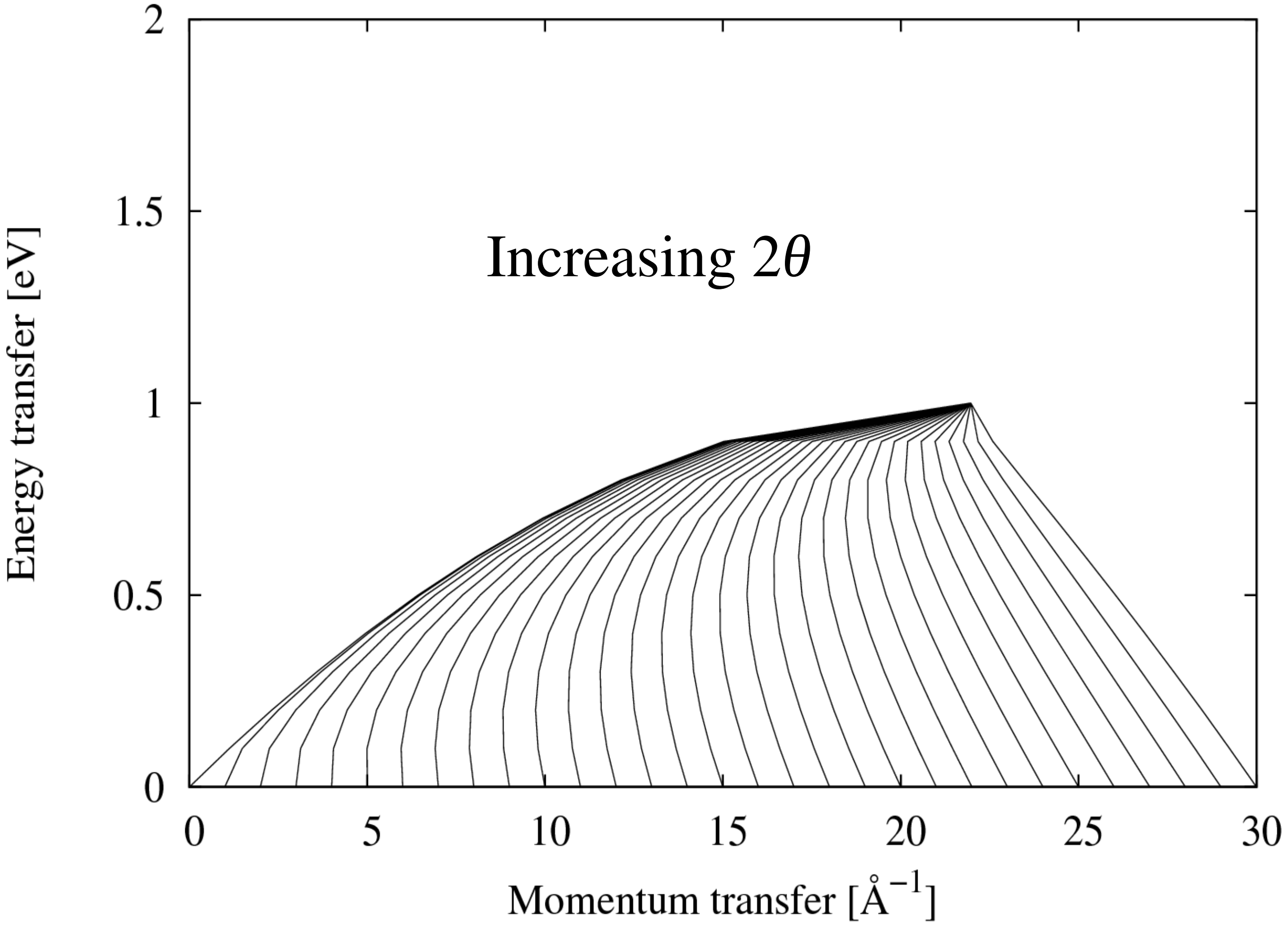
- Kinematics of neutron scattering:-

$$Q^2 = k_i^2 + k_f^2 - 2\mathrm{k}_i k_f \cos\theta$$

$$\varepsilon = \frac{\hbar^2}{2\mathrm{m}}\left(k_i^2 - k_f^2\right)$$

- In a diffraction experiment the neutron detector integrates $S(Q,\varepsilon)$ at constant θ, NOT constant Q.

