Disordered Materials:

Lecture I

Concepts of disorder:

How we quantify it

and

How we measure it

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Disordered Materials Group

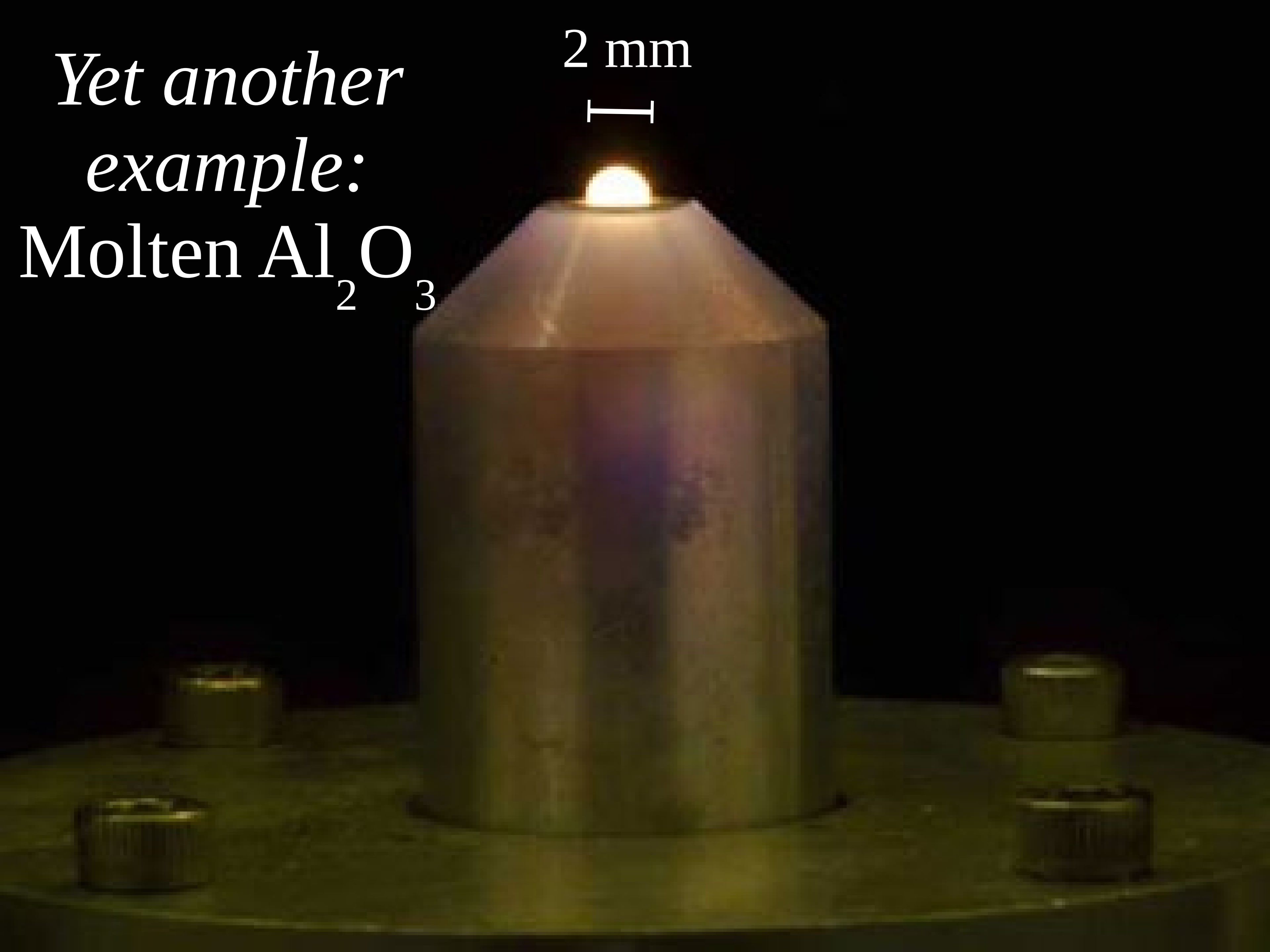
ISIS

A well known example of disorder…

And another…

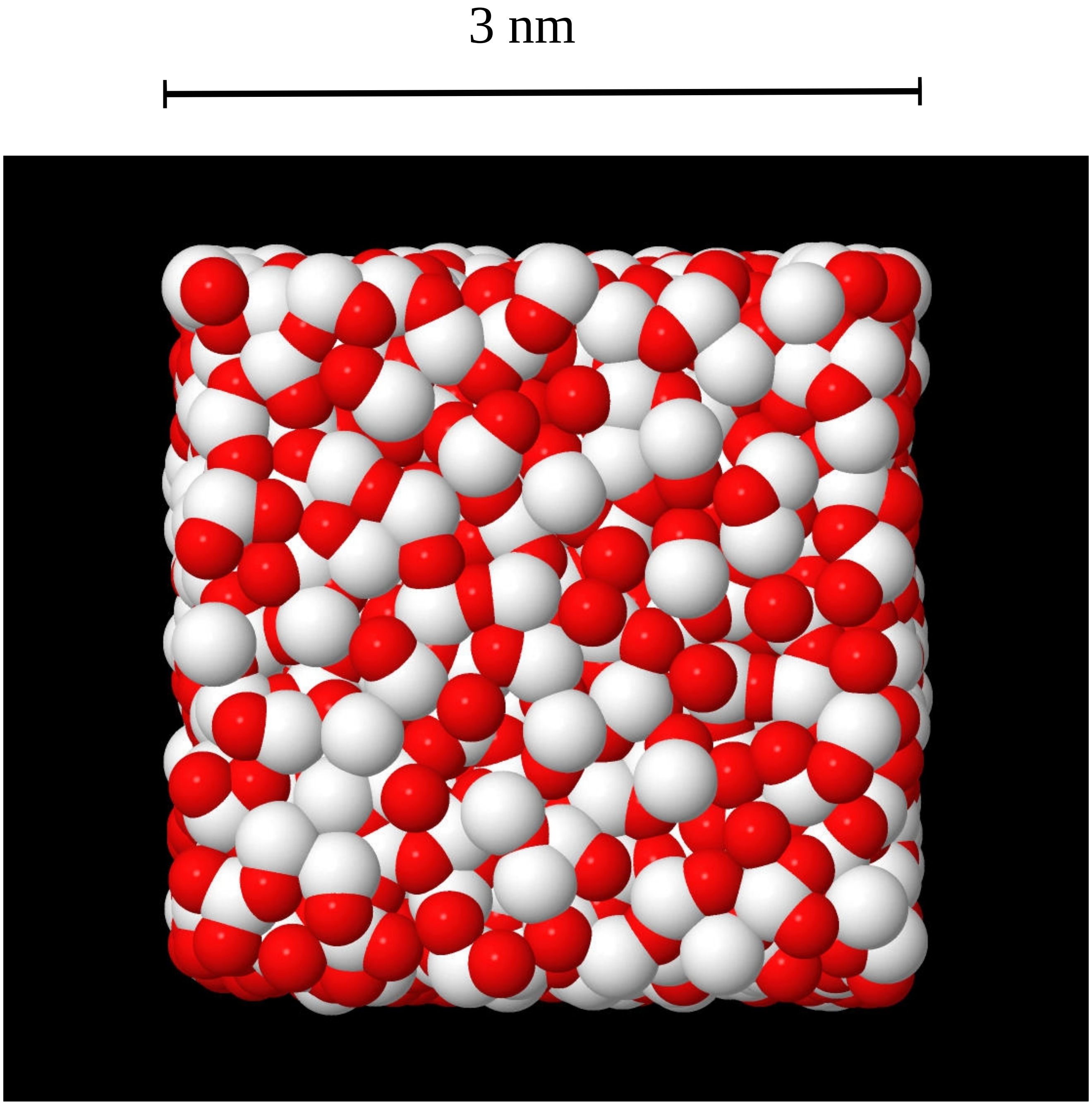
A yet another example of disorder…

Yet another example: Molten Al_2O_3



Molten Al_2O_3

(Atomistic simulation 2500 atoms)



Disorder affects us in many different ways…

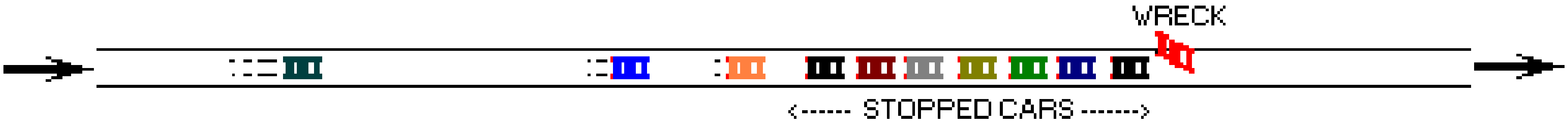
- Congestion in shopping centres, etc.
- Traffic jams
- Sand, shingle and earth piles
- Avalanches
- Blood clots
- …
- Gases, liquids and glasses

