Disordered Materials:
Lecture I

Concepts of disorder:
How we quantify it
and
How we measure it

Alan Soper

Disordered Materials Group

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Disordered Materials:

Lecture II

Finding and refining a structural model

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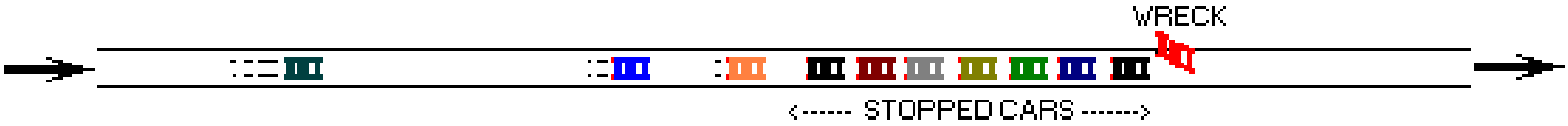
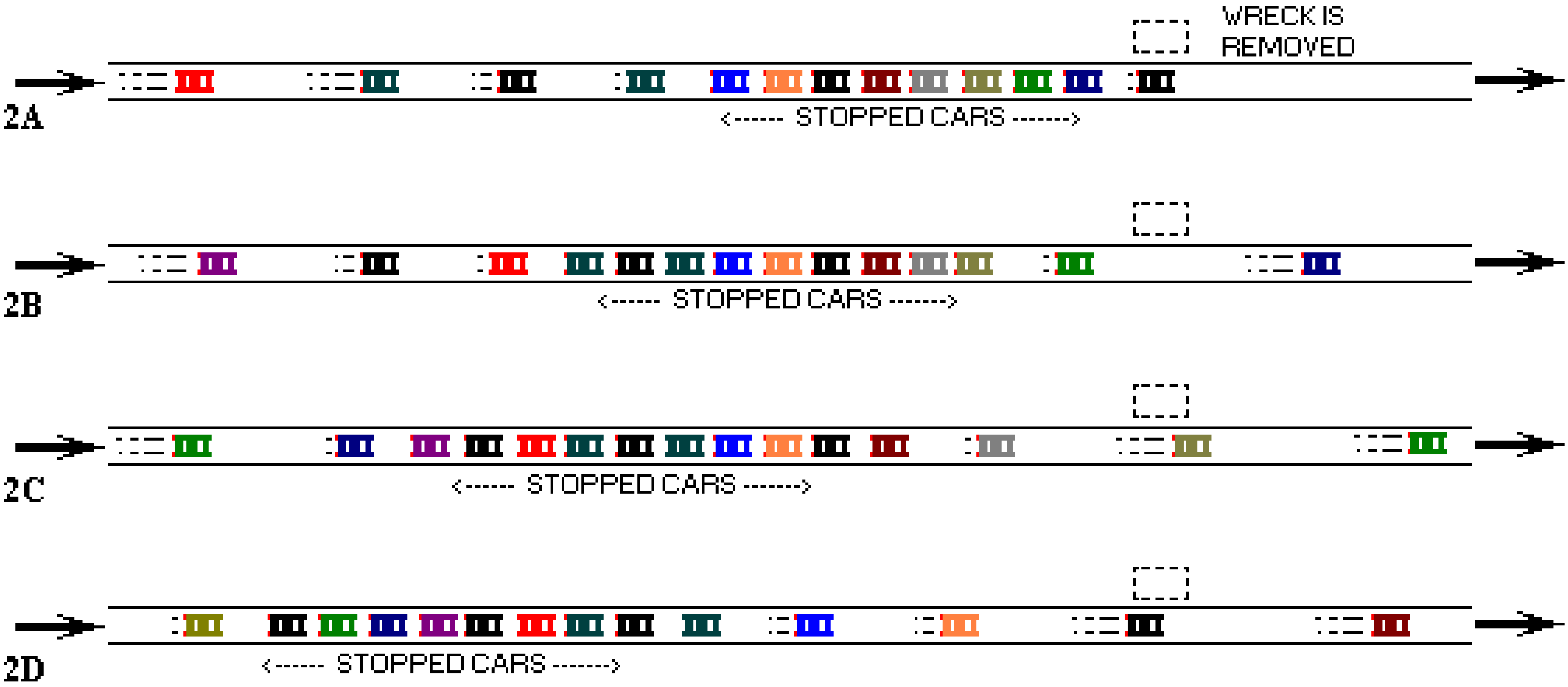
A well known example of disorder…

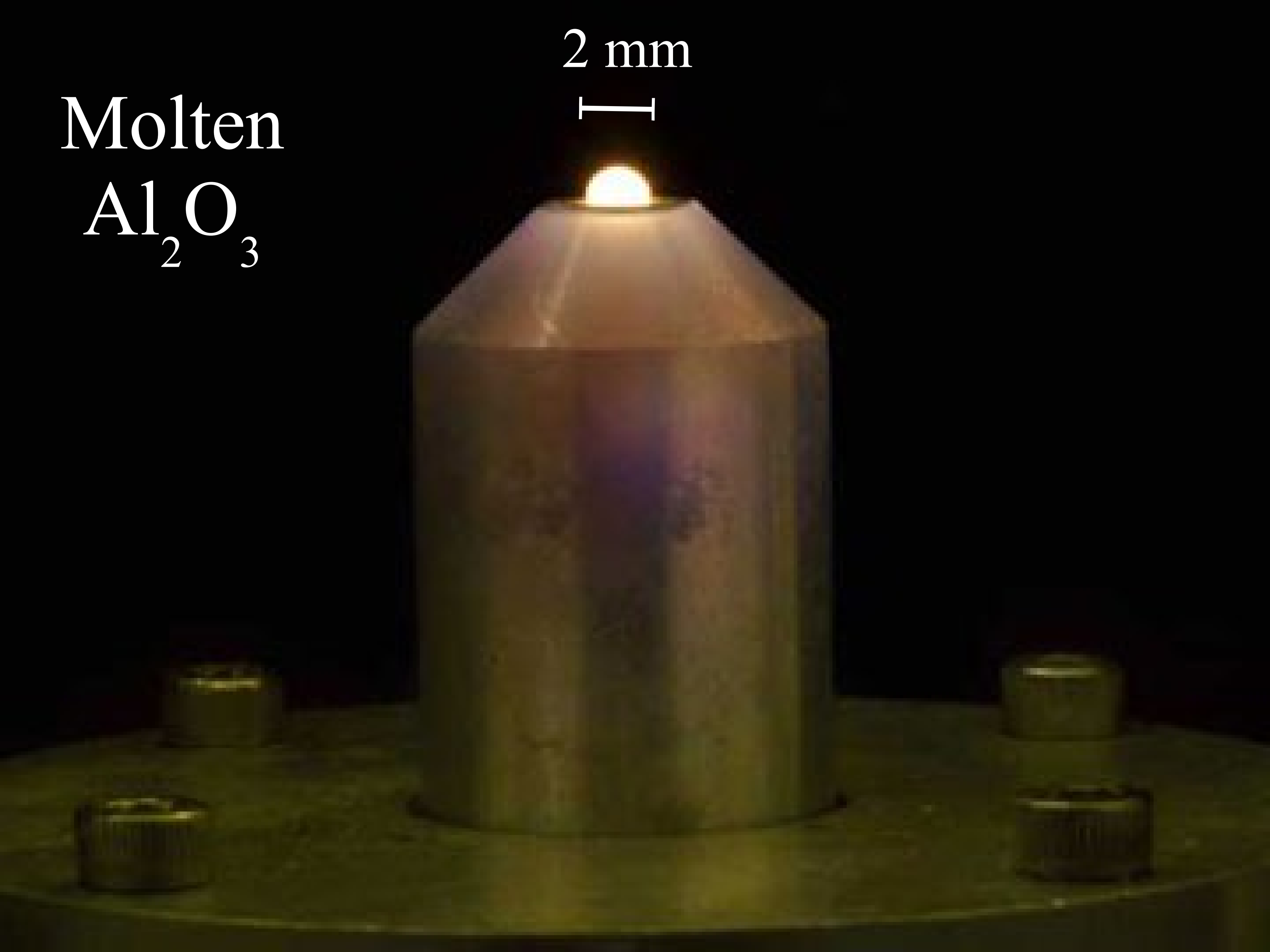


(Courtesy of http://www.amasci.com/amateur/traffic/traffic1.html)

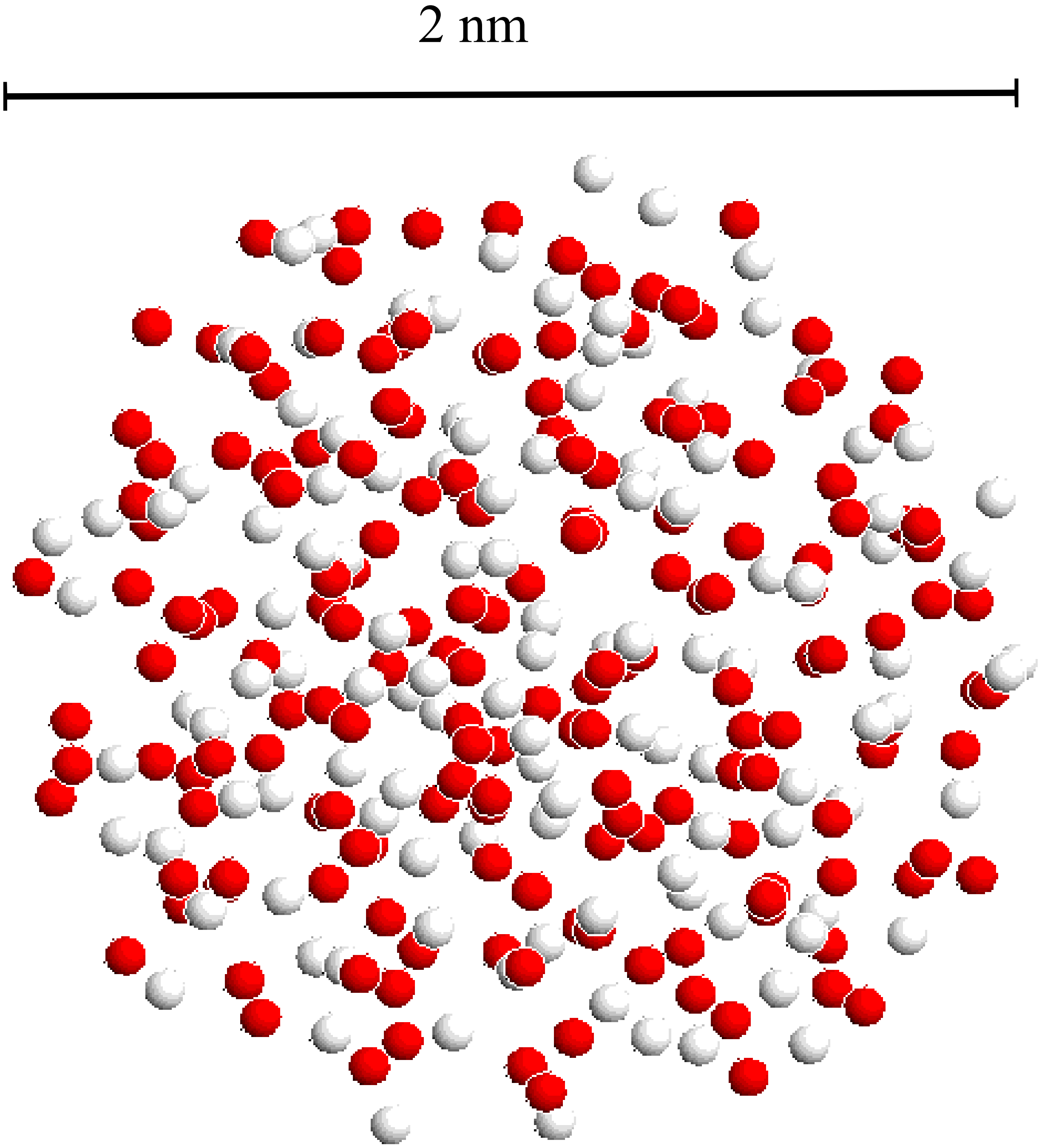

WRECK IS
REMOVED
2A
<------ STOPPED CARS ------->
2B
<------ STOPPED CARS ------->
2C
<------ STOPPED CARS ------->
2D
<------ STOPPED CARS ------->

How to avoid traffic congestion...


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


Molten Al_2O_3
2 mm

Molten Al_2O_3



Disorder affects us in many different ways…

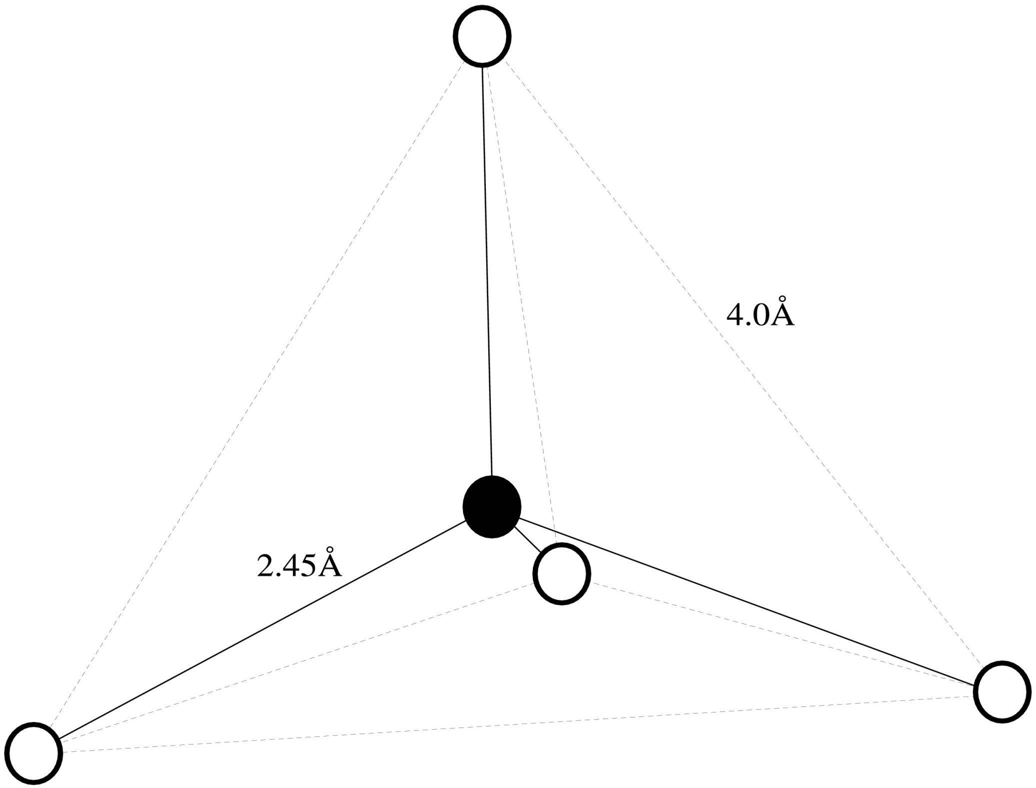
- Avalanches
- Sand, shingle and earth piles
- Congestion in shopping centres, etc.
- Football crowds
- Blood clots
- …
- Gases, liquids and glasses

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 positions.

Disordered materials can be classified as: "Atom jams with marked positional correlations."