Fixed incident energy plot
E_i = 1eV



Effect of energy transfer

- For distinct scattering (Placzek, 1952):-

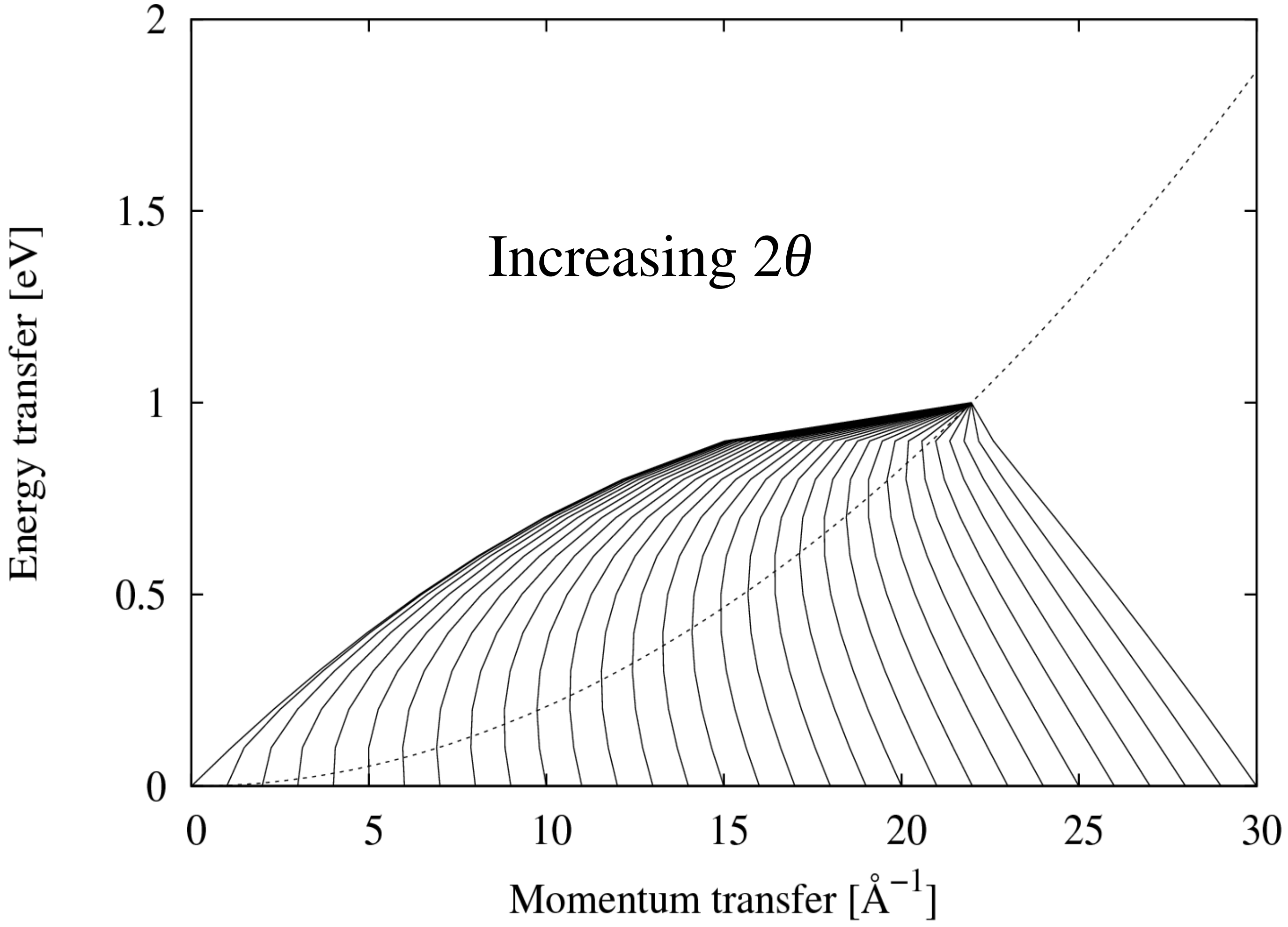
$$\int_Q \varepsilon \; S_d(Q,\varepsilon) = 0$$