What is common to all these examples?

Answer…

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

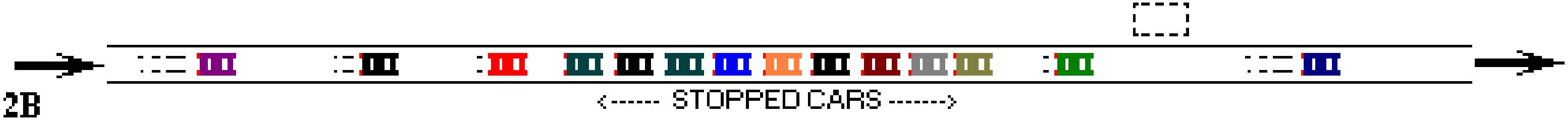
Traffic jam correlations



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


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

2A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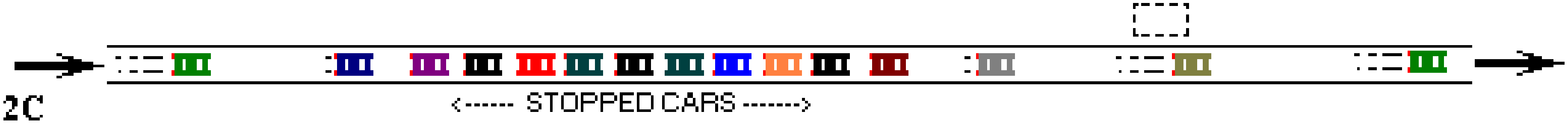
2B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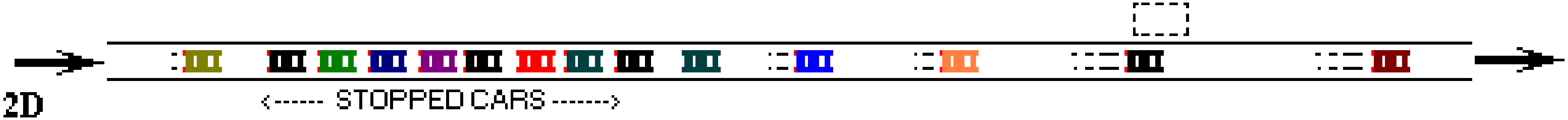
2C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2D

What are the fundamental requirements for disordered correlation to occur?

- Some attractive forces…
- Some repulsive forces…
- High packing fractions.
- Random positions.