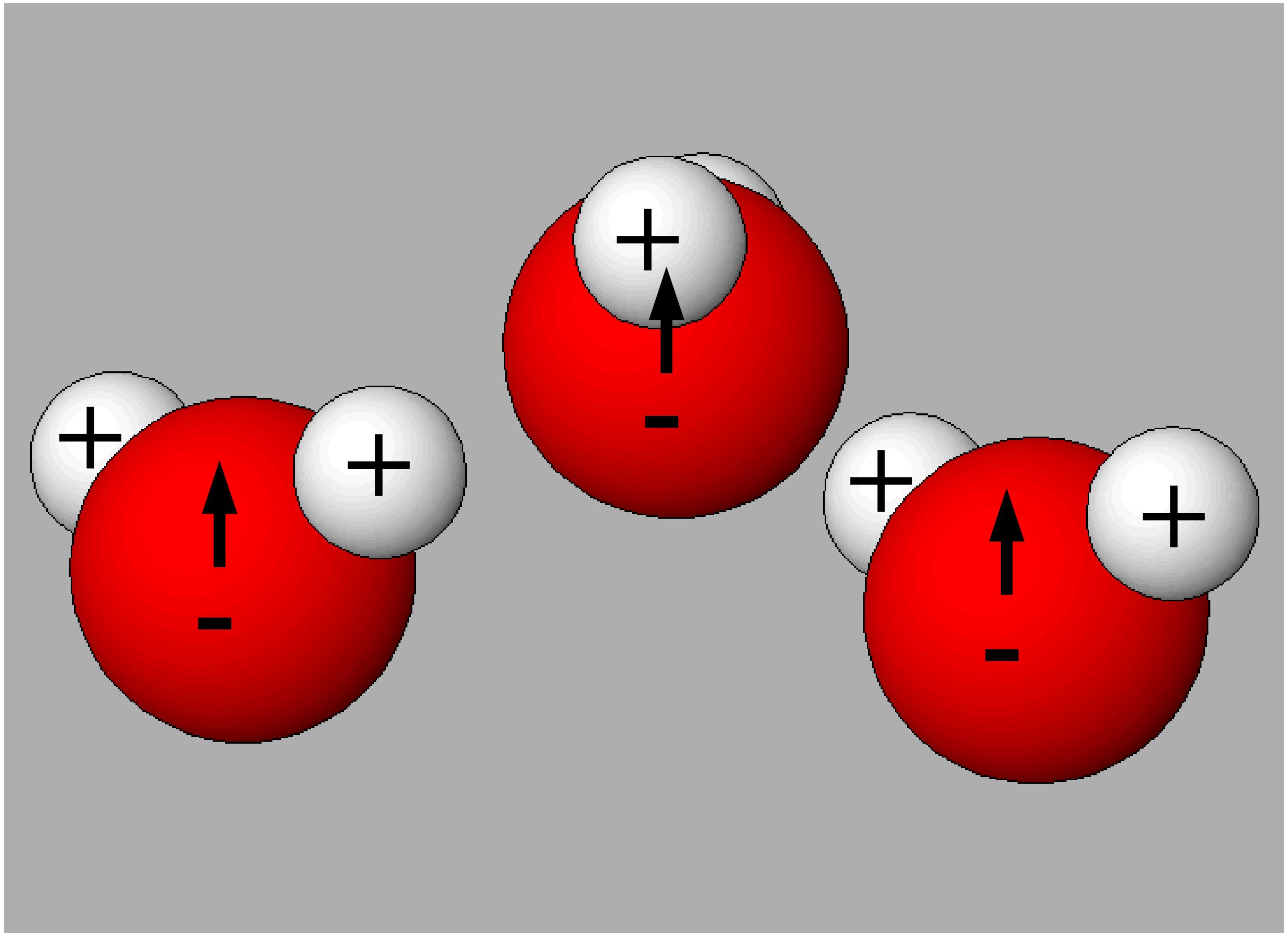
In a gas the atoms are free to move (almost) anywhere.

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

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

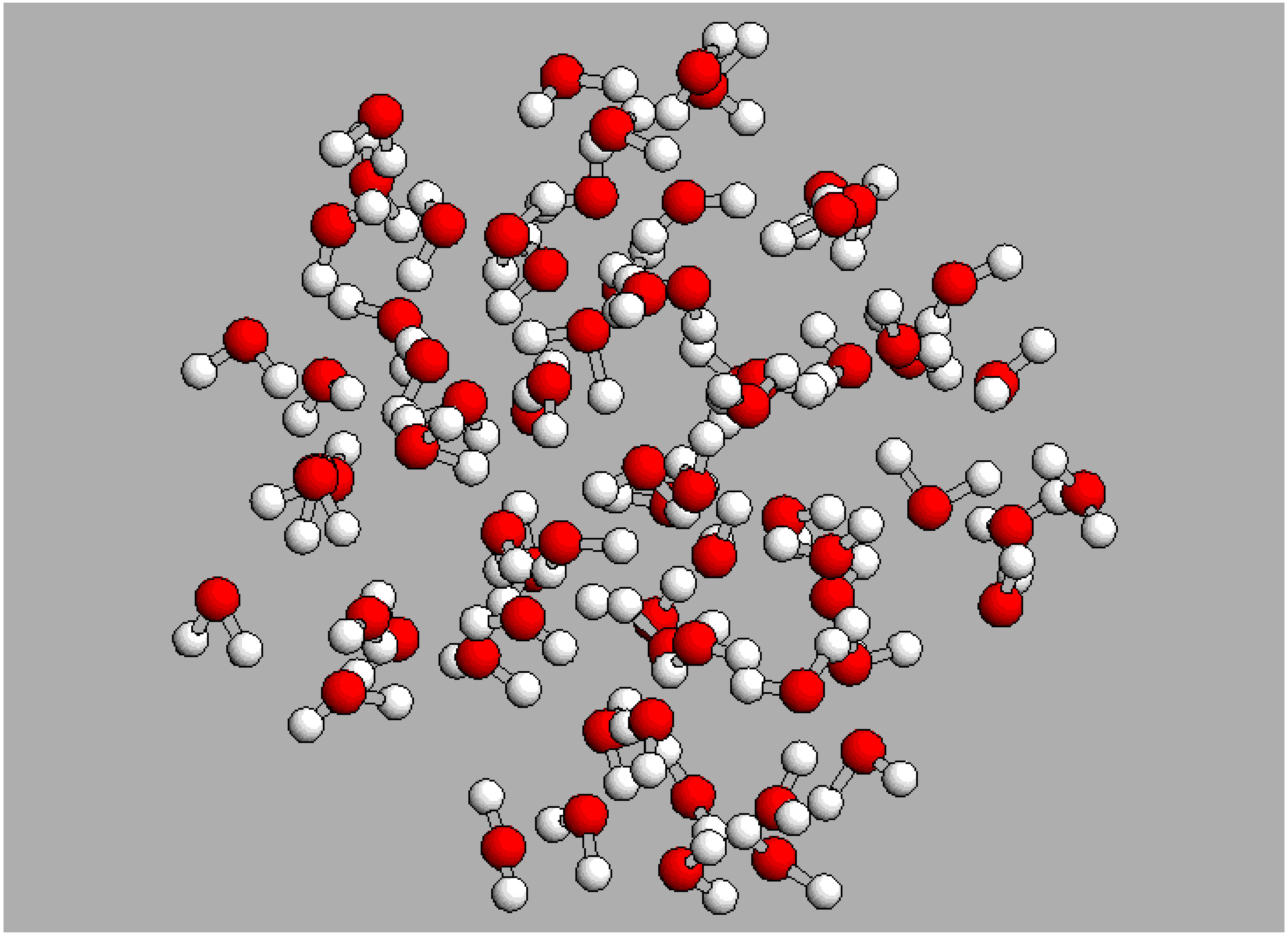
A “typical” liquid, water…

The water molecule



This results in a material which looks like this:-

and this:-



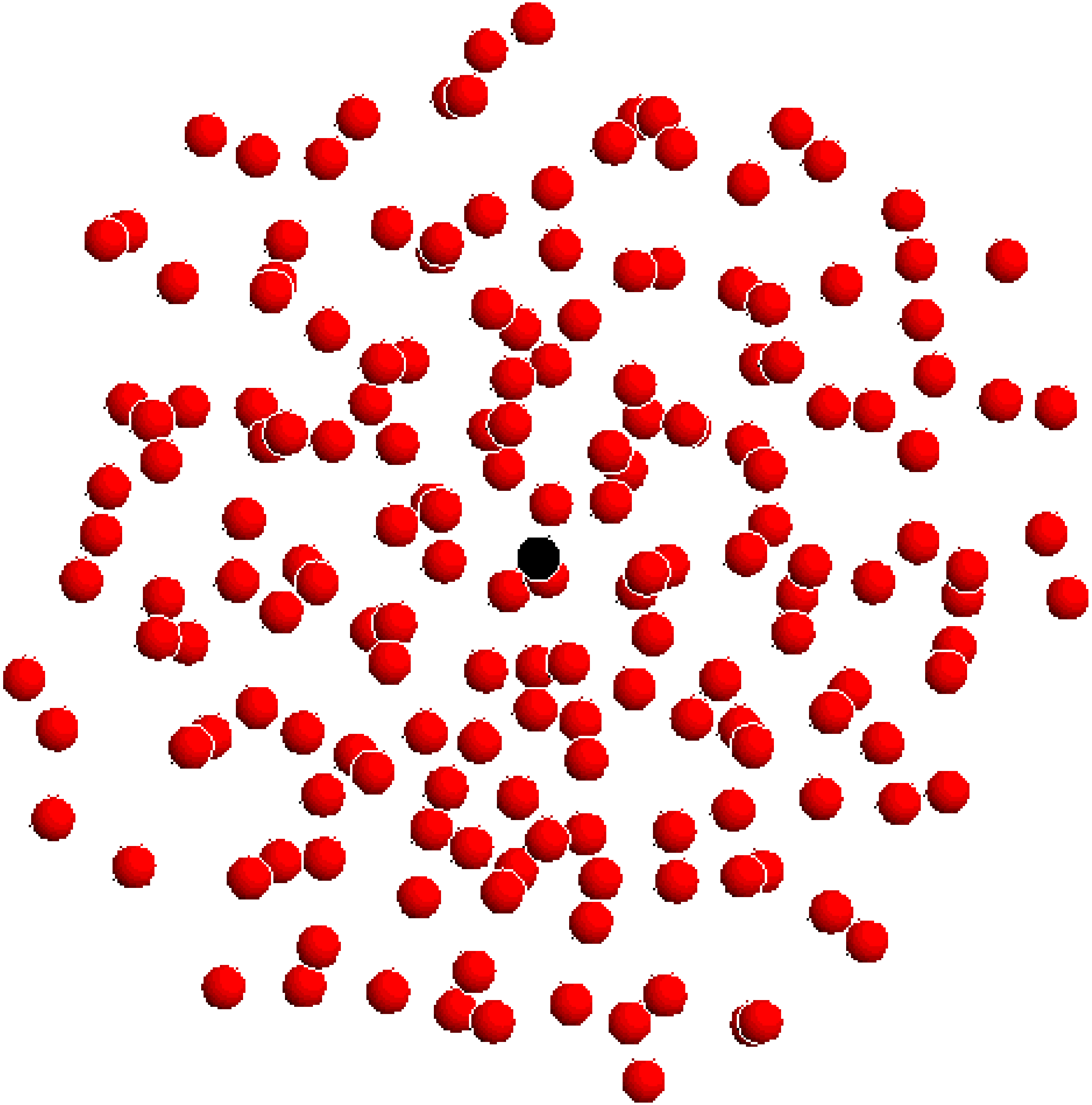
An interesting fact about water:

- *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!).*

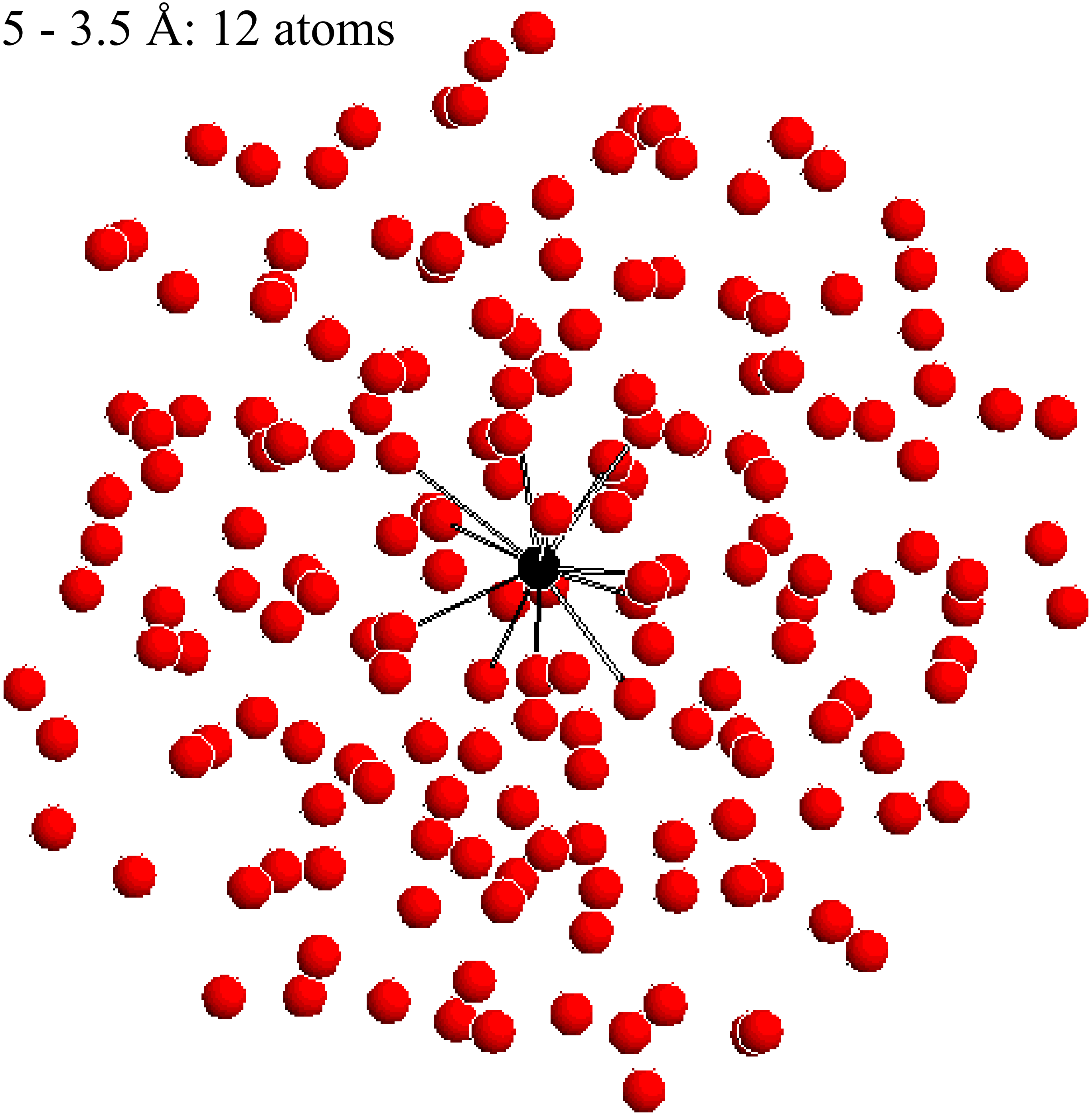
So how do you characterise structure in a disordered system?

By counting.