- For self scattering:-

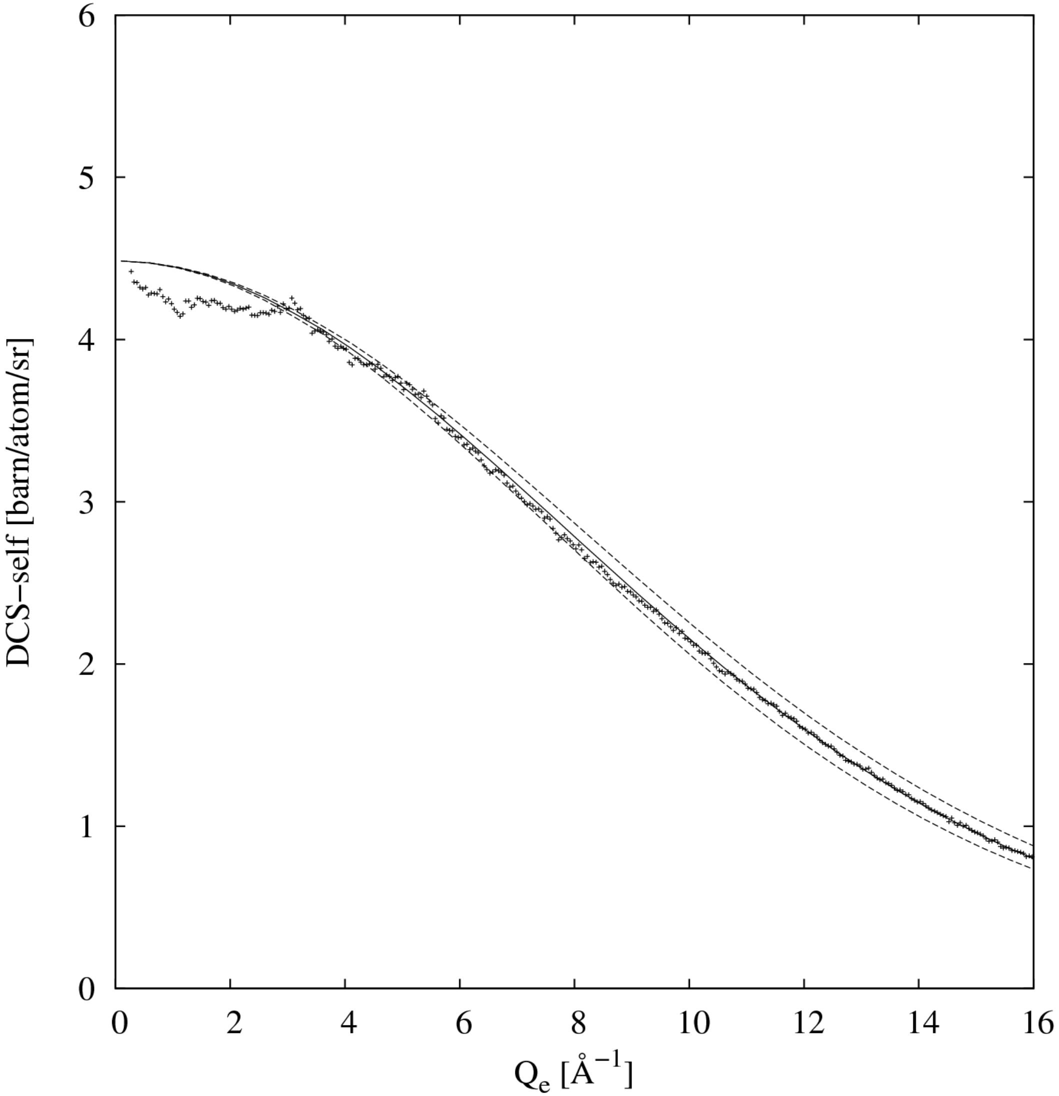
$$\int_Q \varepsilon \; S_s(Q,\varepsilon) = \frac{\hbar^2 Q^2}{2\mathrm{M}}$$

- $M_p \approx M_n$ means significant energy loss on scattering by protons.