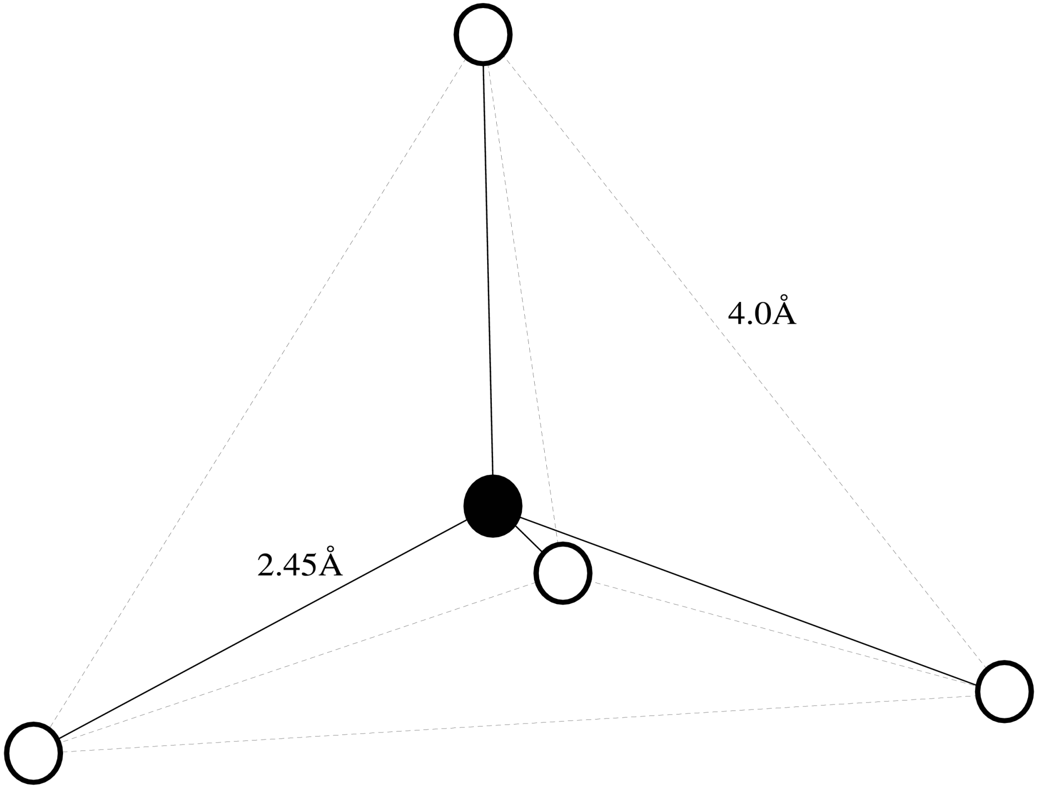
Disordered materials can be classified as: "Atom jams with marked positional correlations."

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.