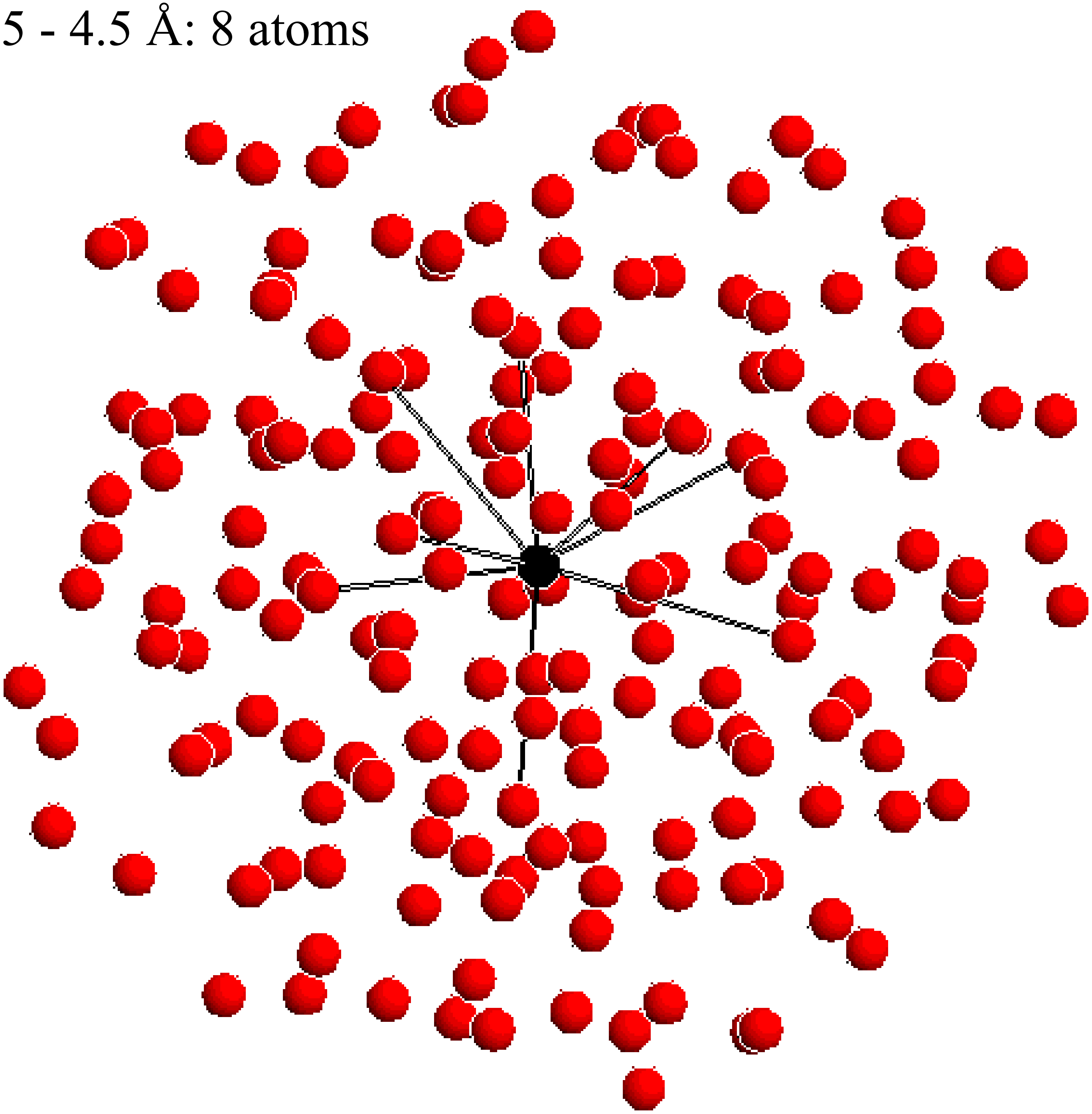
This gives the “radial distribution function ”, $g(r)$:



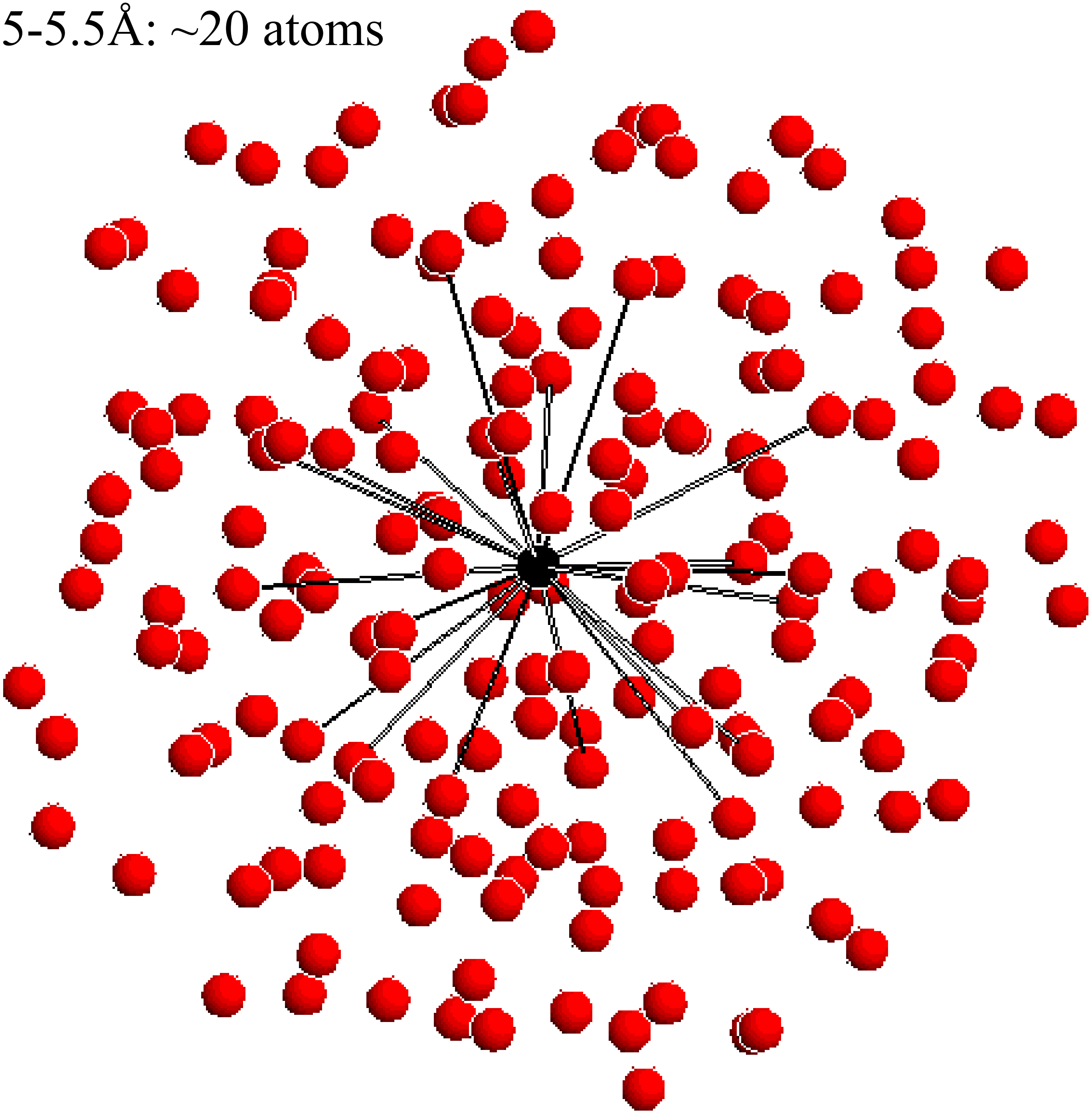
2.5 - 3.5 Å: 12 atoms



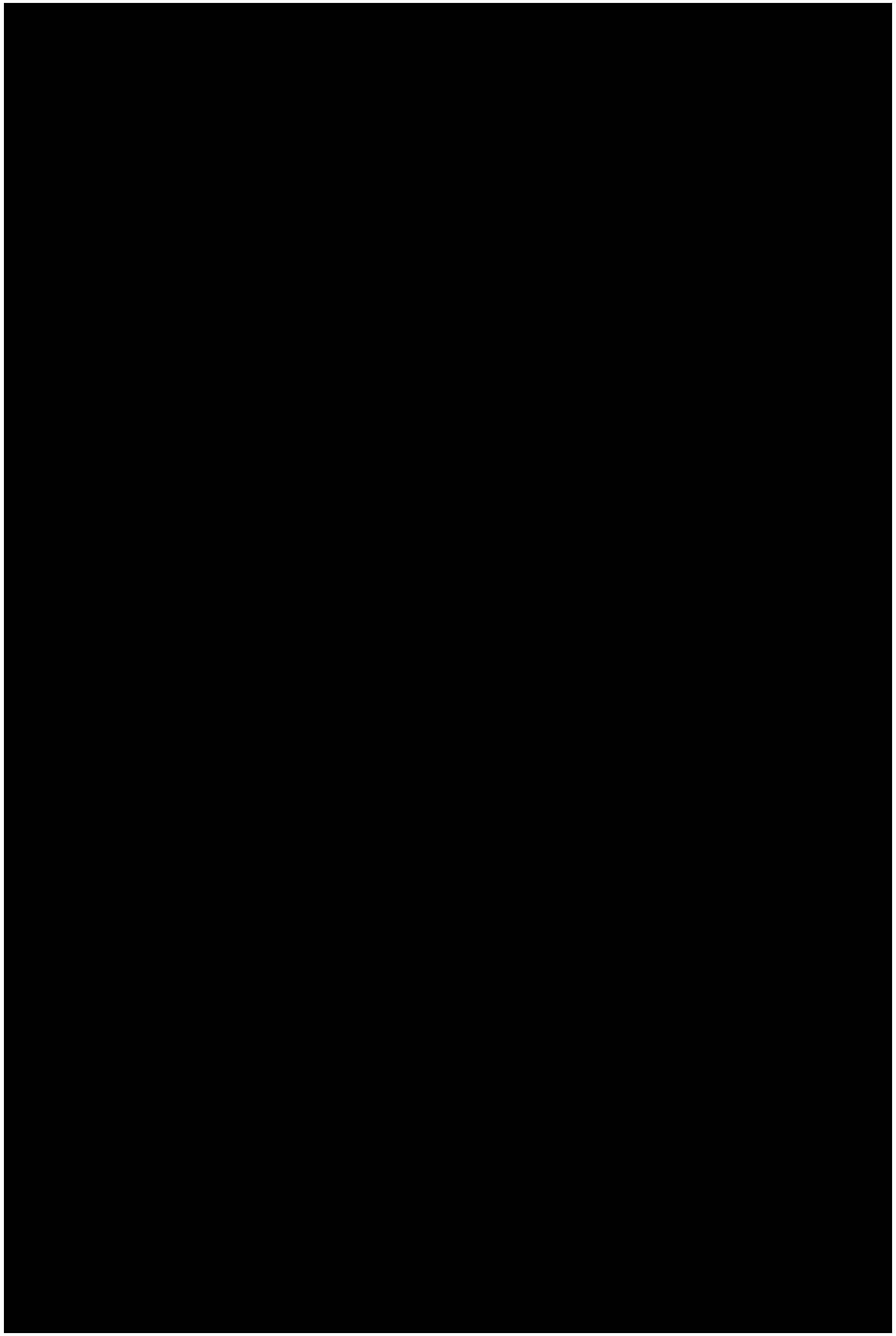
3.5 - 4.5 Å: 8 atoms



4.5-5.5Å: ~20 atoms



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

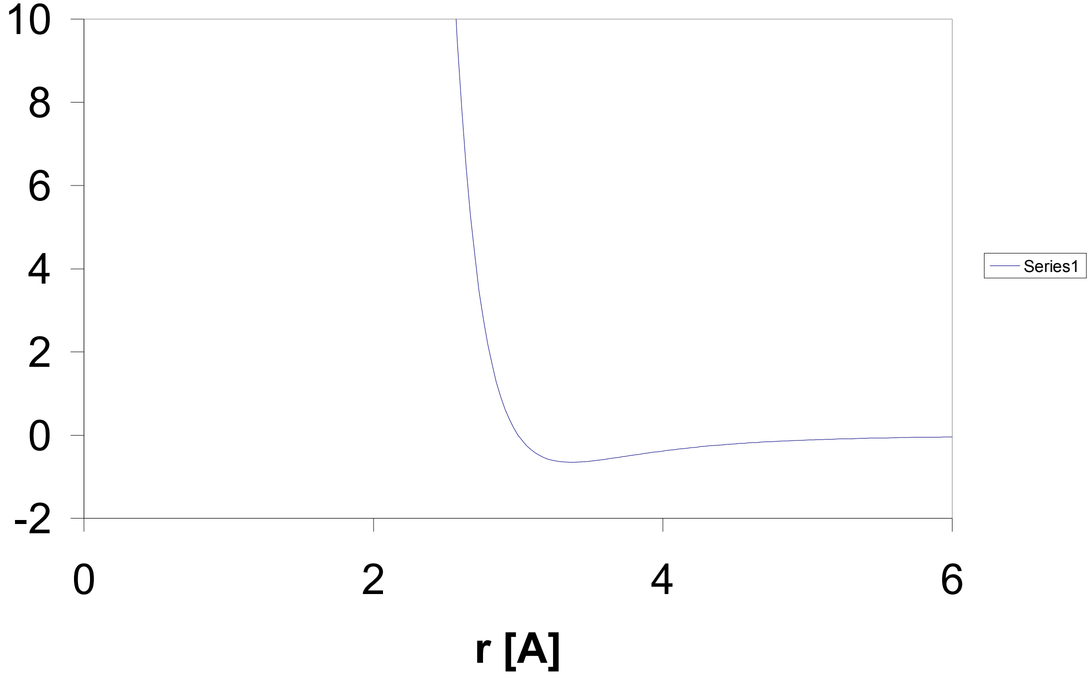


What is this radial distribution function, g(r), telling us?

- 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…

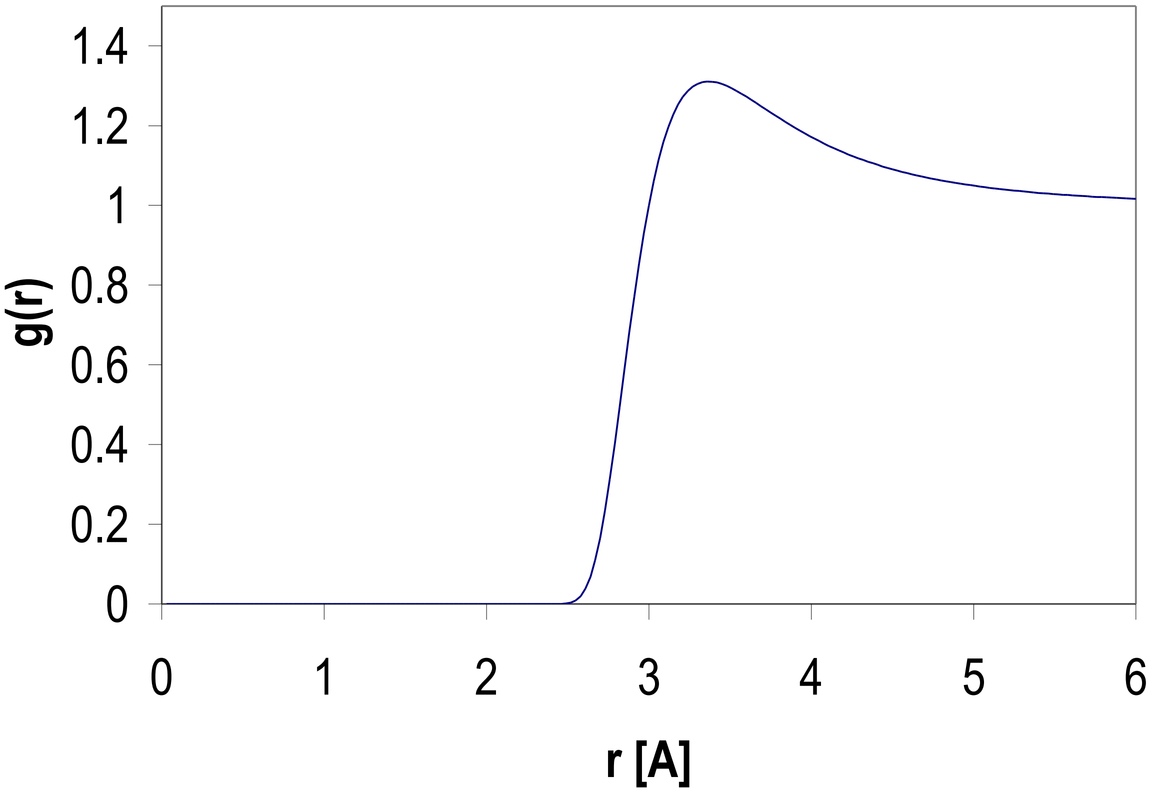
- Typical interatomic potentials are not oscillatory – they have a repulsive core and are attractive beyond the core – van der Waals forces.