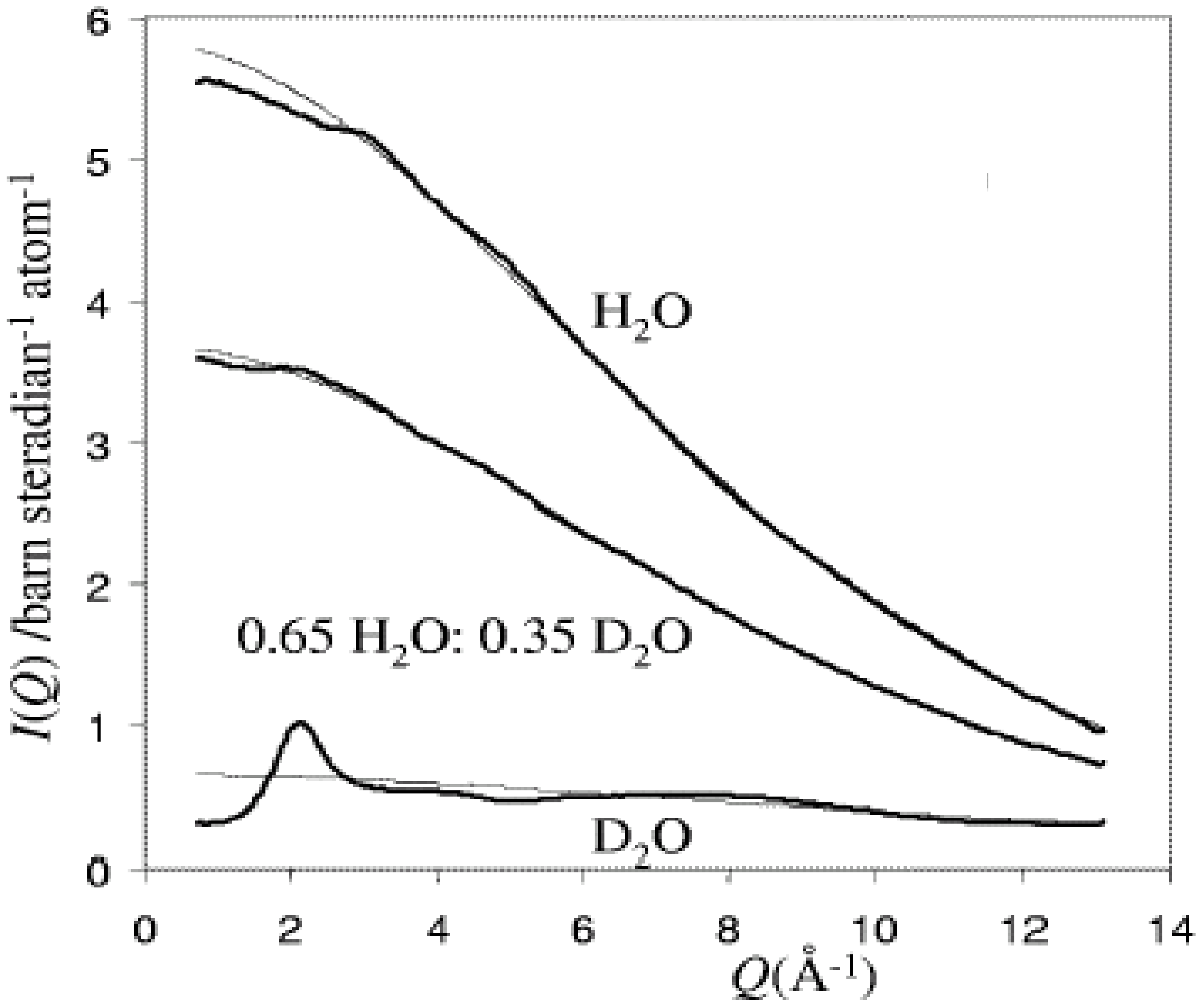
Fixed incident energy plot
E_i = 1eV



Fixed incident energy integration



Reactor data



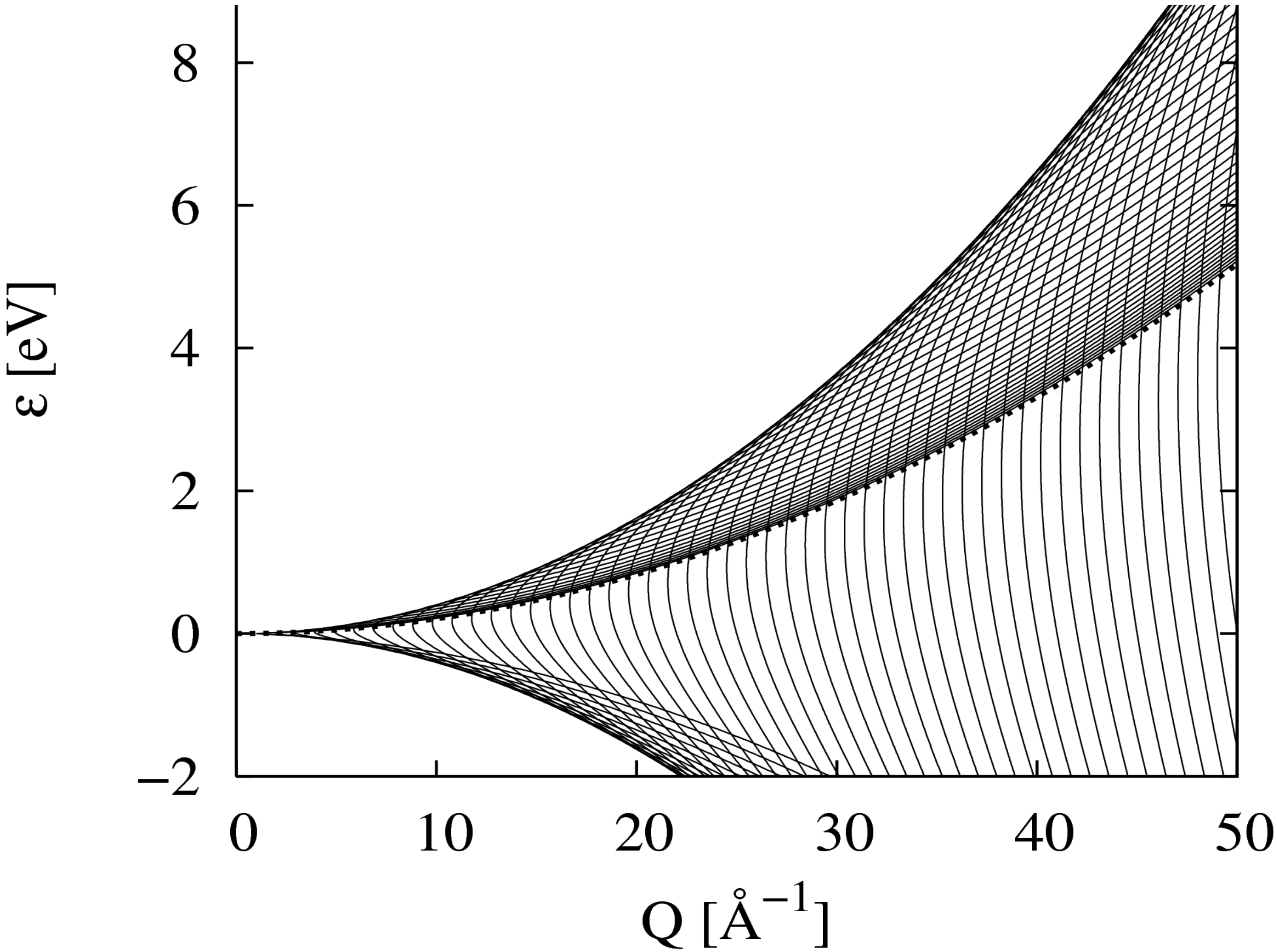
Time of Flight diffraction

- Energy dispersive.
- Detector at fixed scattering angle.
- Detector still integrates at constant angle, but *each* time of flight channel corresponds to a *range* of incident energies:

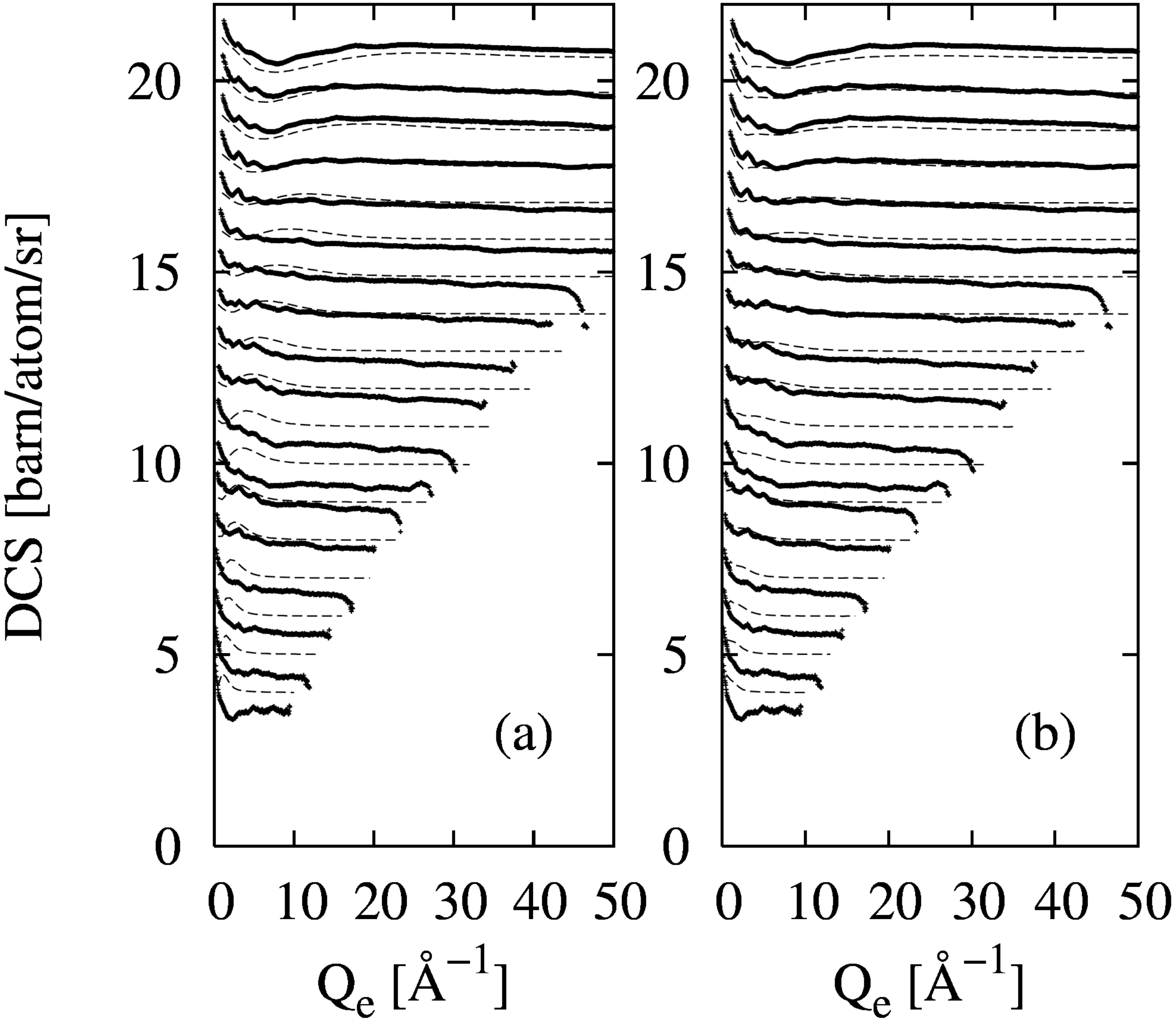
$$\frac{(1+R)}{k_e} = \frac{1}{k_i} + \frac{R}{k_f}, \quad k_e = \frac{Q_e}{2\sin\theta}$$

Constant time-of-flight plots:

$2\theta = 30^{\circ}$



Pulsed Source Data



Our raw diffraction data need to be corrected:

- Normalise to incident beam monitor readings.
- Correct for background.
- Put on absolute scale by comparison with vanadium scattering
- Correct for multiple scattering
- Correct for attenuation and container scattering
- Produce differential scattering cross-section per atom or molecule of sample.
- Remove the single atom scattering.
- Merge detectors into a single pattern.