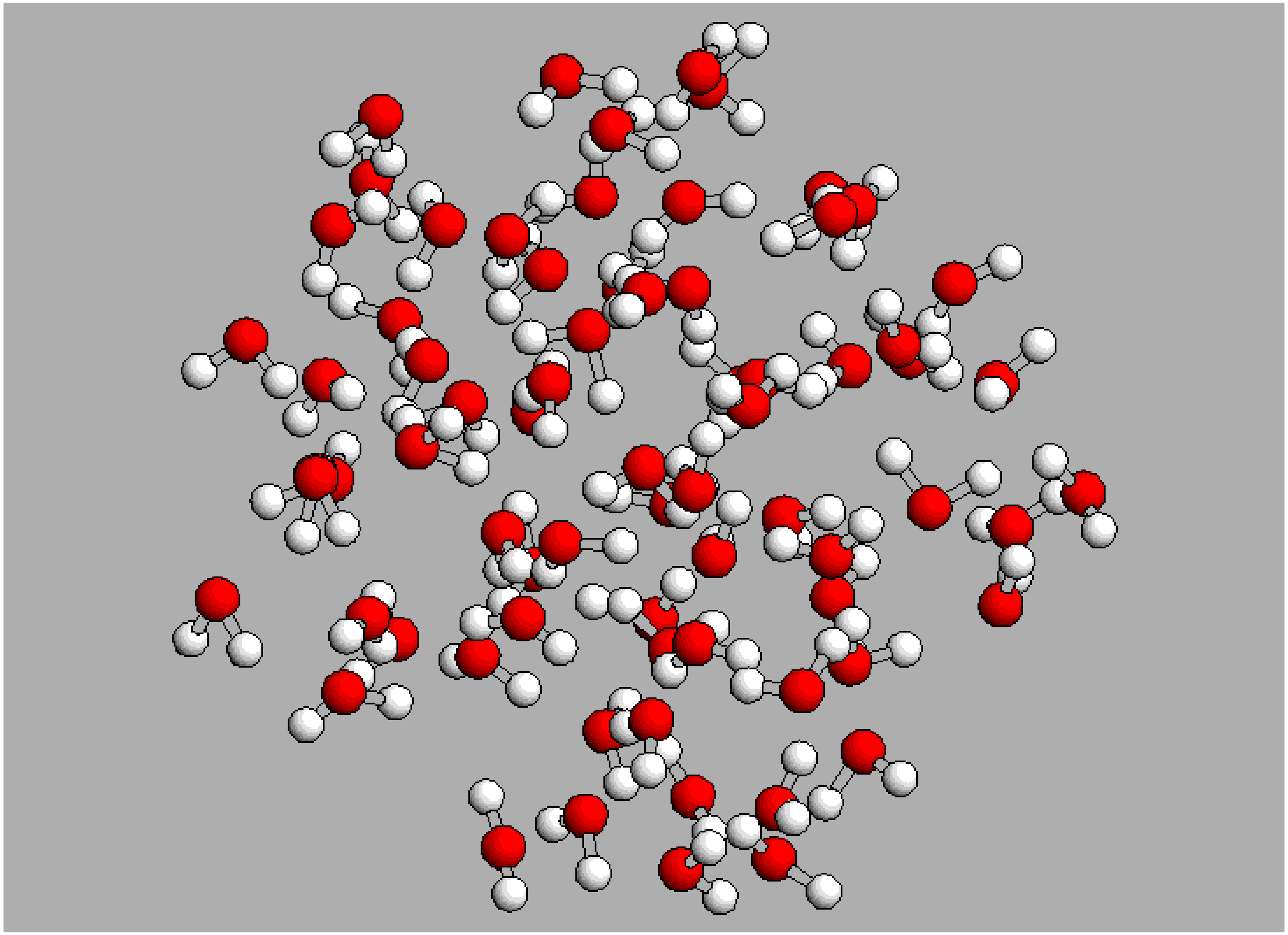
In reality not quite so simple…



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

Another common liquid, water…

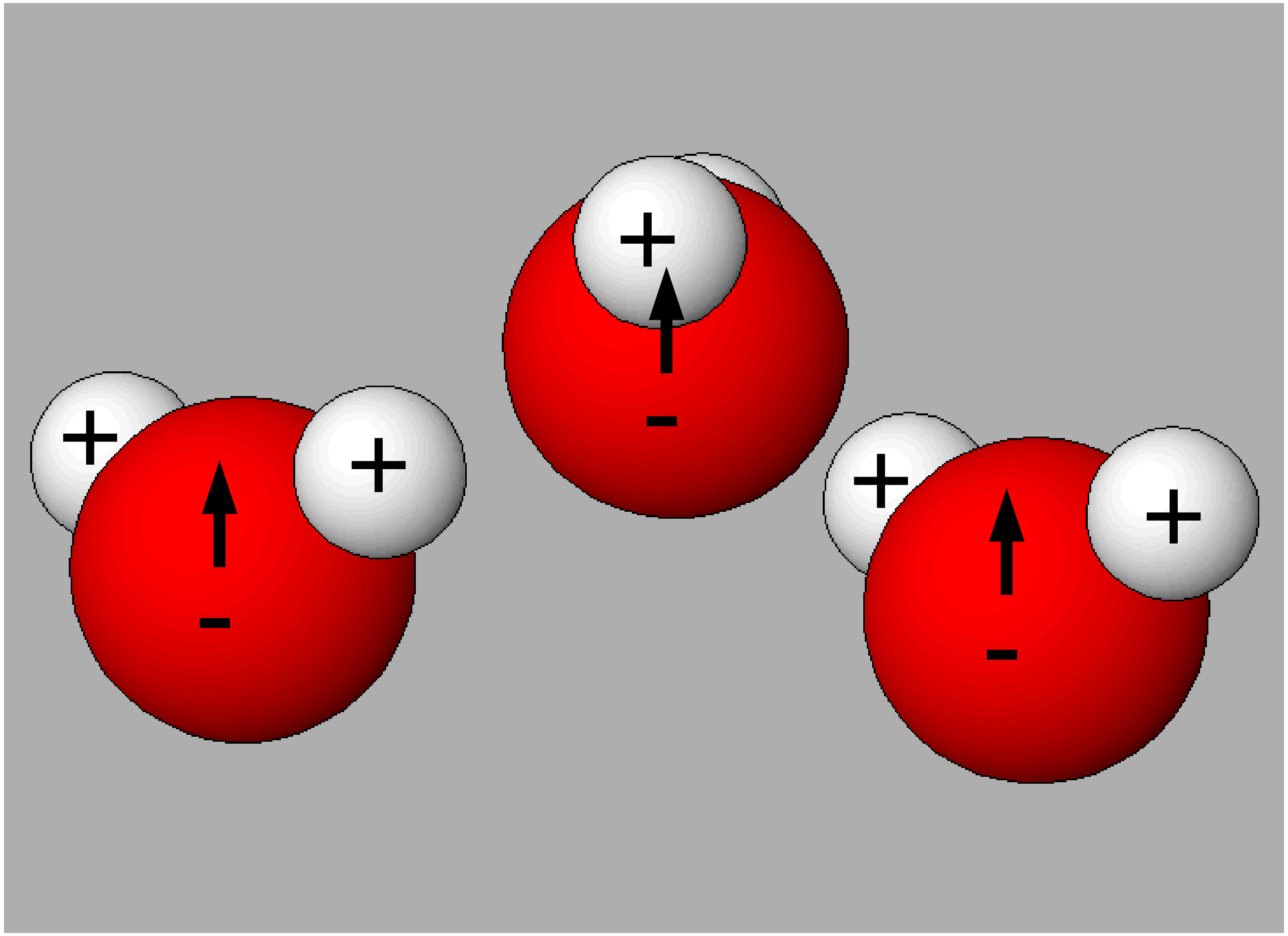
Atomistically this material looks like this:-



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 that when 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!).*
- *Where does this heat come from?*