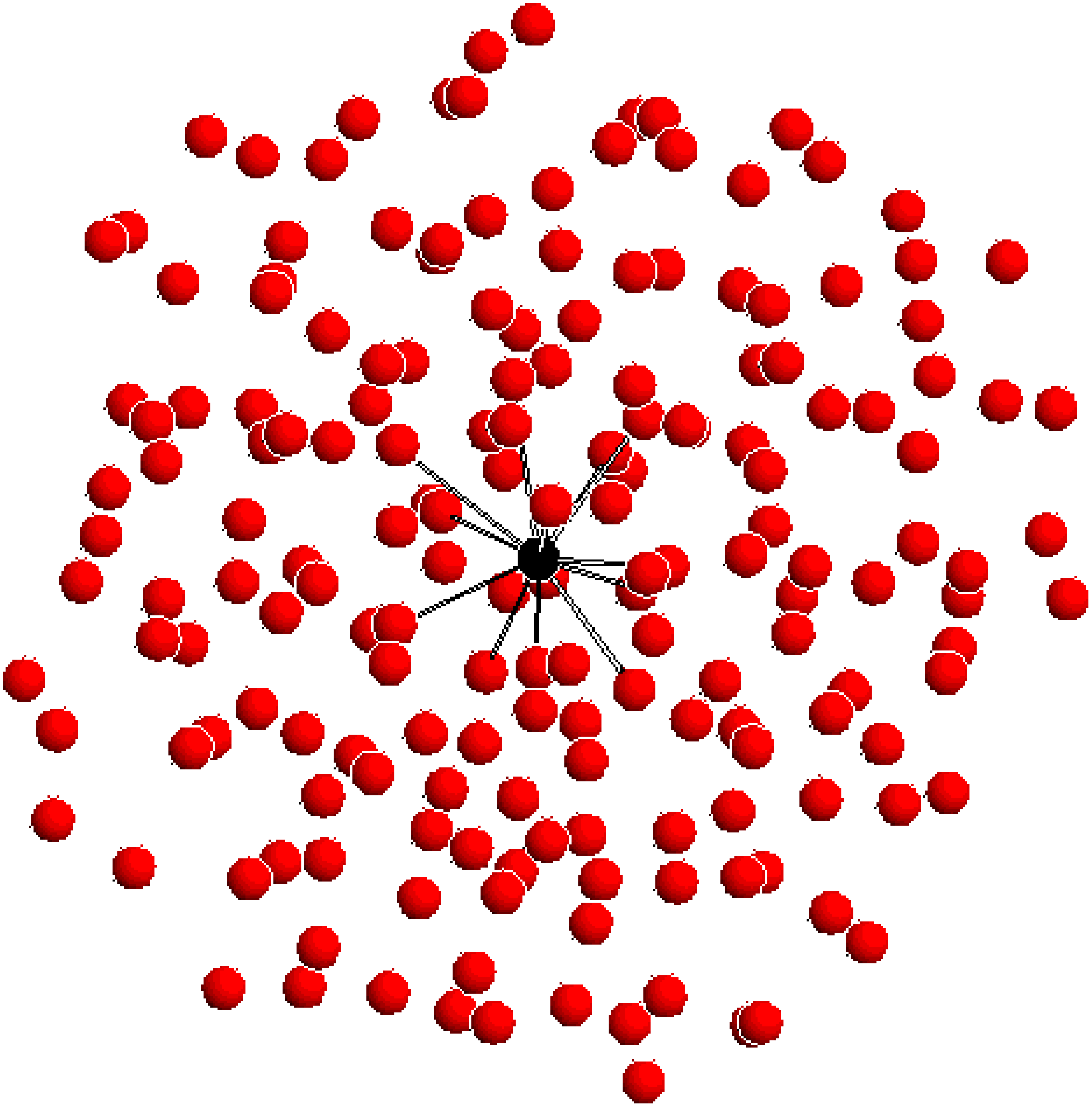
Corresponding g(r):

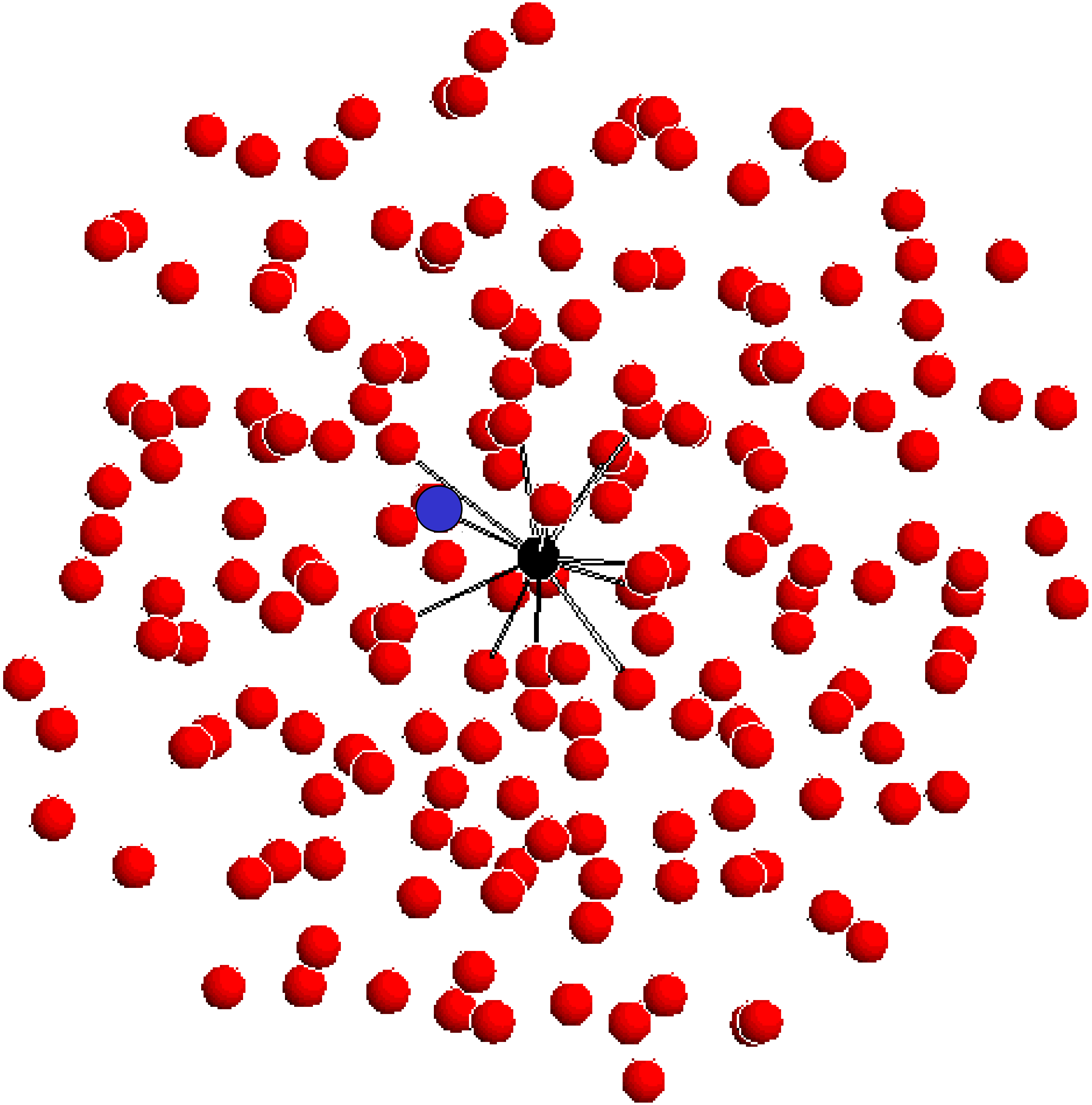
- At zero density, formally exact result:

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



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

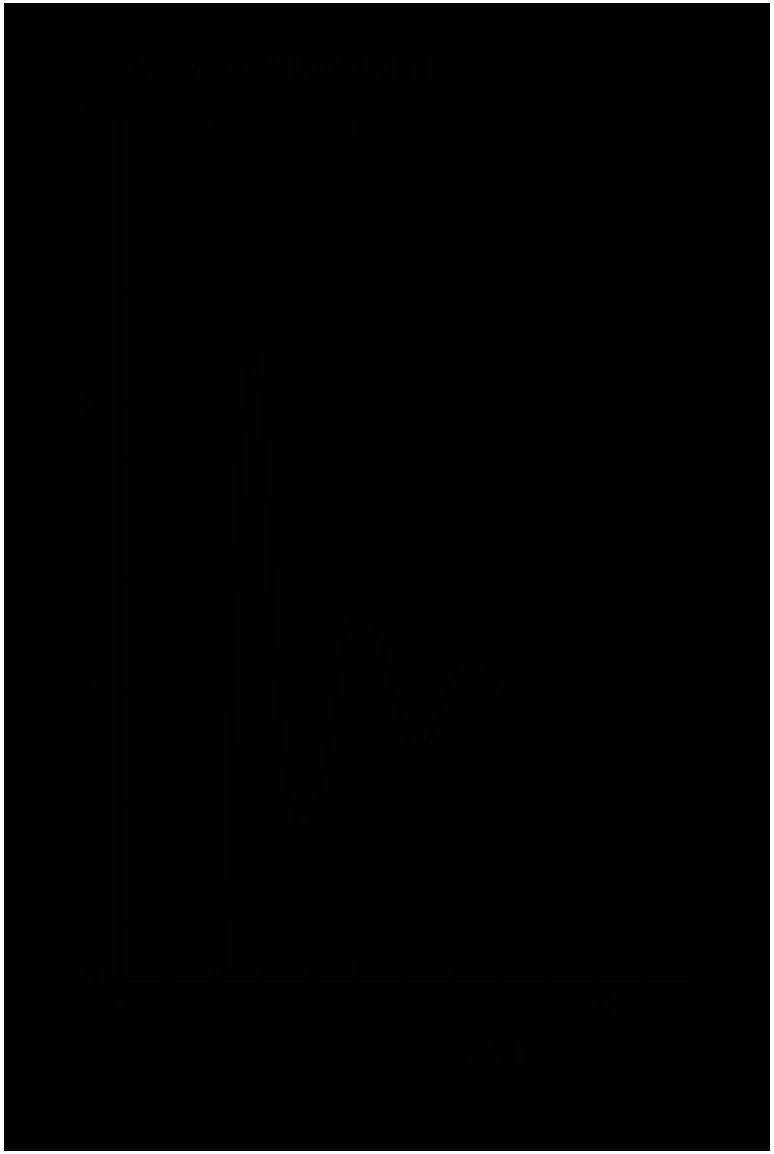




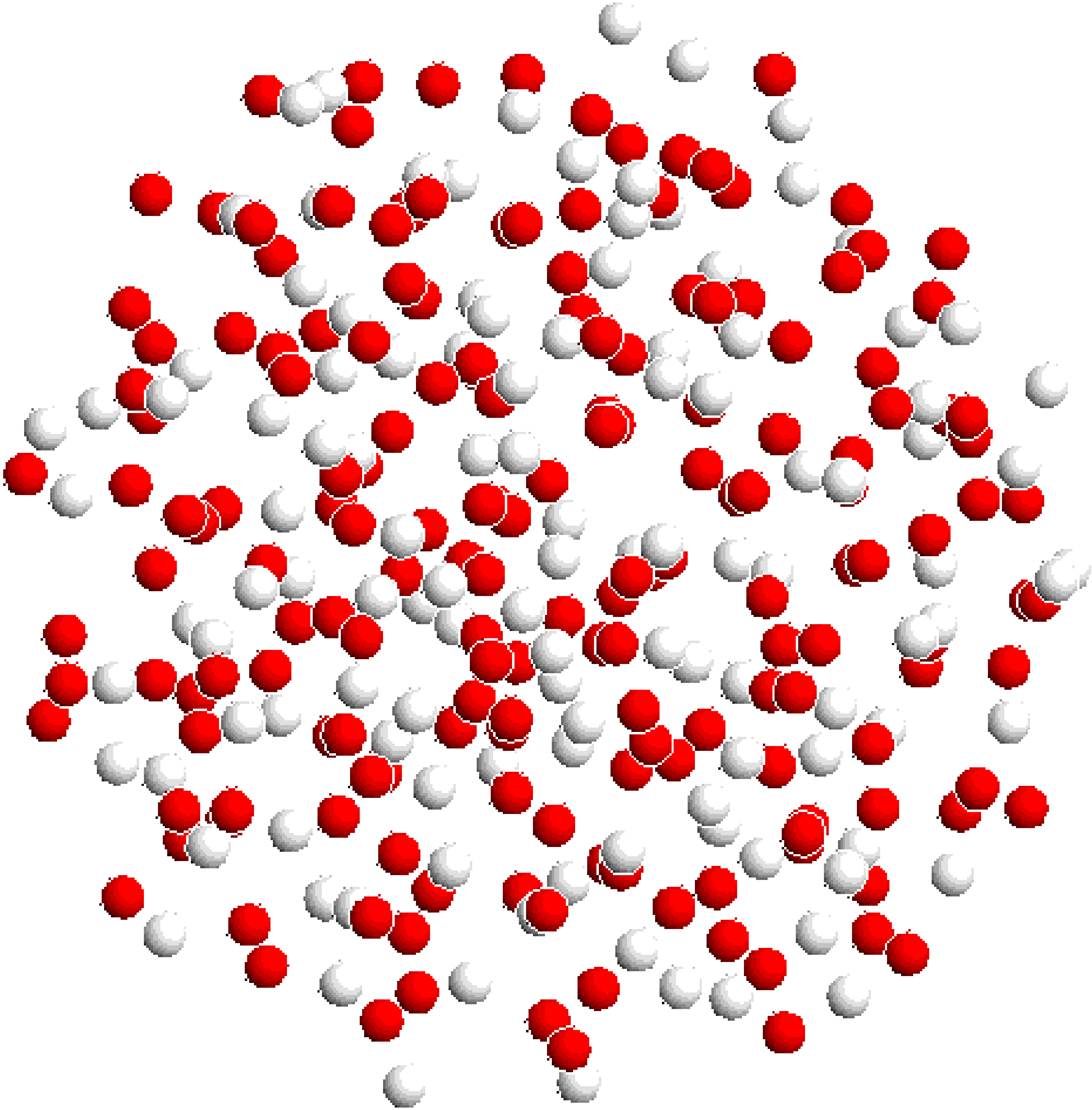
Effect of many body correlations

Many body correlations give rise to the oscillations...