The structure factor:

The partial structure factors, $H_{\alpha\beta}(Q)$

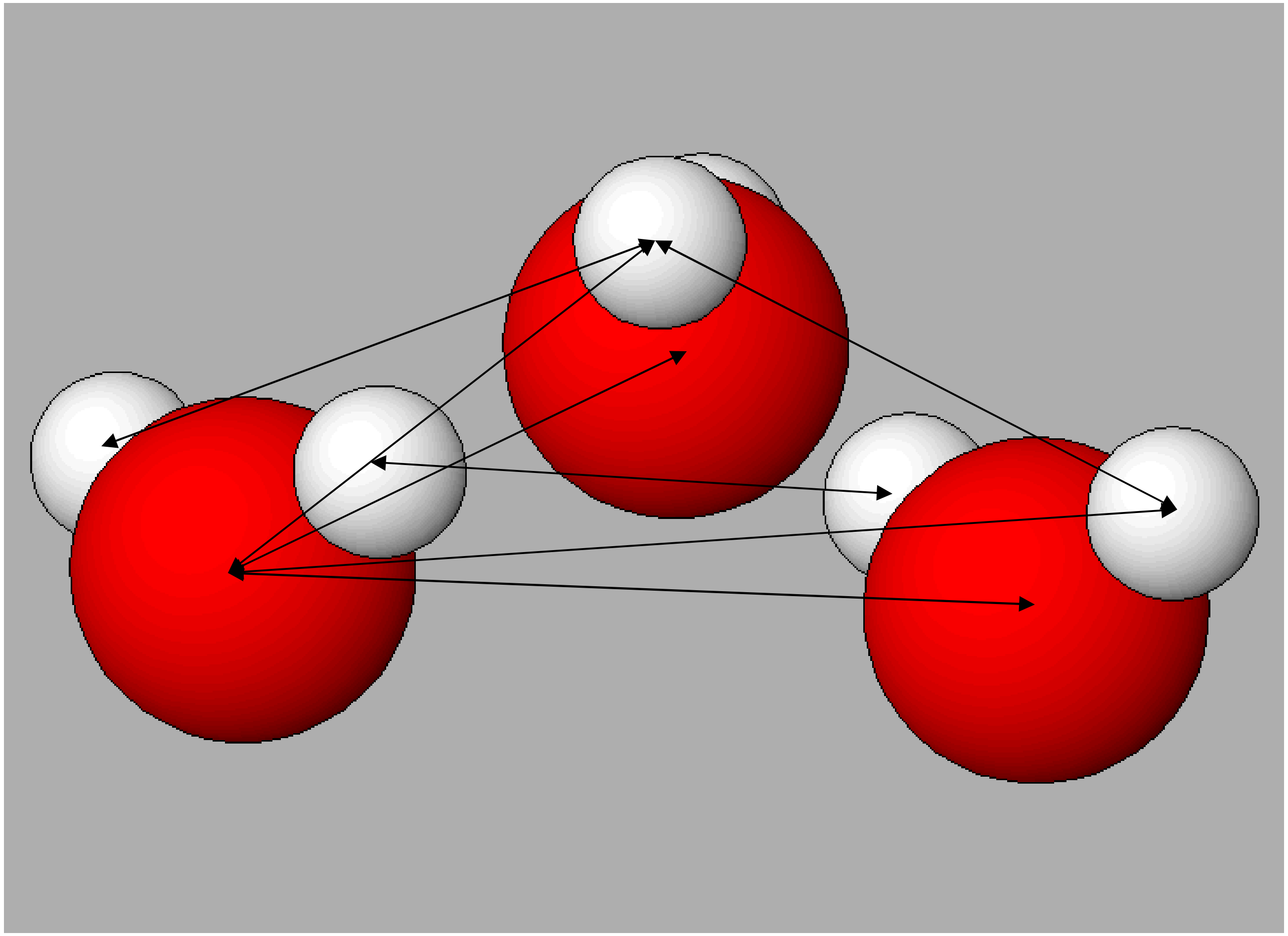
The site-site radial distribution functions, $g_{\alpha\beta}(r)$

$$F_d(Q)=\sum_{\alpha,\beta\geq\alpha}(2-\delta_{\alpha\beta})\,c_\alpha c_\beta b_\alpha b_\beta\left\{4\pi\rho\int r^2\left(g_{\alpha\beta}(r)-1\right)\frac{\sin Qr}{Qr}\,dr\right\}$$

Atomic fraction of component “α”

The atom scattering factor or “form factor”