The water molecule

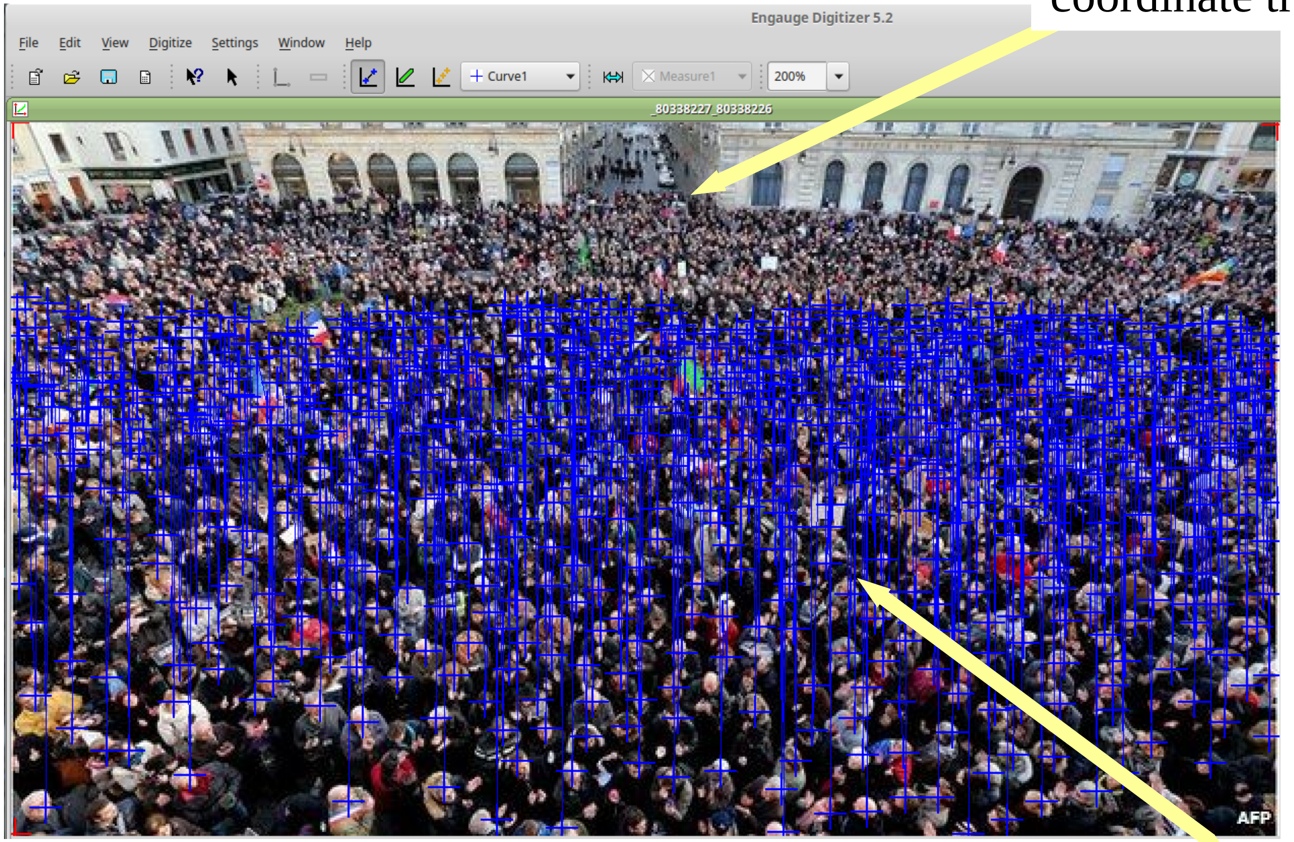


So how do you characterise structure in a disordered system?

By counting.

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

Let's examine the crowd picture once more:

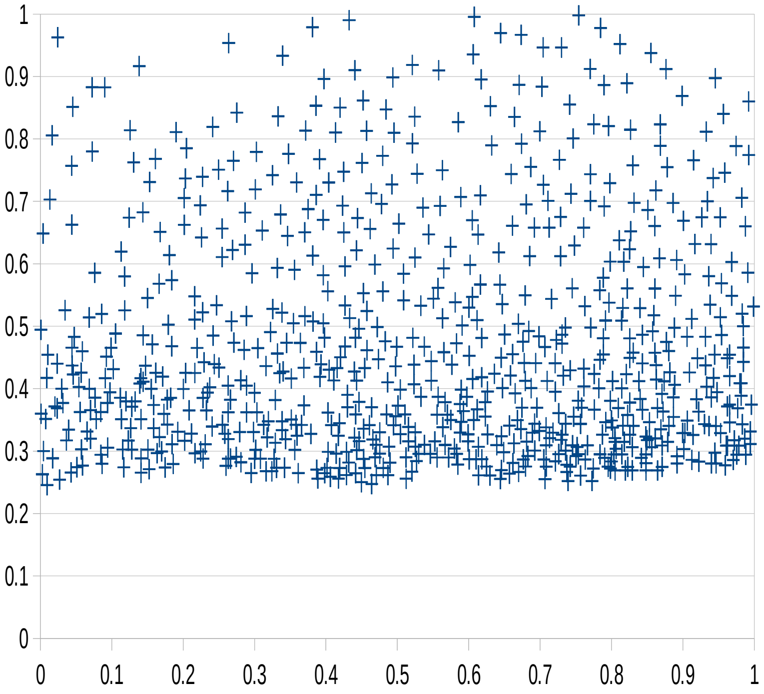


Use street to calibrate coordinate transformation.