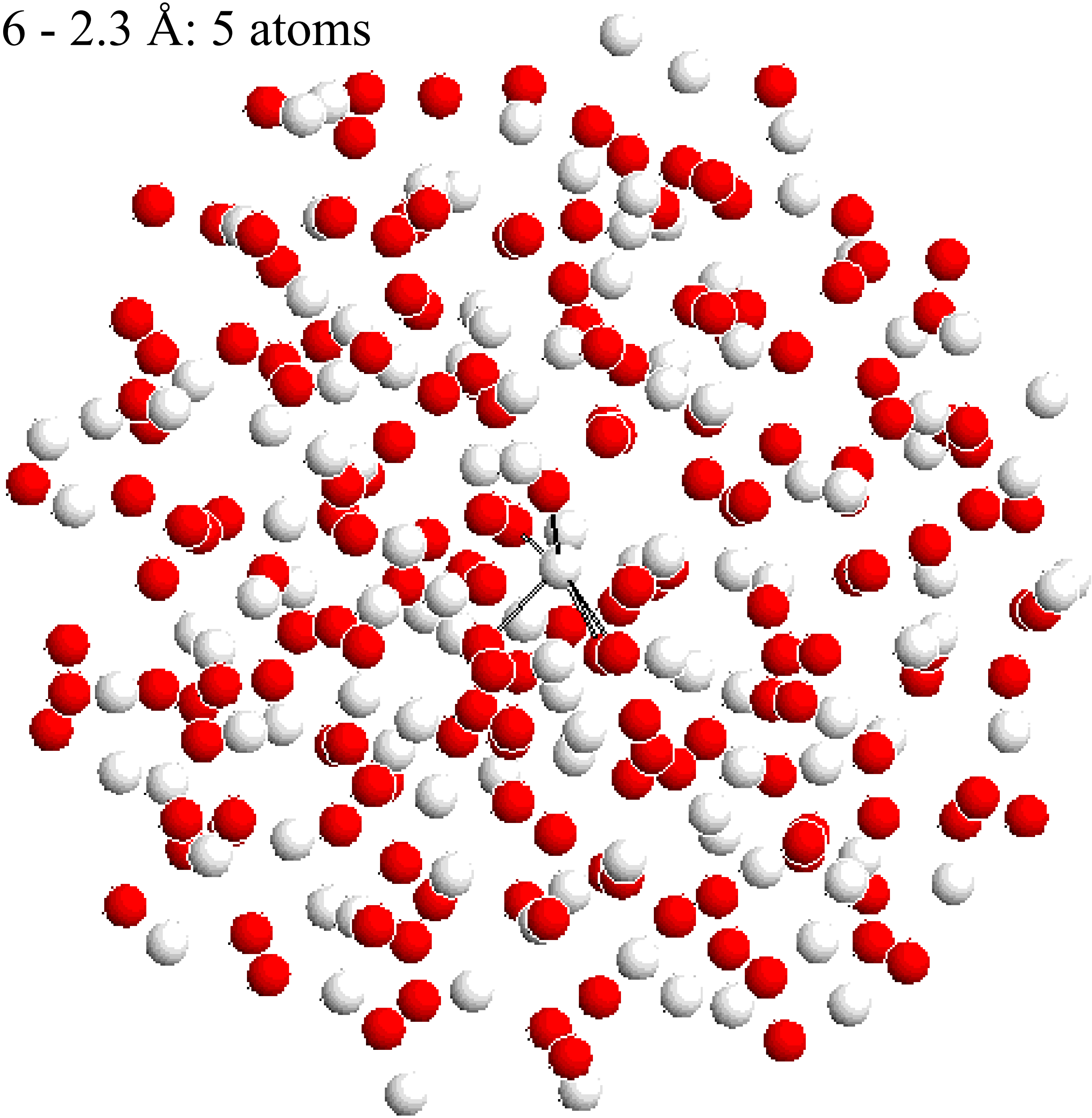
BUT we can’t estimate them without the aid of computer simulation



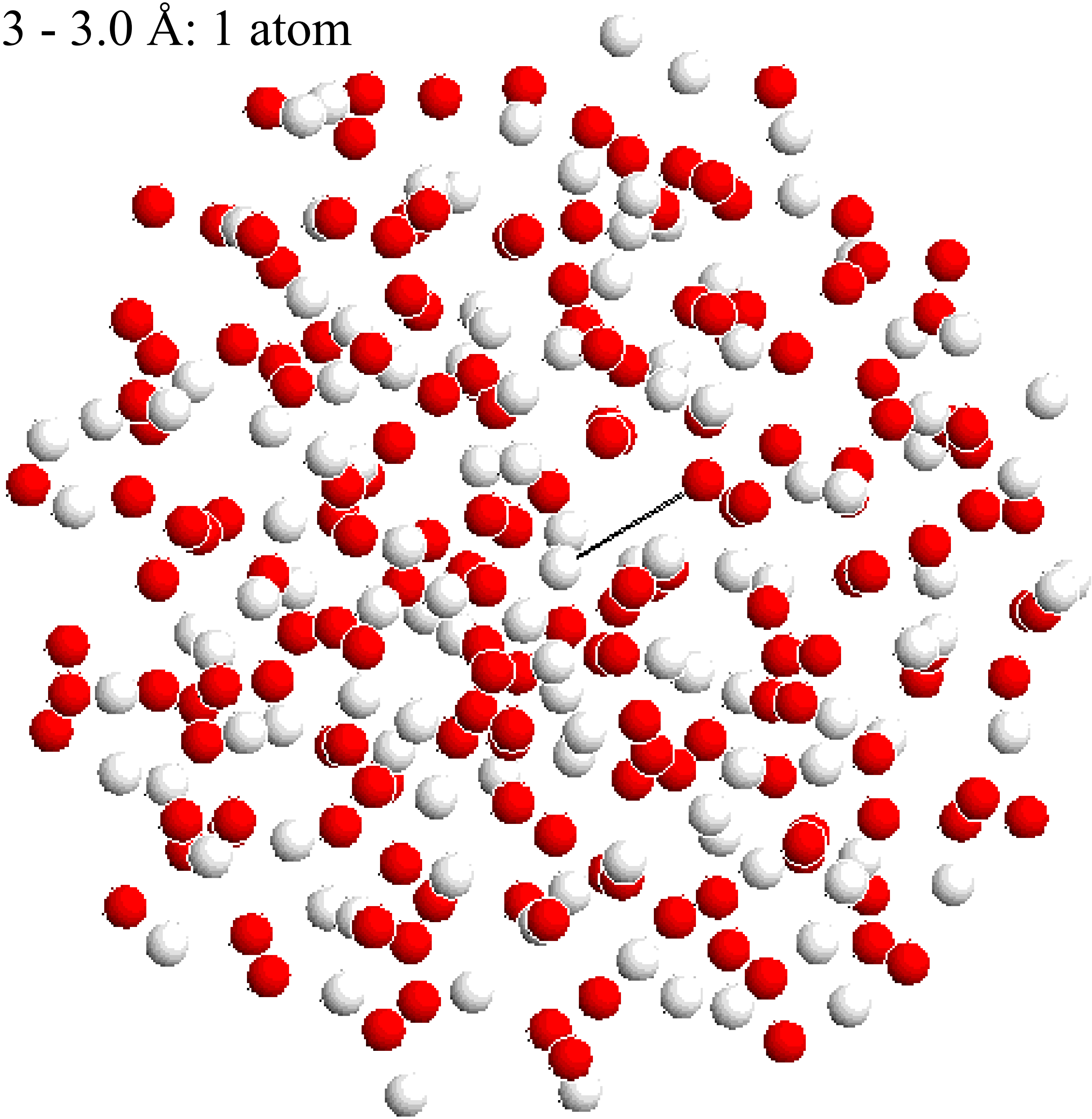
Now consider a 2-component system:



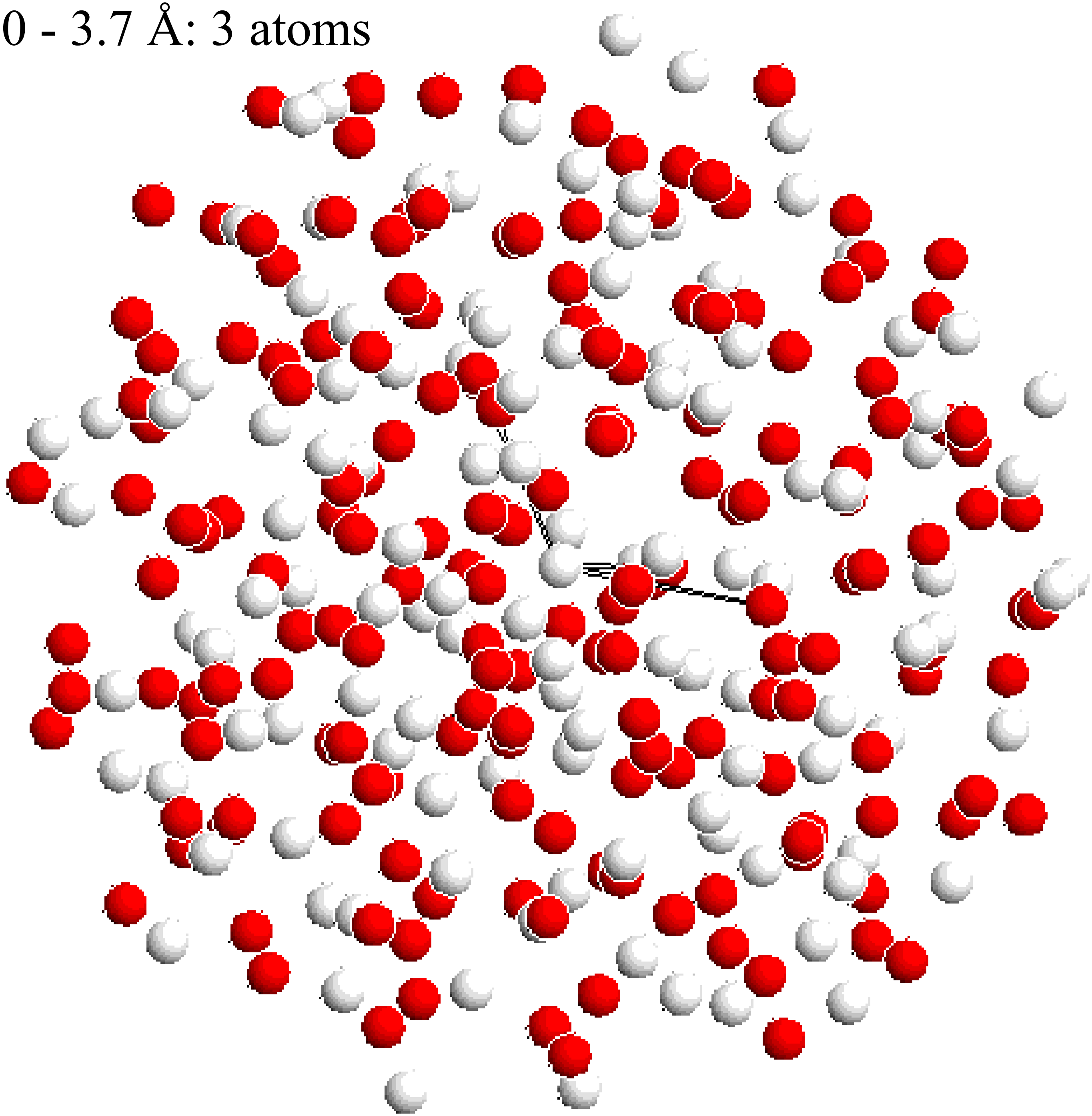
1.6 - 2.3 Å: 5 atoms



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)*

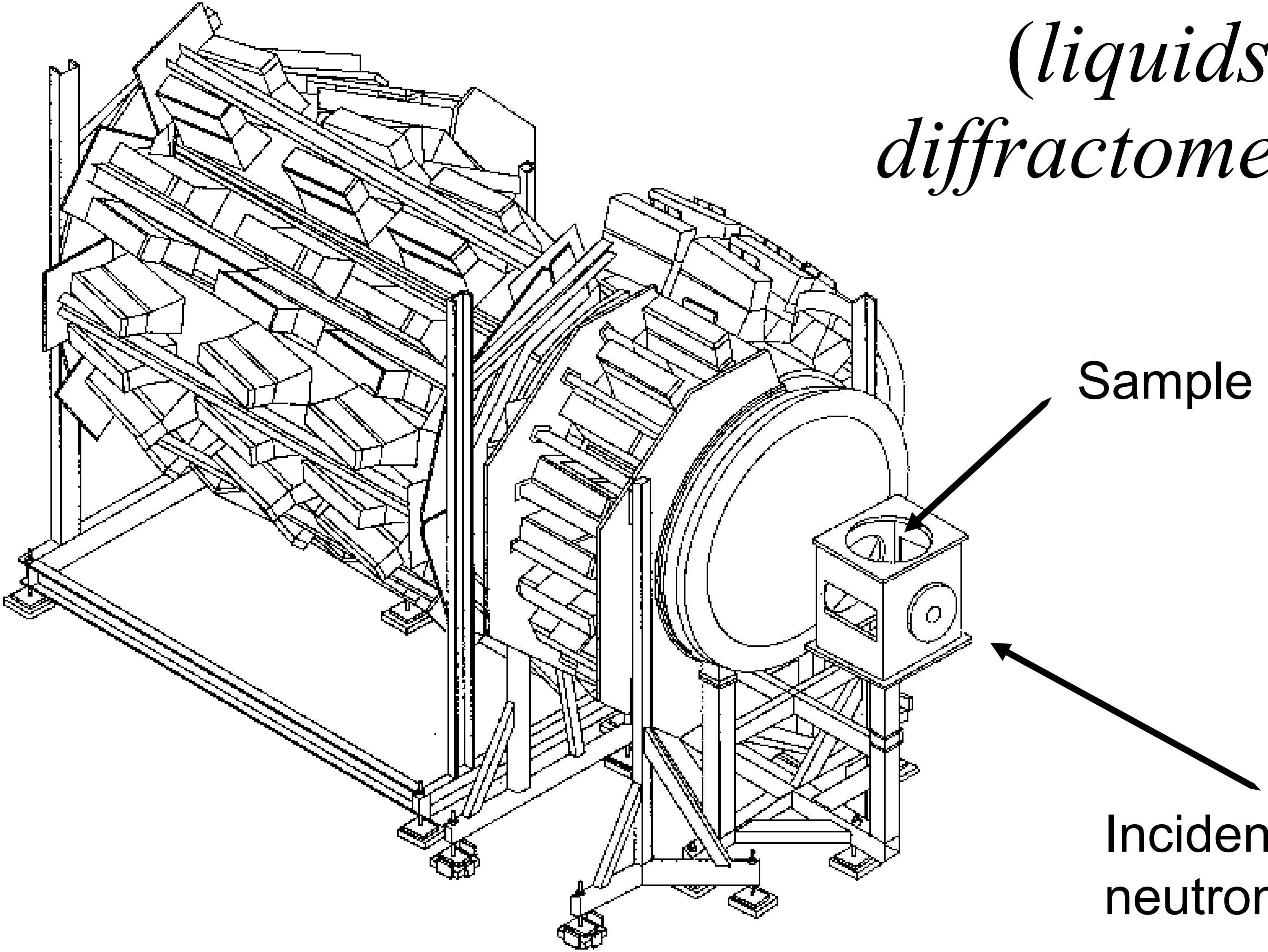
Instead you have to use a diffractometer to do the atom counting.

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!