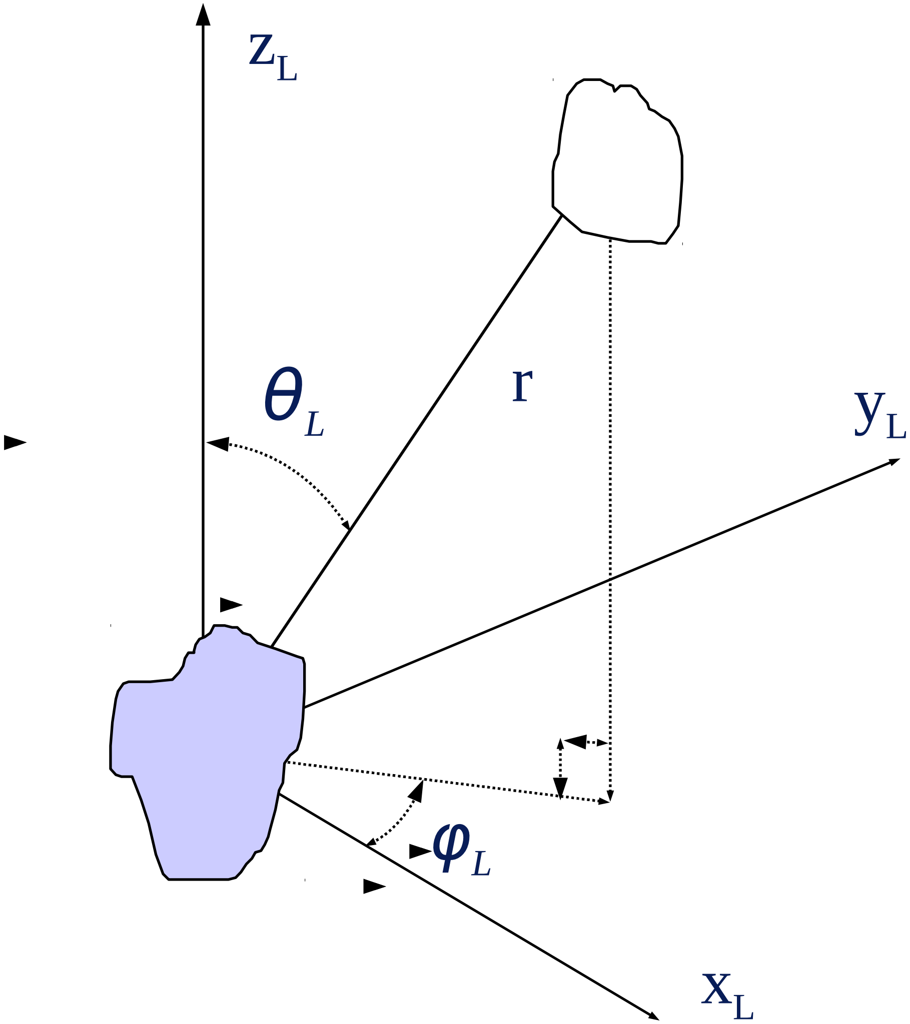
What do we measure if there are molecules present?



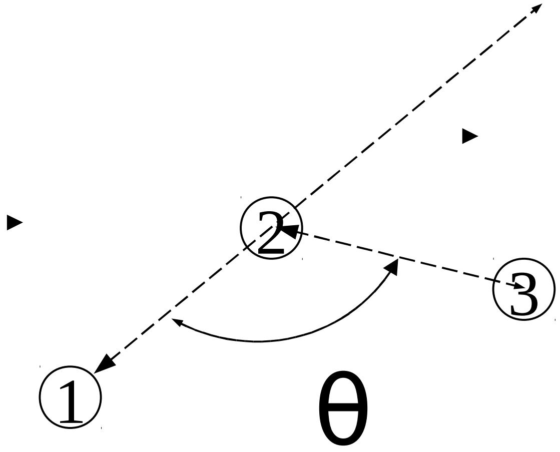
However, two issues need to be addressed:-

- *Issue 1: Often not possible to measure all partial structure factors.*
- *Issue 2: Even if we could, what do they mean?*

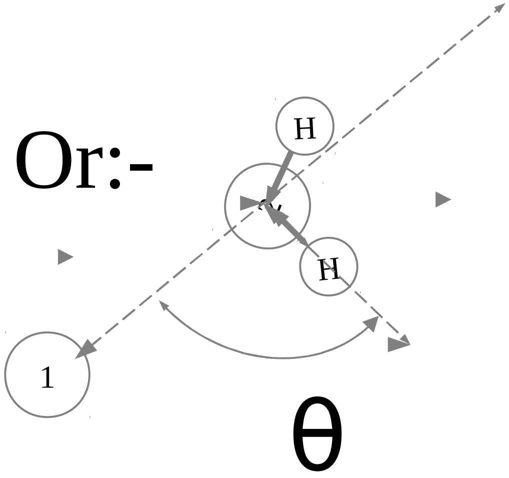
Beyond g(r): the spatial density function