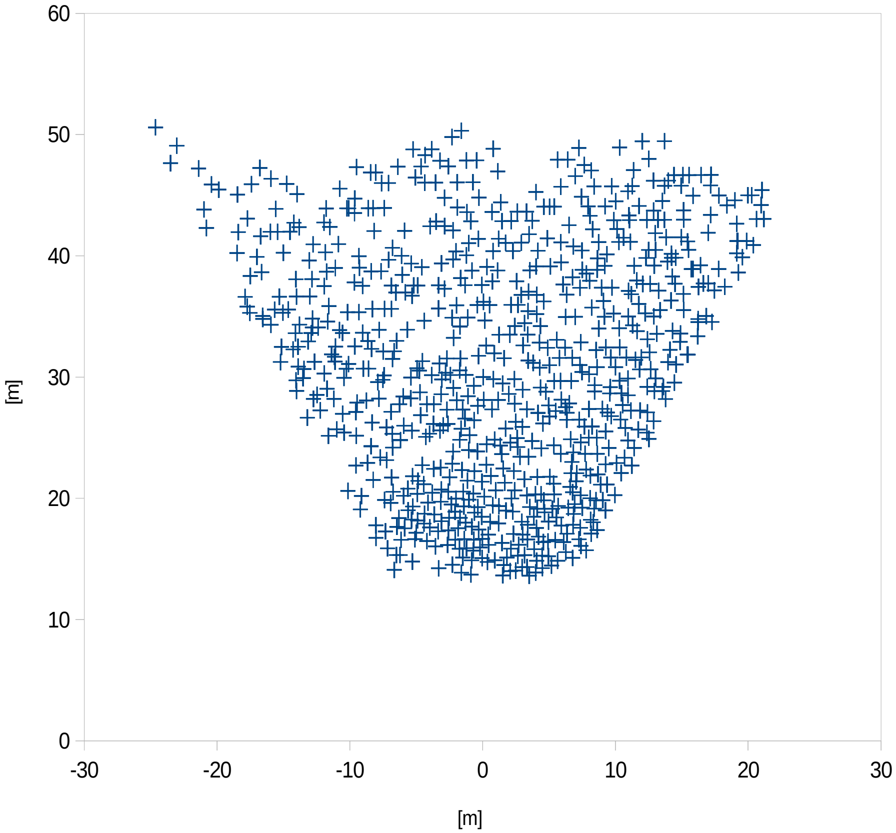
Digitize positions of people

People coordinates

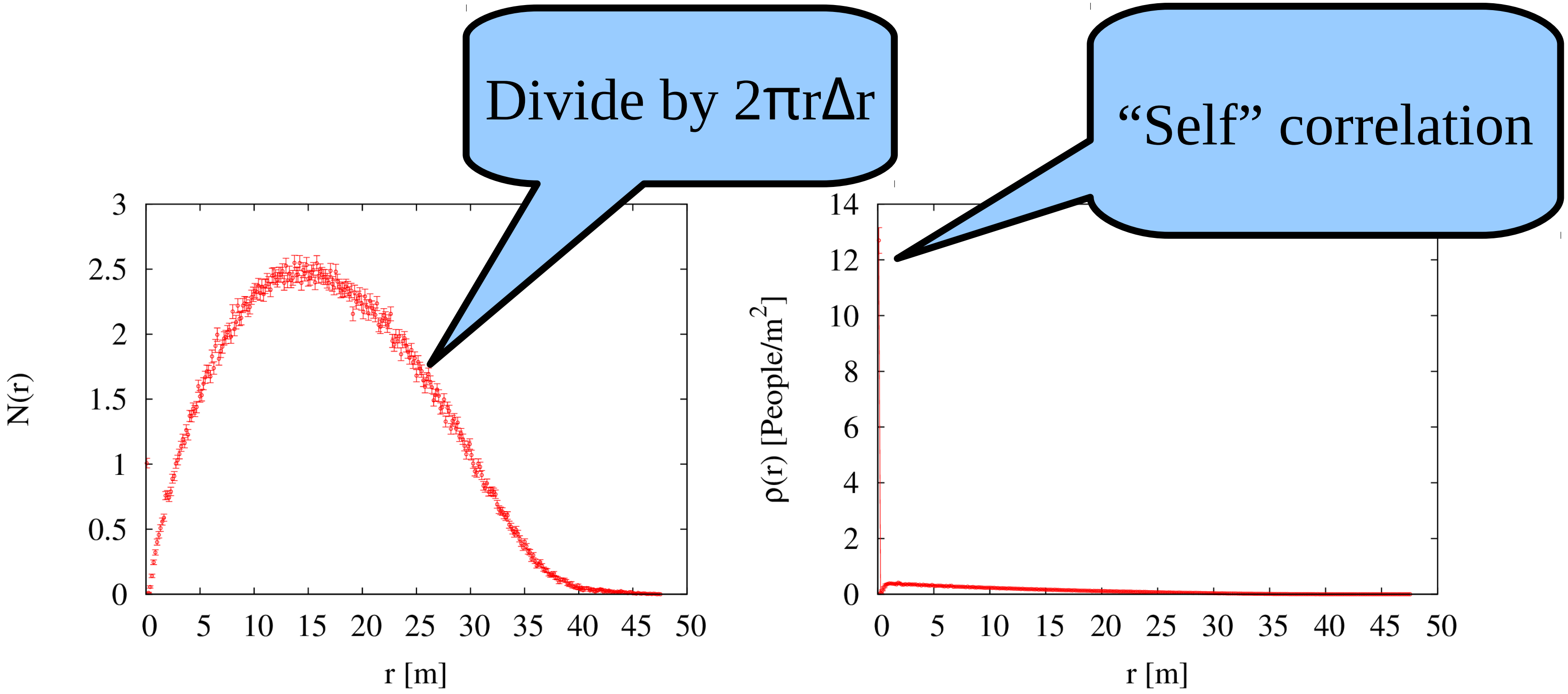
- Original coordinates



- Re-mapped coordinates