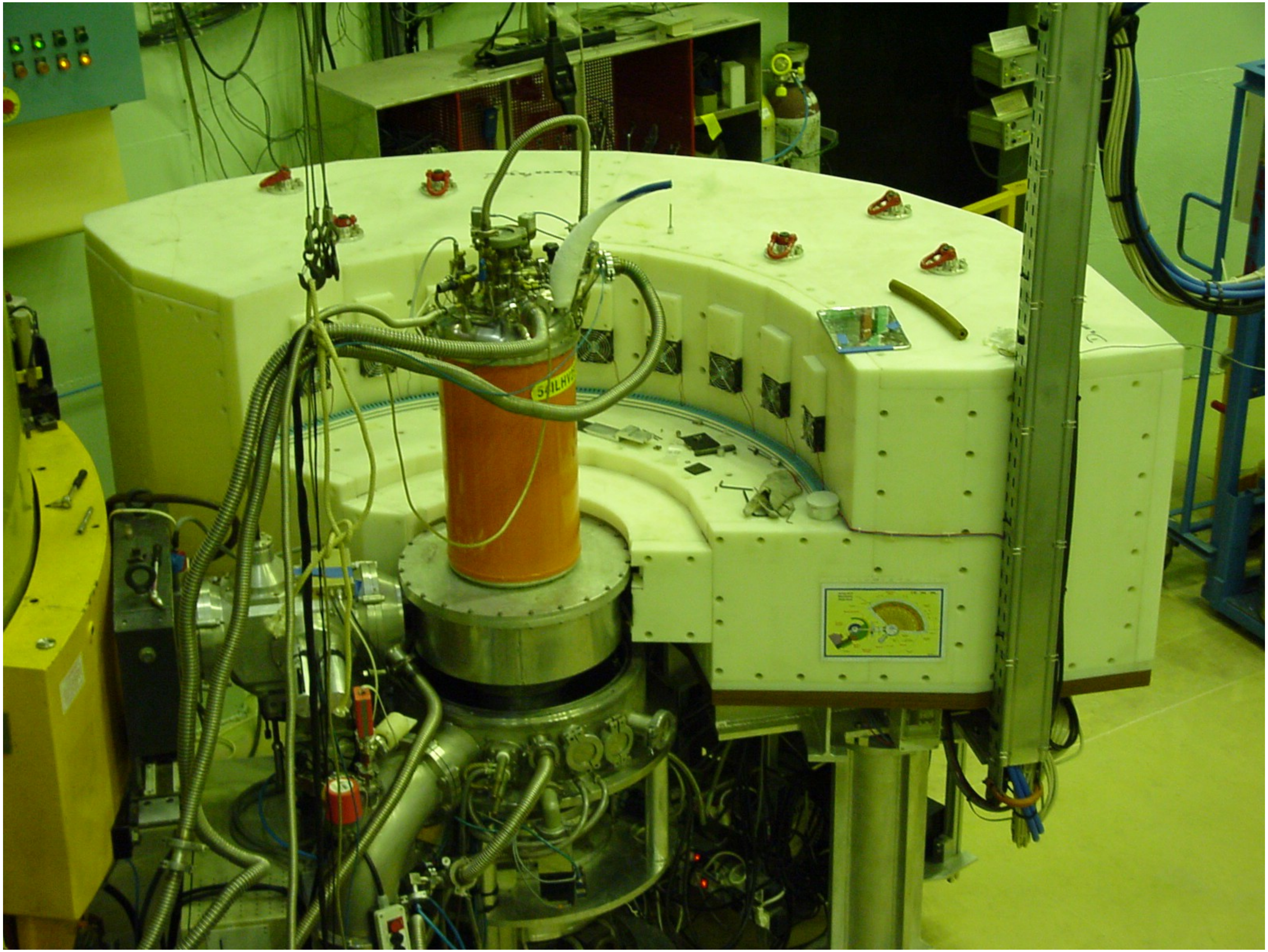
ISIS SANDALS (*liquids diffractometer*)



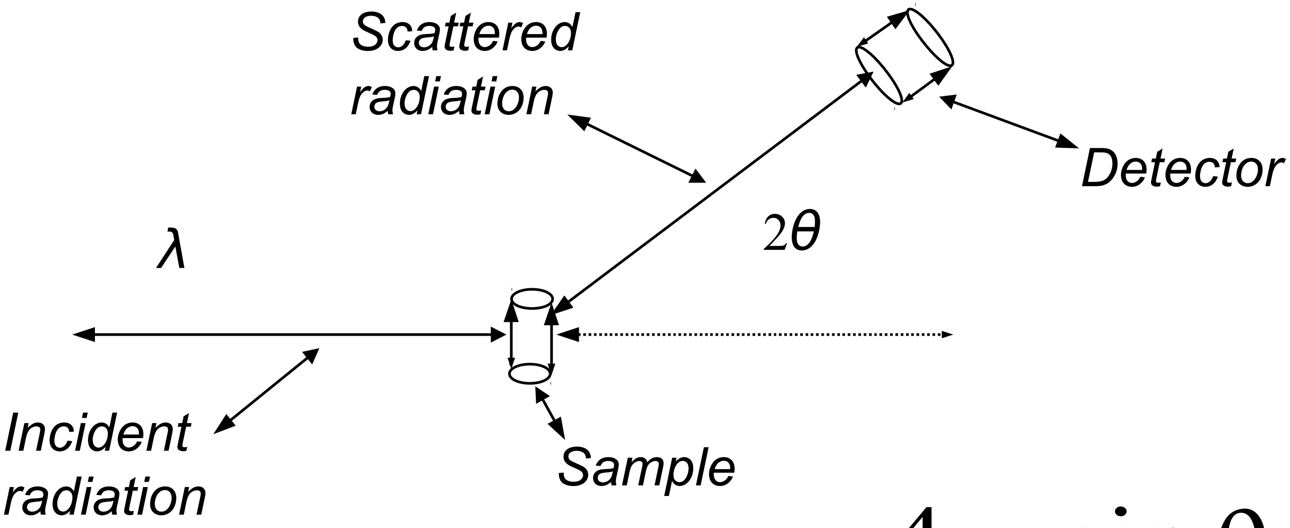
Sample position

Incident
neutron beam

ILL – D4C

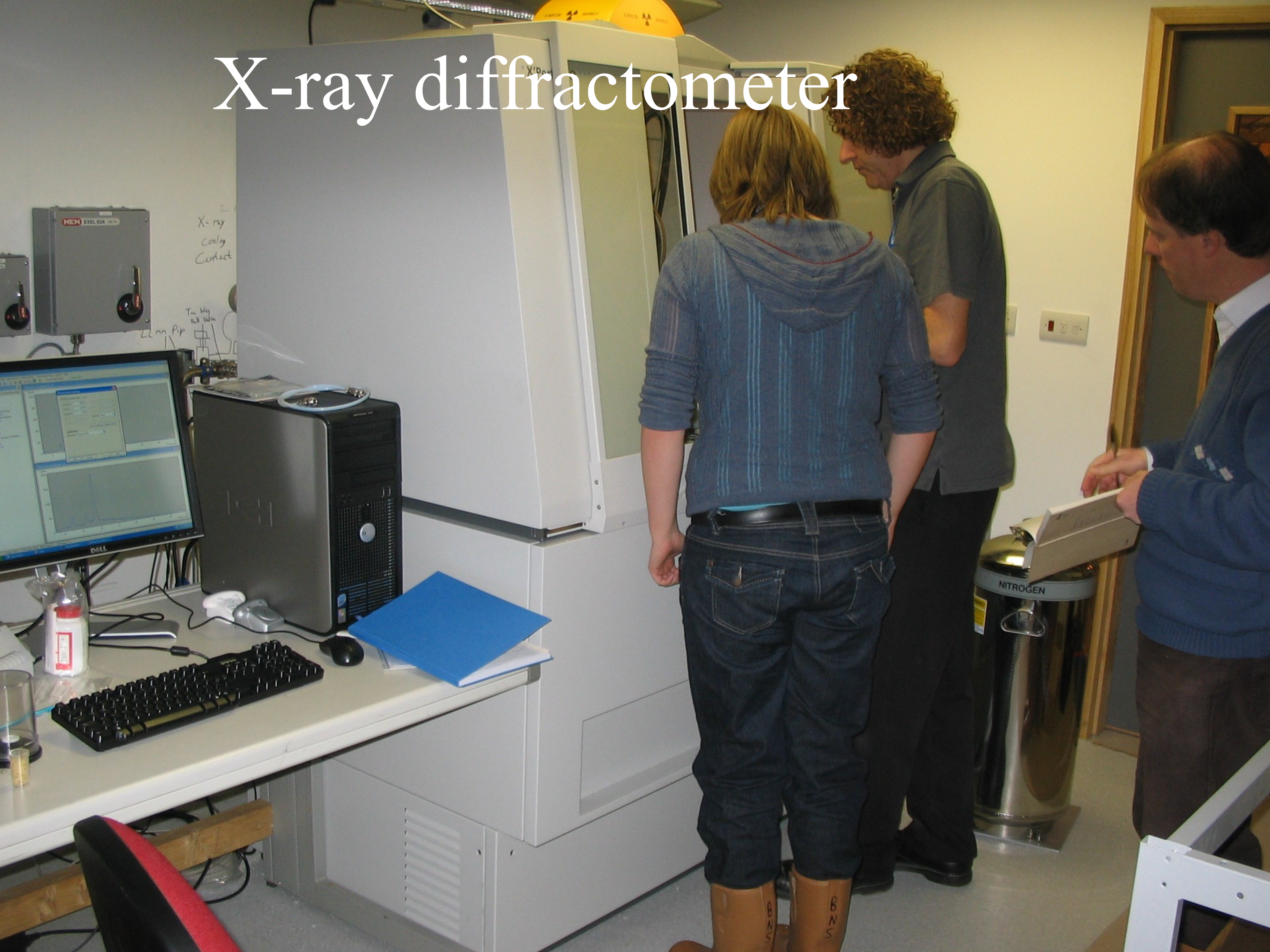


Diffraction from disordered materials - a simple experiment in principle:

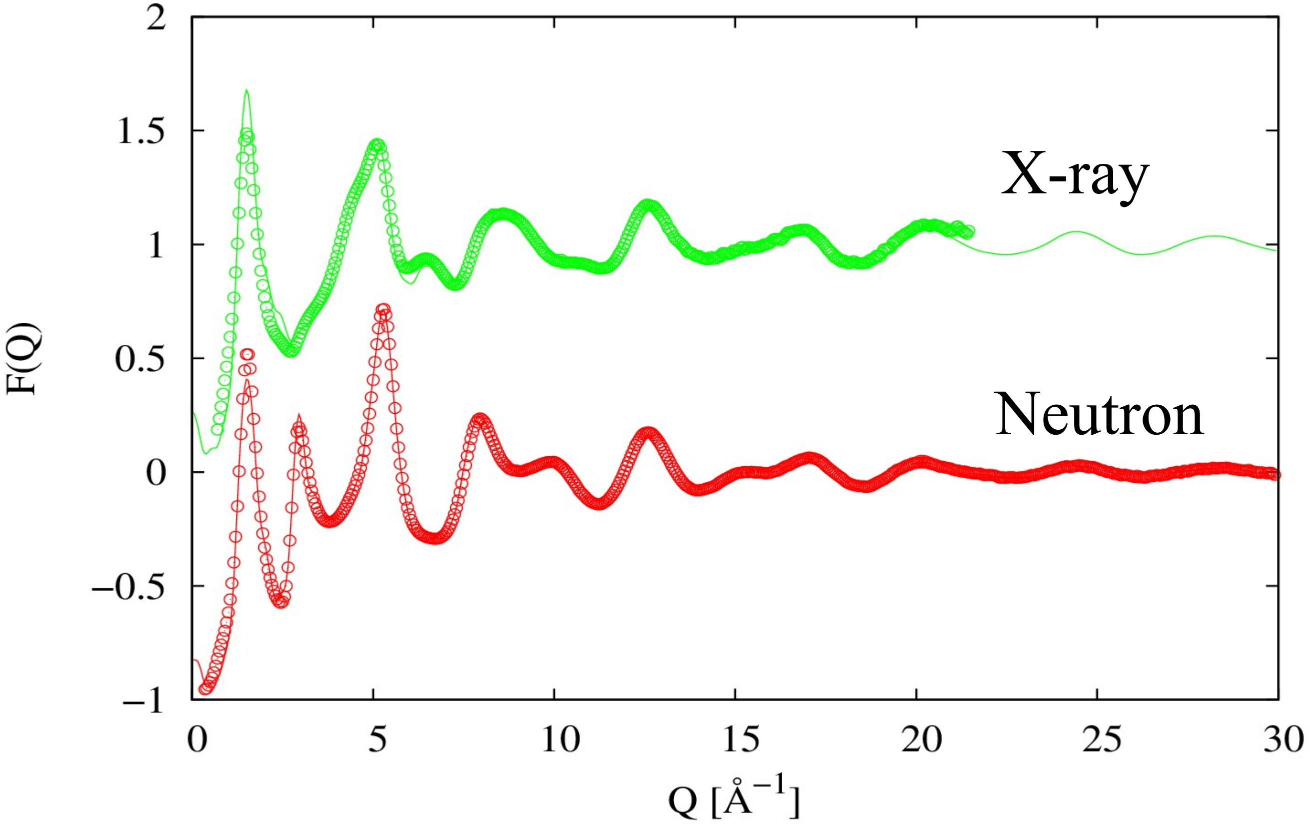


$$Q = \frac{4\pi \sin\theta}{\lambda}$$

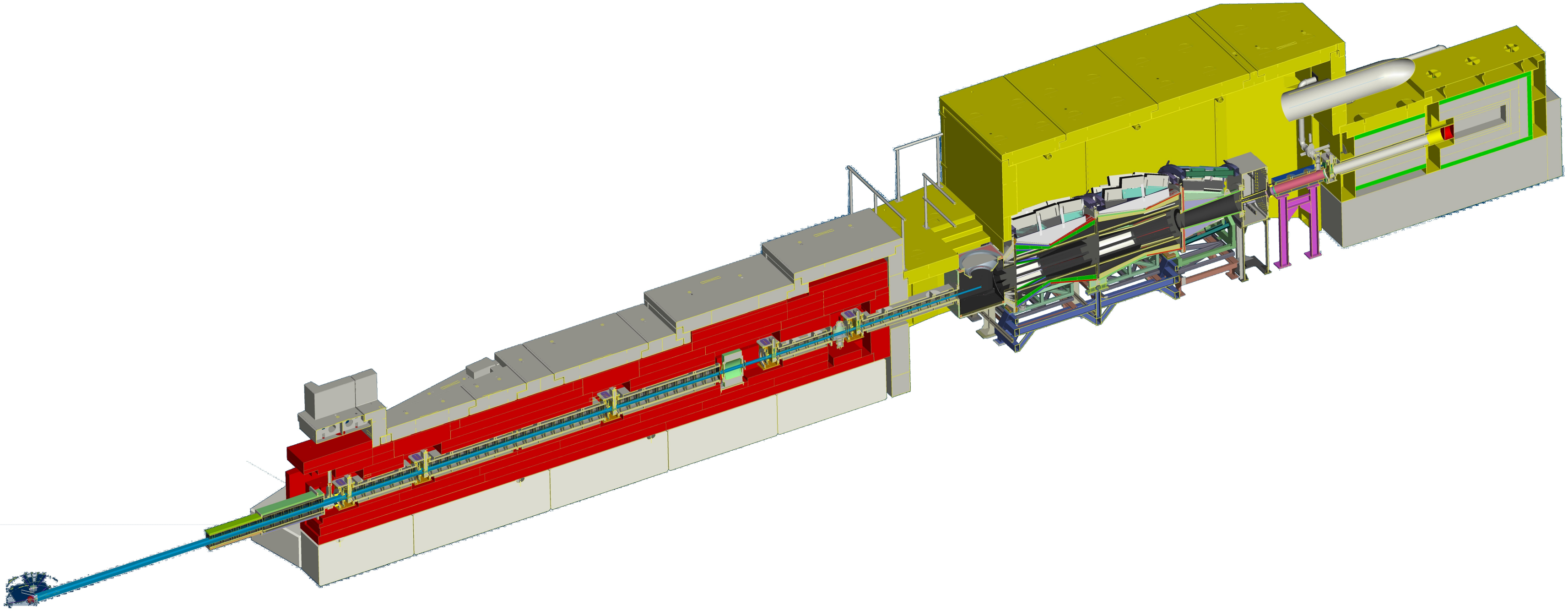
X-ray diffractometer



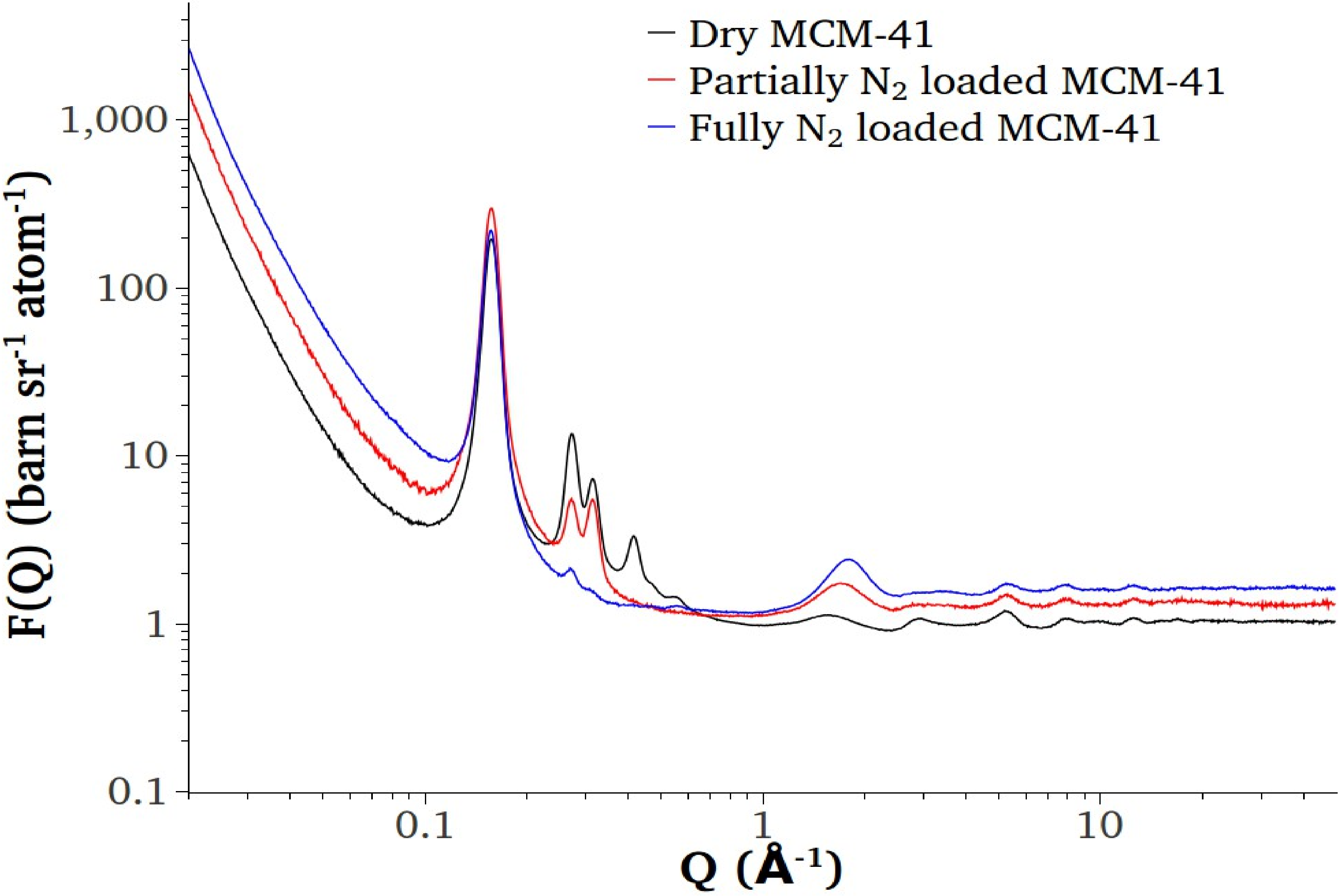
... *gives some data:*



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, $S(Q,\varepsilon)$, 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 :-

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

  - "Instantaneous structure" averaged over positions

- This must be carefully distinguished from the **<u>elastic</u>** structure factor from Bragg scattering

$$S_d(Q,\epsilon=0)\equiv\int S_d(Q,\Delta t)\,d\Delta t$$

  - "Time averaged structure"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Time averaged structure

Sum rules: the “static” structure factor

- For self scattering:-

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

Effect of energy transfer

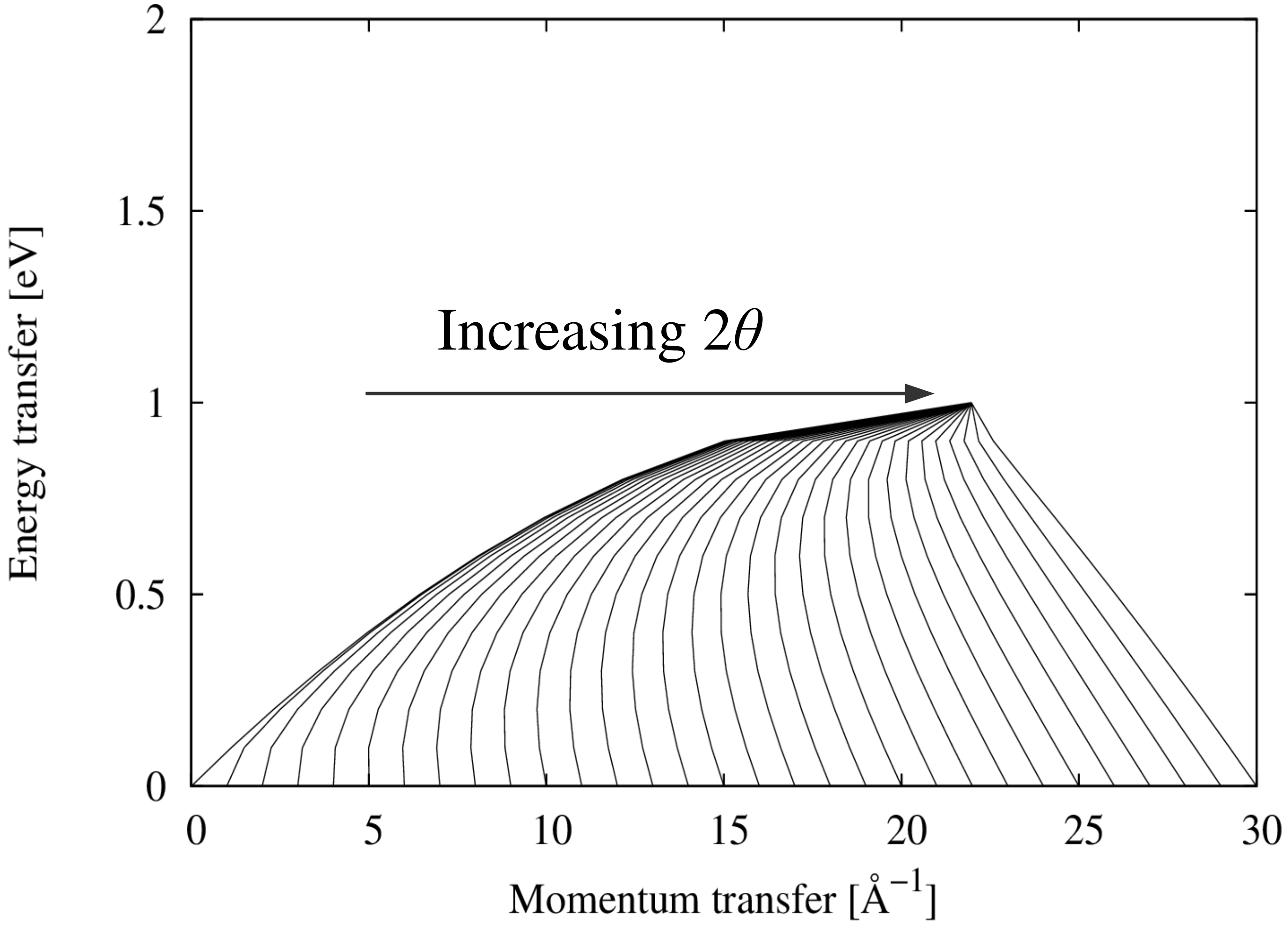
- Kinematics of neutron scattering:-

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

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

- In a diffraction experiment the neutron detector integrates *S(Q,ε)* at constant *θ*, NOT constant *Q*.

Fixed incident energy plot
$E_i = 1eV$



Effect of energy transfer

- For distinct scattering (Placzek, 1952):-

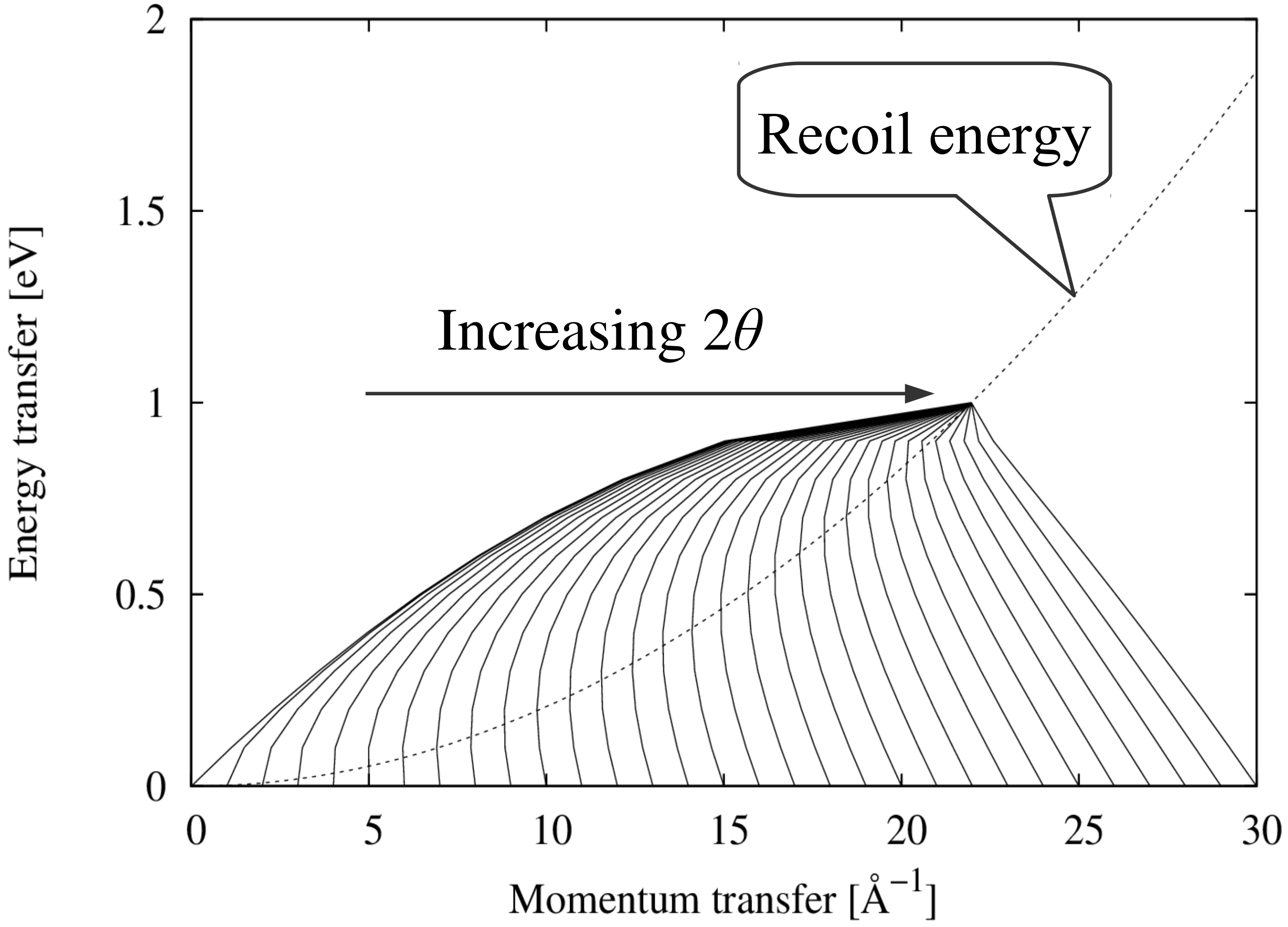
$$\int_Q \epsilon S_d(Q,\epsilon)\, d\epsilon = 0$$

- For self scattering:-

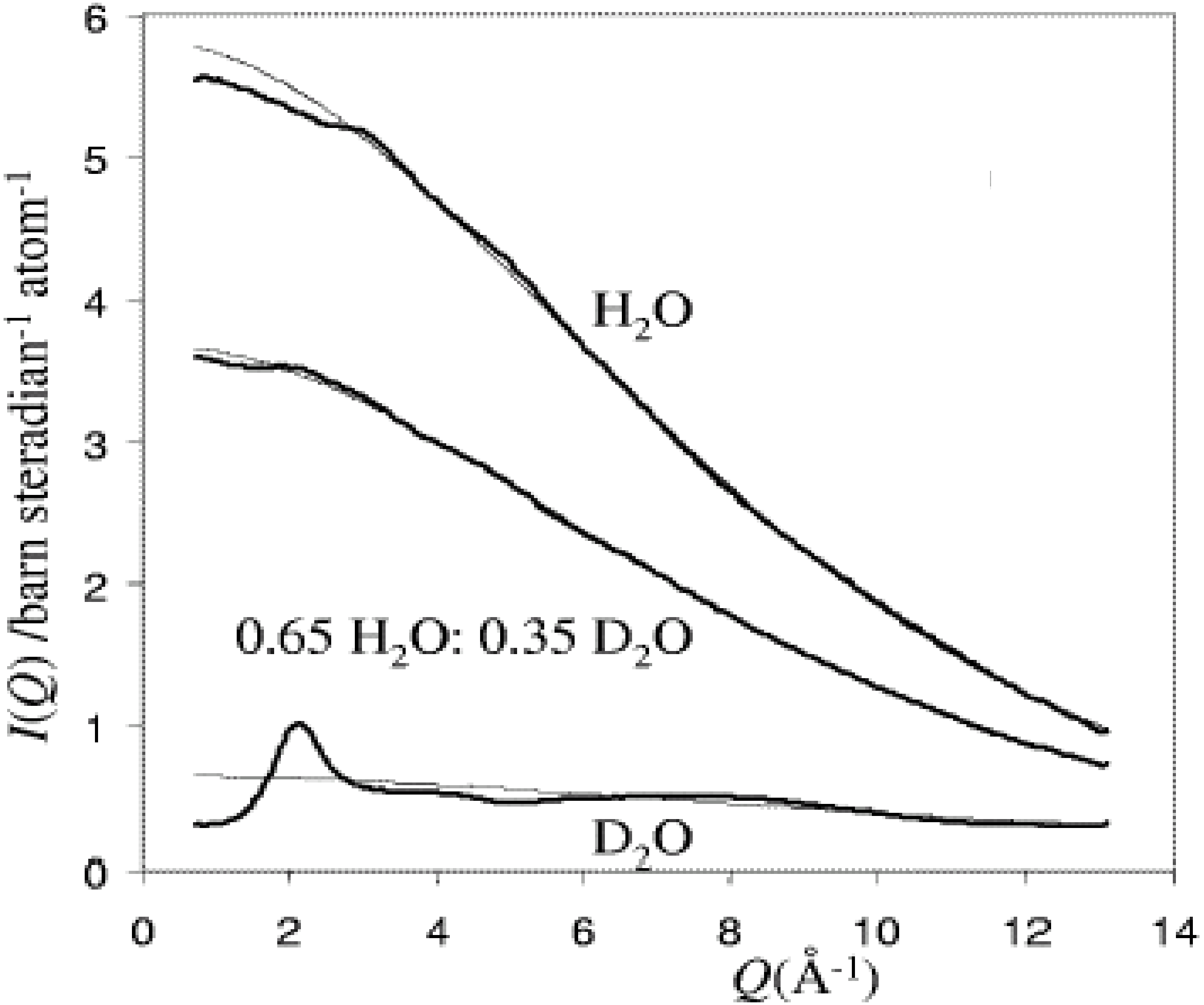
$$\int_Q \epsilon S_s(Q,\epsilon)\, d\epsilon = \frac{\hbar^2 Q^2}{2\mathrm{M}}$$