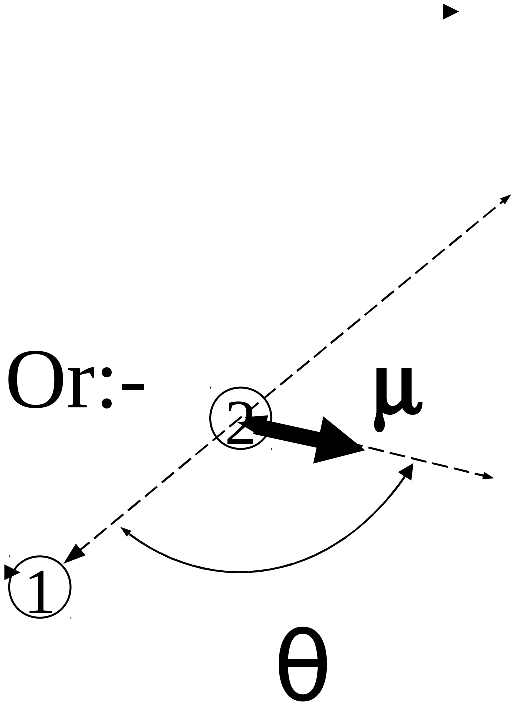
Bond angle distributions



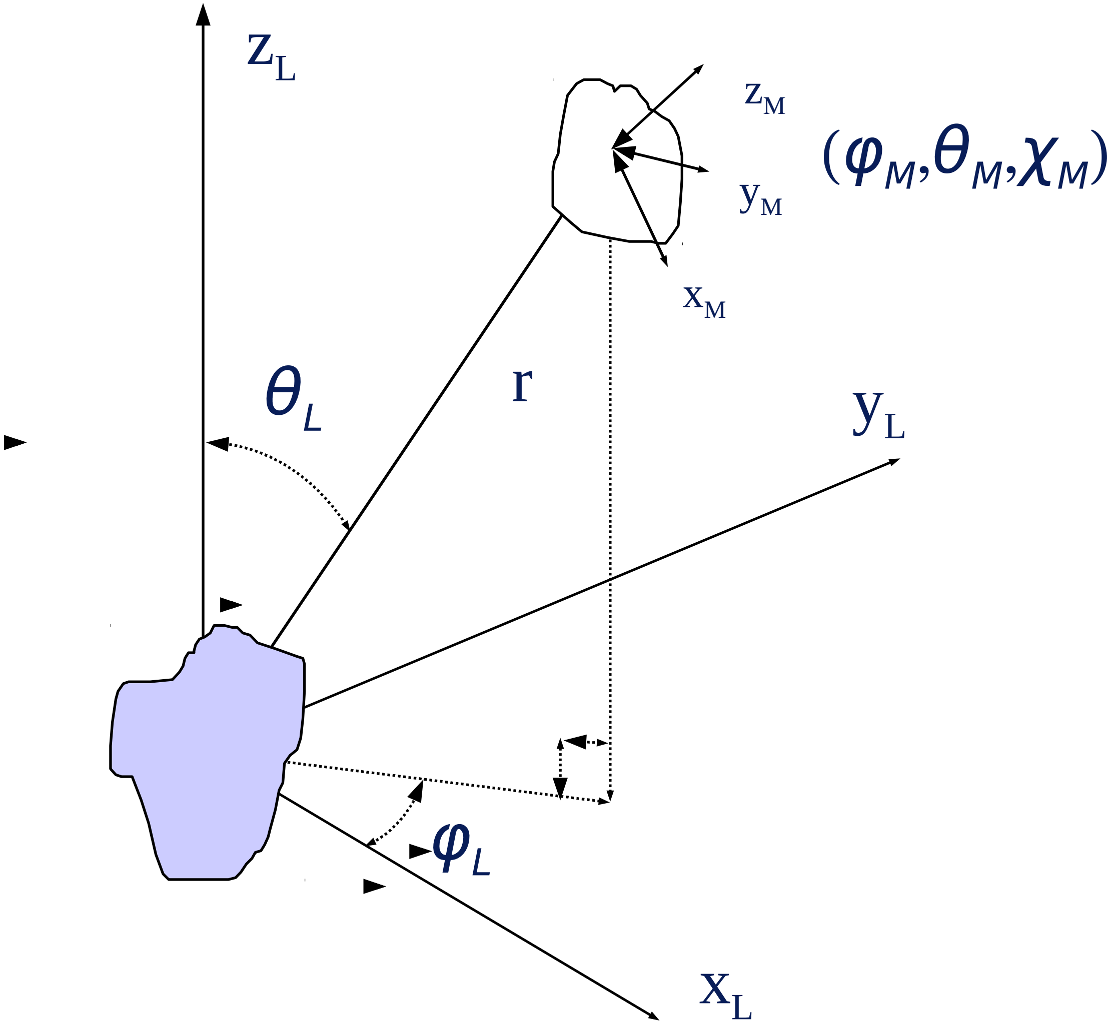
Or:-



Or:-



A step further: the orientational pair correlation function



Summary of Lecture I

- Discussion of disorder in our world.
- Concept of correlation in disordered systems.
- Use of radial distribution function to characterise the correlations in a disordered system.
- Use of diffraction to count atoms as a function of distance.
- How to characterise structure in molecular systems:
  - SDF, bond angle distributions, OPCF

Lecture II

- Computer simulation as a tool to model disordered materials
- Use of computer simulation to go from measurements ($S(Q)$, $g(r)$) to SDF, bond angle distribution, OPCF, etc.
- Some case studies: molten alumina, water, amorphous B_2O_3, silica, silicon...