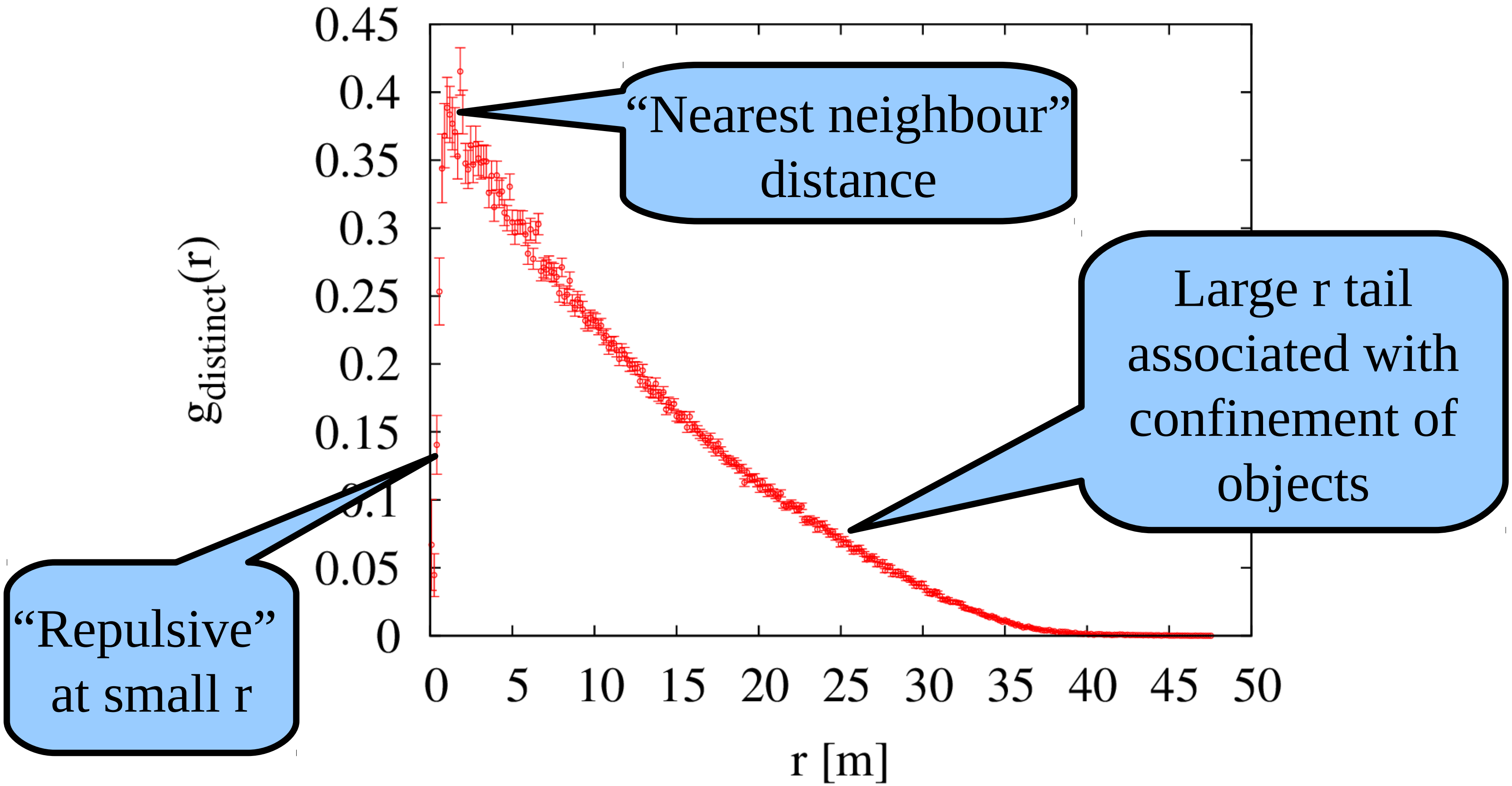
Crowd radial distribution function



Divide by 2πrΔr

“Self” correlation

“Distinct” radial distribution function

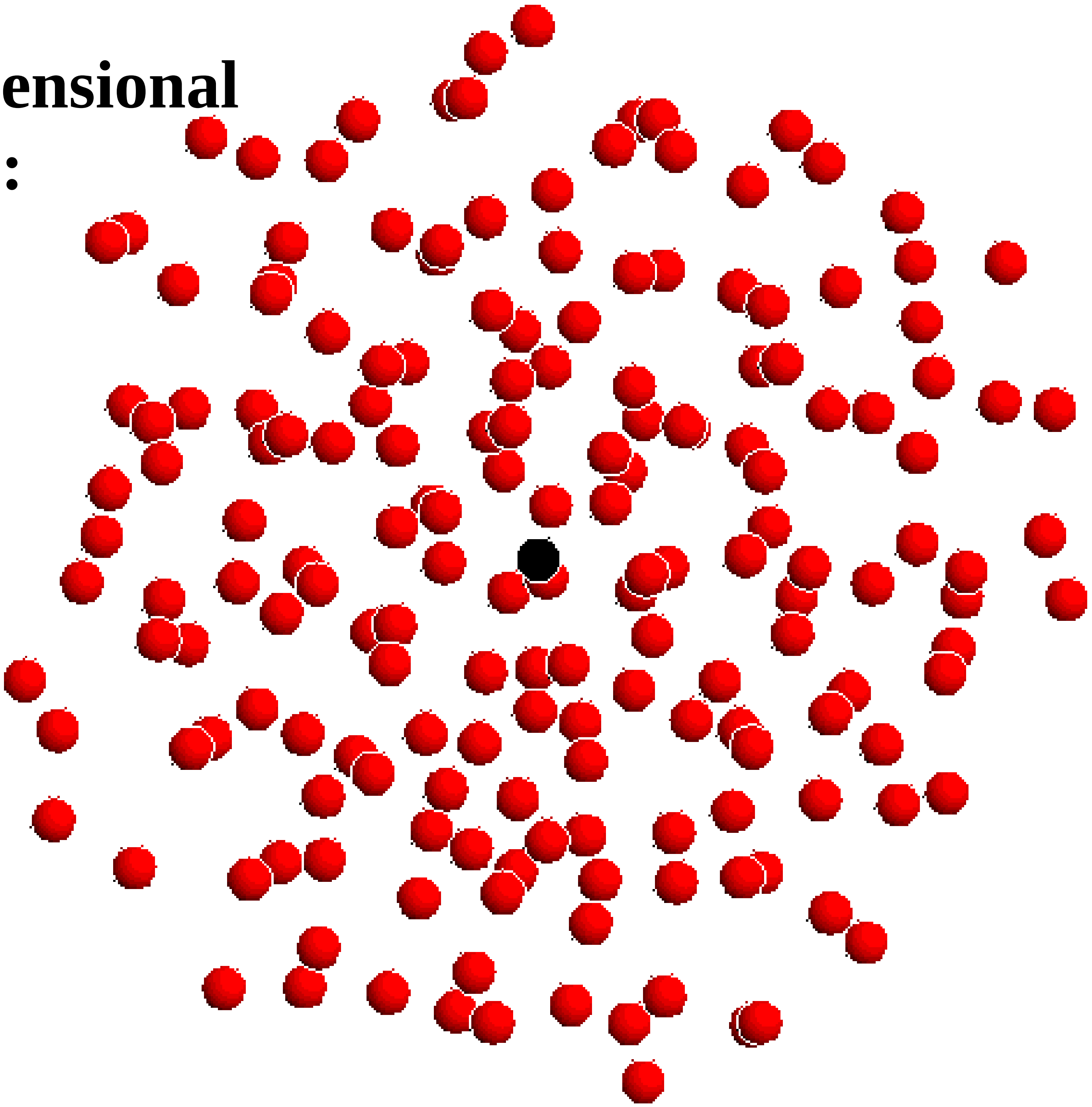