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

Fixed incident energy plot
E_i = 1eV



Reactor data



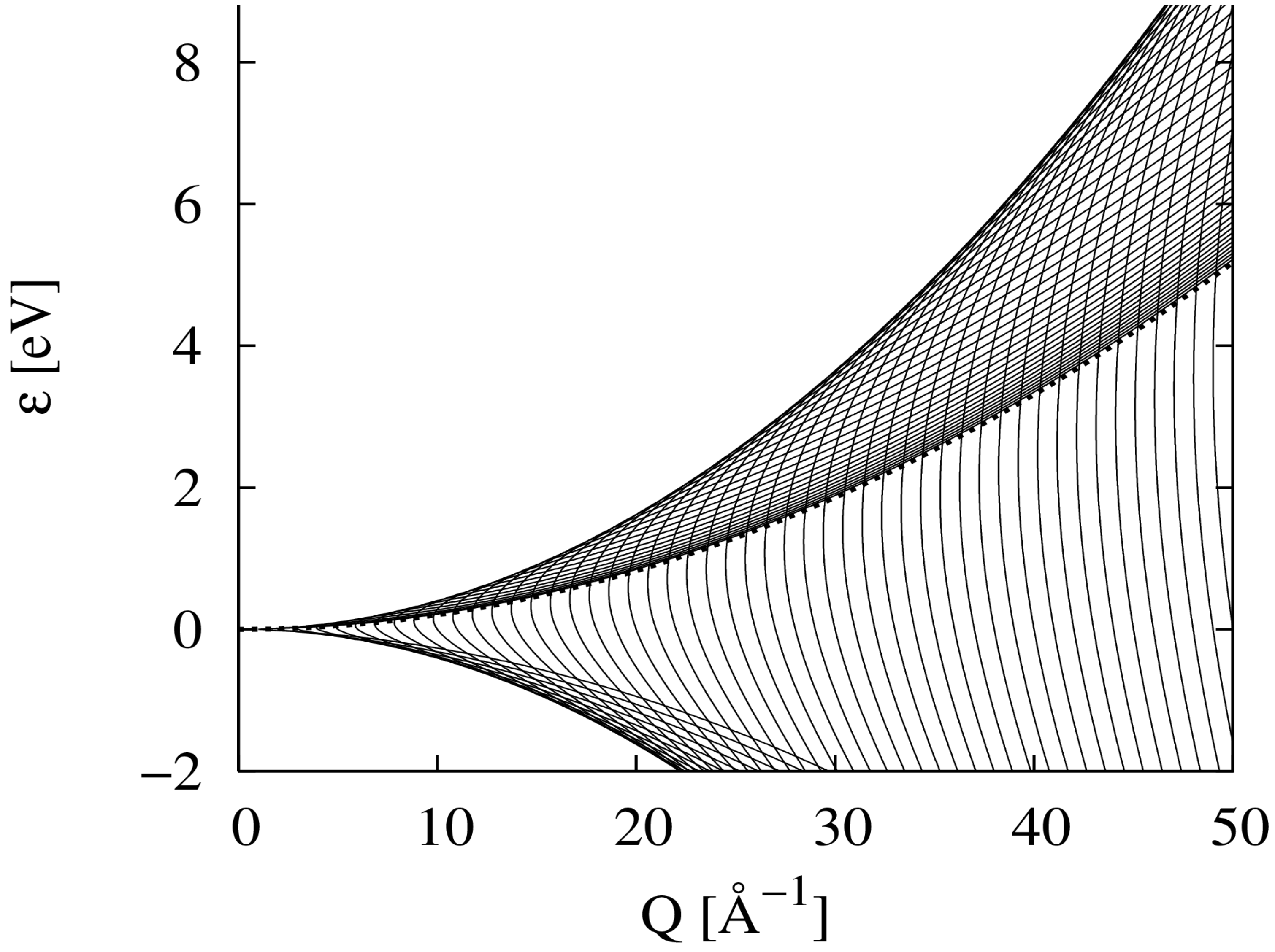
Time of Flight diffraction

- 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:

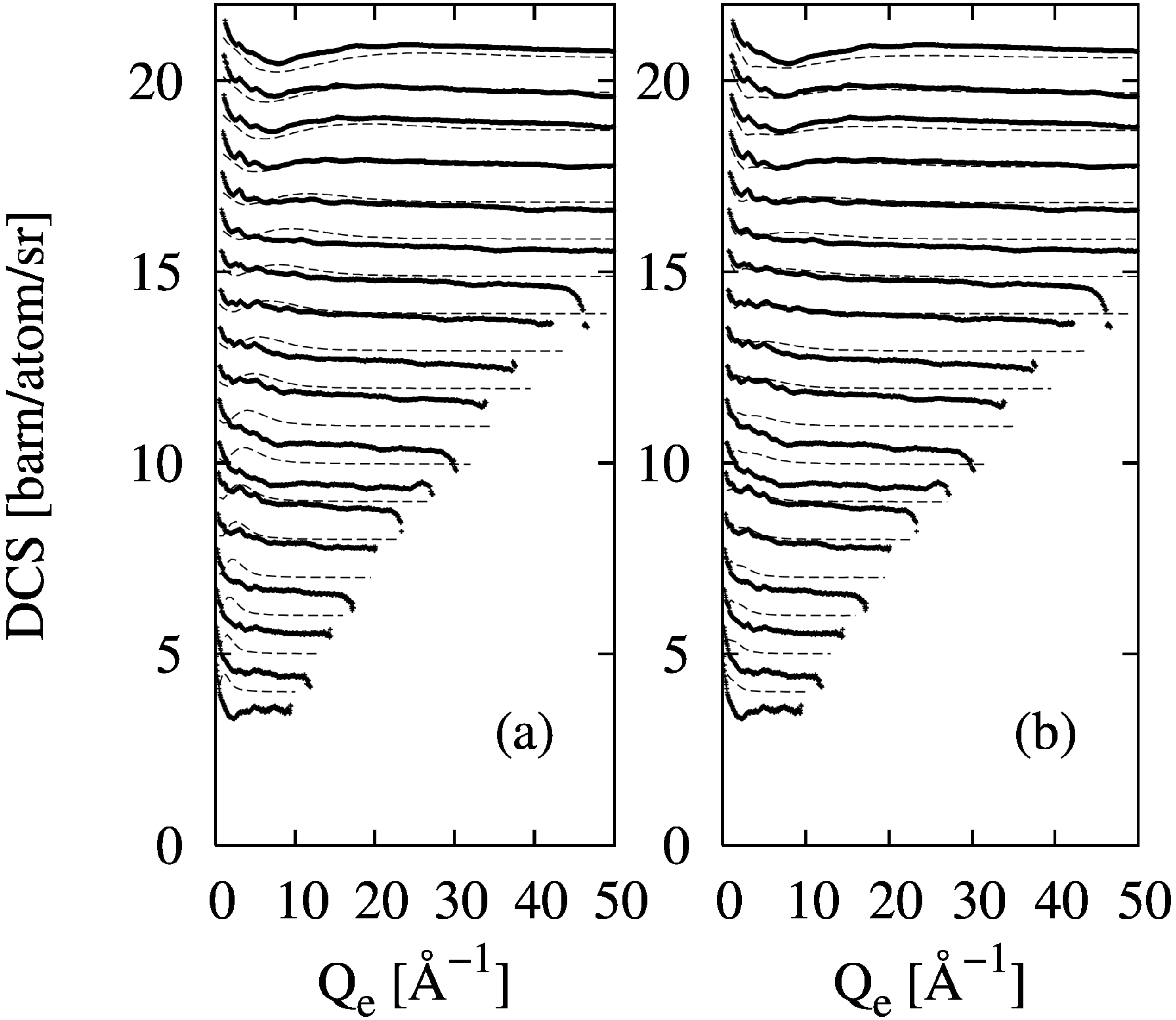
$$\frac{(1+R)}{k_e} = \frac{1}{k_i} + \frac{R}{k_f}, \quad k_e = \frac{Q_e}{2\sin\theta}$$

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, $g_{\alpha\beta}(r)$

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

Atomic fraction of component “α”

The atom scattering factor or “form factor”

A much more tricky question: how do we interpret the data?

- For many years the next step was to simply invert our scattering equation:

$$d(r) = \frac{1}{2\pi^2\rho}\int_0^\infty Q^2 D(Q)\frac{\sin Qr}{Qr}\,dQ$$

$$= \sum_{\alpha,\beta\geq\alpha}\left(2-\delta_{\alpha\beta}\right) c_\alpha c_\beta b_\alpha b_\beta\left(g_{\alpha\beta}(r)-1\right)$$

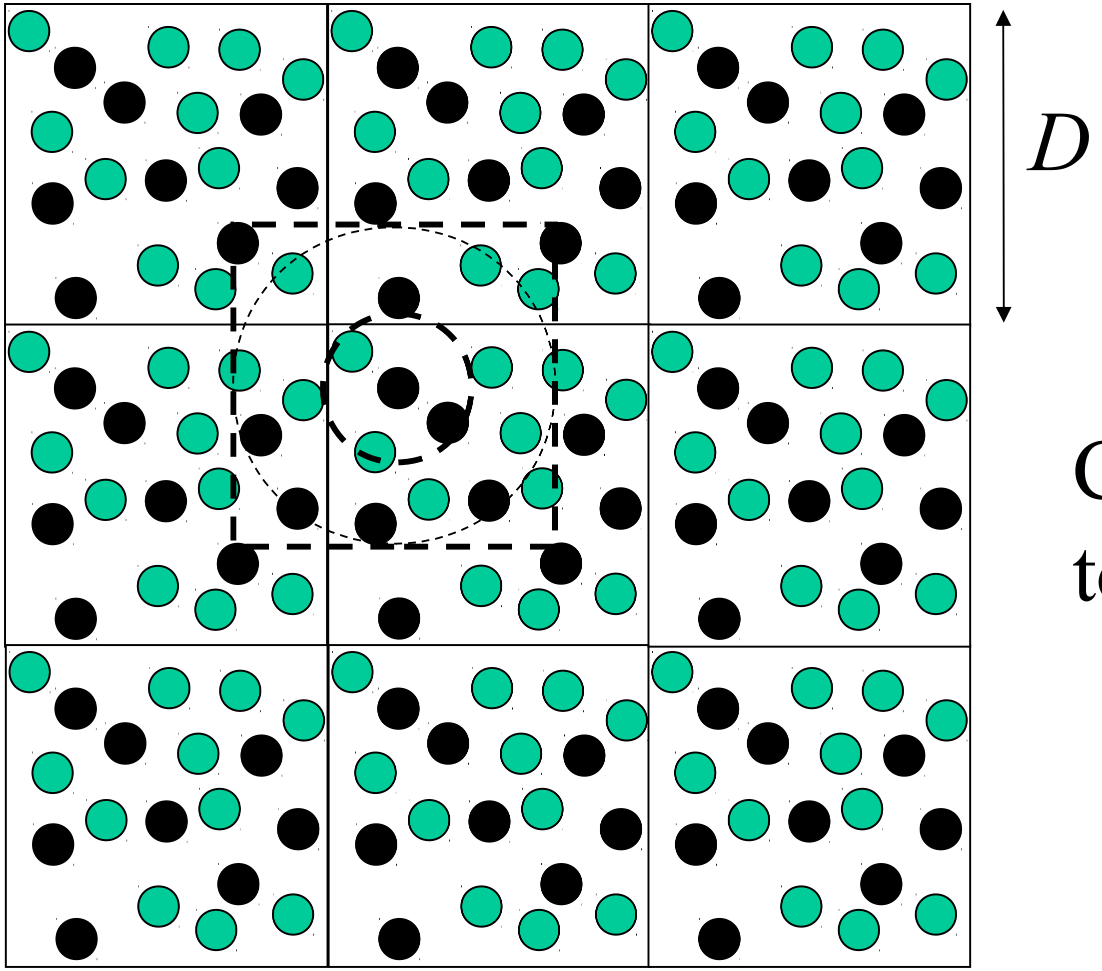
This leads to many problems

- Truncation errors.
- Systematic errors.
- Finite measuring statistics.
- Some site-site terms are more strongly weighted than others.
- These all make interpretation of the data unreliable.
- Radial distribution functions ($g(r)$) do not yield the Orientational Pair Correlation Function (OPCF).

Introduce: computer simulation

- Requires an atom-atom potential energy function.
- Place computer atoms in a (parallelpiped) box at same density as experiment.
- Apply periodic boundary conditions
  - the box repeats itself indefinitely throughout space.
- Apply minimum image convention.

Minimum image convention



Count atoms out to *D/2*

Monte Carlo computer simulation

1. Using the specifed atom-atom potential function, calculate energy of atomic ensemble.
2. Displace one atom or molecule by a random amount in the interval $\pm\delta$.
3. Calculate change in energy of ensemble, ΔU.
4. Always accept move if $\Delta U < 0$
5. If $\Delta U > 0$, accept move with probability $\exp[-\Delta U/kT]$.
6. Go back to 2 and repeat sequence.

But there is a problem:

We don’t know the potential energy function!

Introduce Reverse Monte Carlo, RMC

1. Build a box of atoms as before. Calculate $\chi^2=[D(Q)-F(Q)]^2/\sigma^2$
2. Displace one atom or molecule by a random amount in the interval ±δ.
3. Calculate change in χ^2 of ensemble, $\Delta\chi^2$.
4. Always accept move if $\Delta \chi^2 < 0$
5. If $\Delta \chi^2 > 0$, accept move with probability $\exp[- \Delta \chi^2]$.
6. Go back to 2 and repeat sequence.

Introduce Empirical Potential Structure Refinement, EPSR

- Use harmonic constraints to define molecules.
- Use an existing “reference” potential for the material in question taken from the literature (or generate your own if one does not exist).
- Use the diffraction data to perturb this reference potential, so that the simulated structure factor looks like the measured data.

Introducing the data

$$F(Q) = \sum_{\alpha, \beta \geq \alpha} \boxed{(2 - \delta_{\alpha\beta})\, c_\alpha c_\beta b_\alpha b_\beta} H_{\alpha\beta}(Q)$$

- *M* measured datasets, *N* partial structure factors: (Usually $M < N$)
- Assign a “feedback” factor *f* for the data:

$$w'_{ij} = f w_{ij}, \quad 1 \leq i \leq M$$

- and (1 – *f*) for the simulation:

$$w'_{ij} = (1 - f)\, \delta_{(i-M),j}, \quad M < i \leq M + N$$

- Form inversion of

$$w'_{ij}, \; 1 \leq i \leq M + N, \; 1 \leq j \leq N$$

Refining the potential: M datasets, N partial structure factors

$$F_{i(=1,M+N)}(Q) = \begin{array}{r|cccccccccc|}
 & fw_{11} & fw_{12} & \cdots & & & & & & \cdots & fw_{1N} \\
\text{Data} & fw_{21} & fw_{22} & \cdots & & & & & & \cdots & fw_{2N} \\
 & \cdots & \cdots & & & & & & & & \cdots \\
 & \cdots & \cdots & & & & & & & & \cdots \\
 & fw_{M1} & fw_{M2} & & & & & & & & fw_{MN} \\
 & (1-f) & 0.0 & 0.0 & \cdots & & & & & \cdots & 0.0 \\
 & 0.0 & (1-f) & 0.0 & \cdots & & & & & \cdots & \cdots \\
 & 0.0 & 0.0 & (1-f) & \cdots & & & & & & \\
 & \cdots & \cdots & \cdots & \cdots & & & & & & \\
 & & & & & \cdots & & & & & \\
 & & & & & & \cdots & & & & \\
\text{Simulation} & & & & & & & \cdots & \cdots & \cdots & \cdots \\
 & \cdots & & & & & & \cdots & (1-f) & 0.0 & 0.0 \\
 & \cdots & \cdots & & & & & \cdots & 0.0 & (1-f) & 0.0 \\
 & 0.0 & \cdots & \cdots & & & & \cdots & 0.0 & 0.0 & (1-f)
\end{array} \times \begin{bmatrix} S_1 \\ S_2 \\ \cdots \\ \\ \\ \\ \cdots \\ S_N \end{bmatrix}$$

$$\Delta U_j(r) = \text{Fourier Transform of} \left\{ \sum_{i=1,M} w'^{-1}_{ij} \left(D_i(Q) - F_i(Q) \right) \right\}, \quad j = 1, N$$

Summary of Lecture I

- Widespread occurrence of disordered systems (macroscopic as well as microscopic).
- Concept of correlation in disordered systems.
- Use radial distribution function (PDF) to characterise the correlations in a disordered system.
- Use diffraction to count atoms as a function of distance.
- Given some diffraction data, what is the atomic arrangement?
  - Introduce computer simulation.

Summary of lecture II

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