“Nearest neighbour” distance

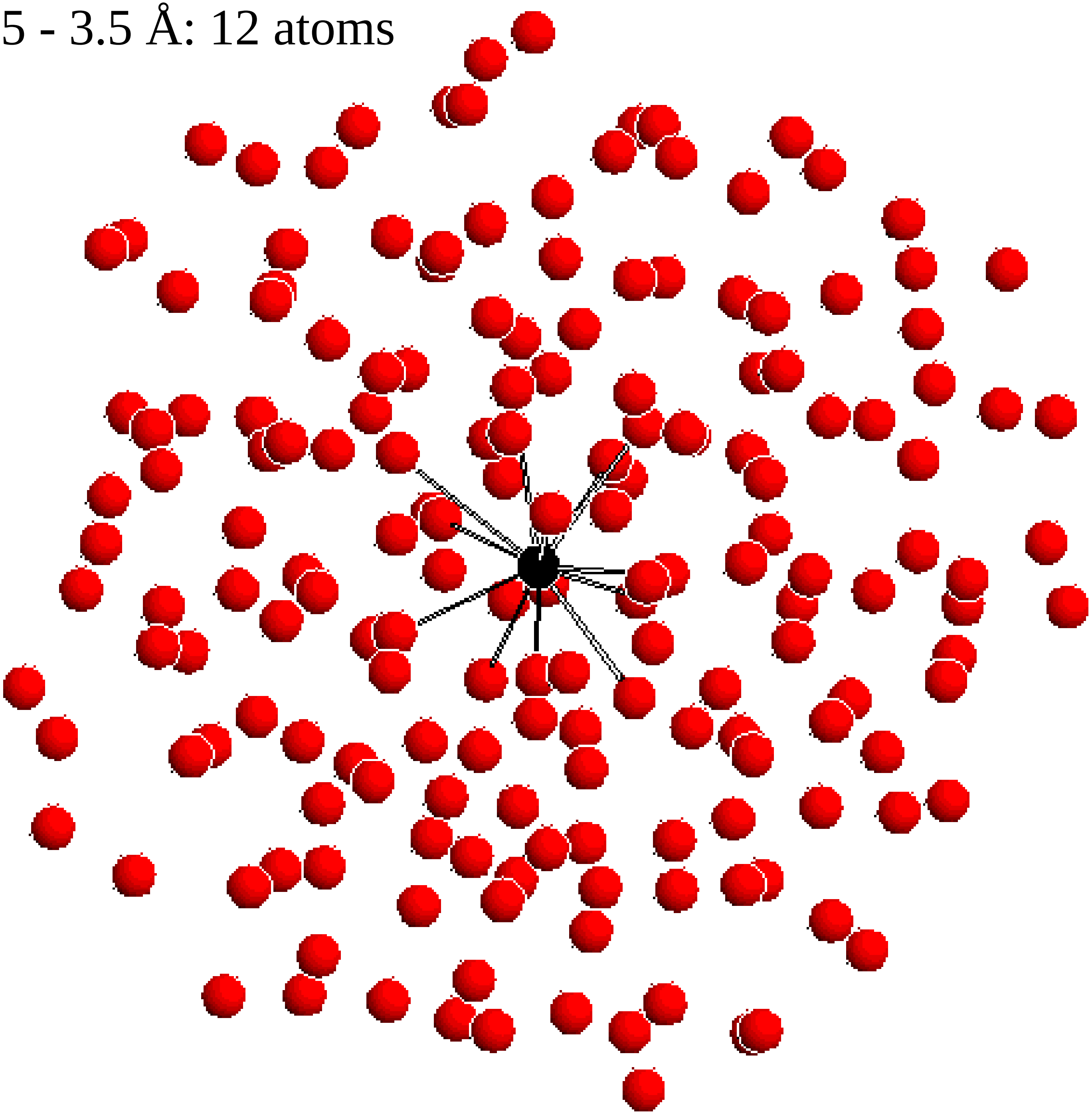
Large r tail associated with confinement of objects

“Repulsive” at small r

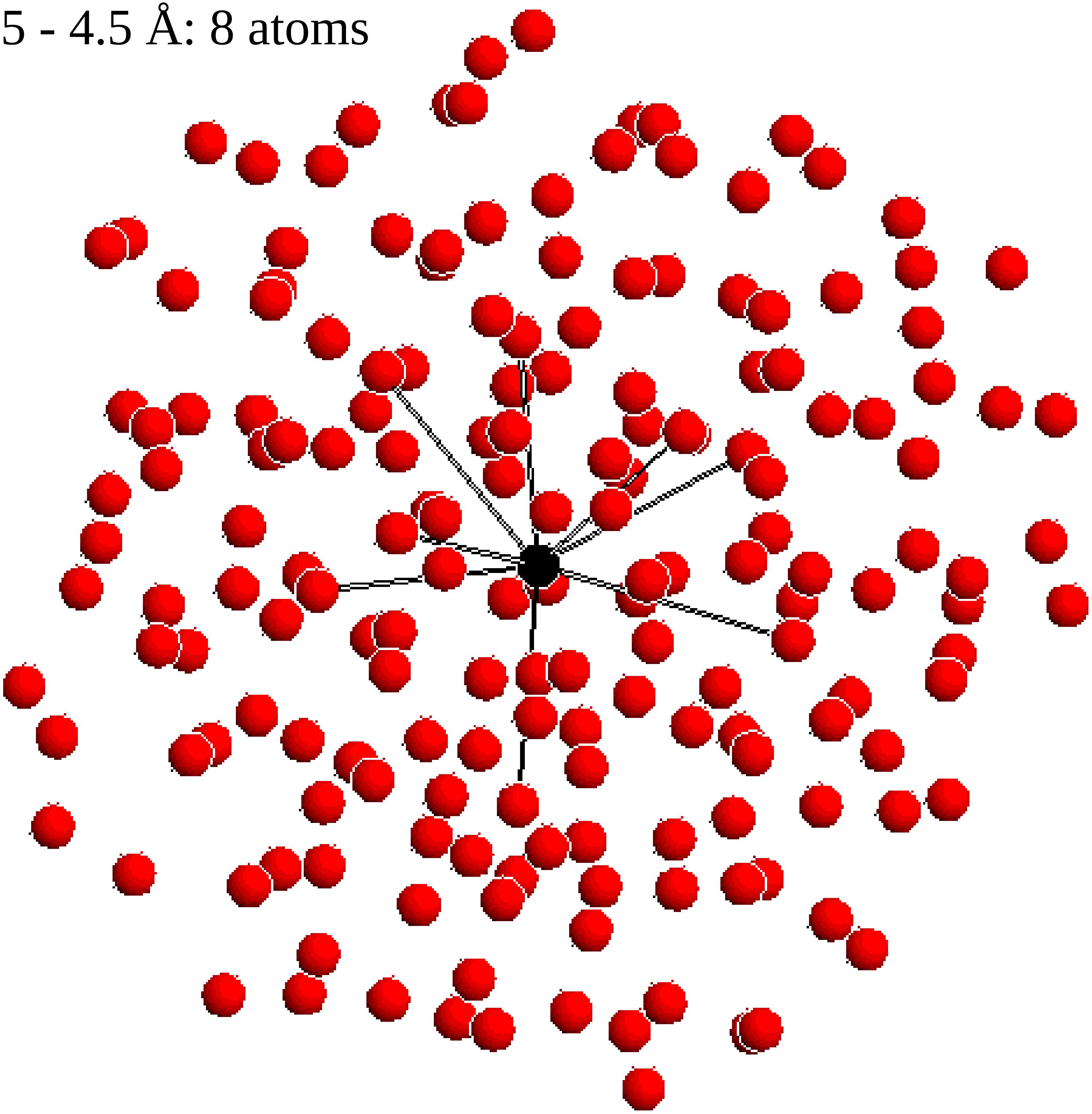
3-dimensional liquid:



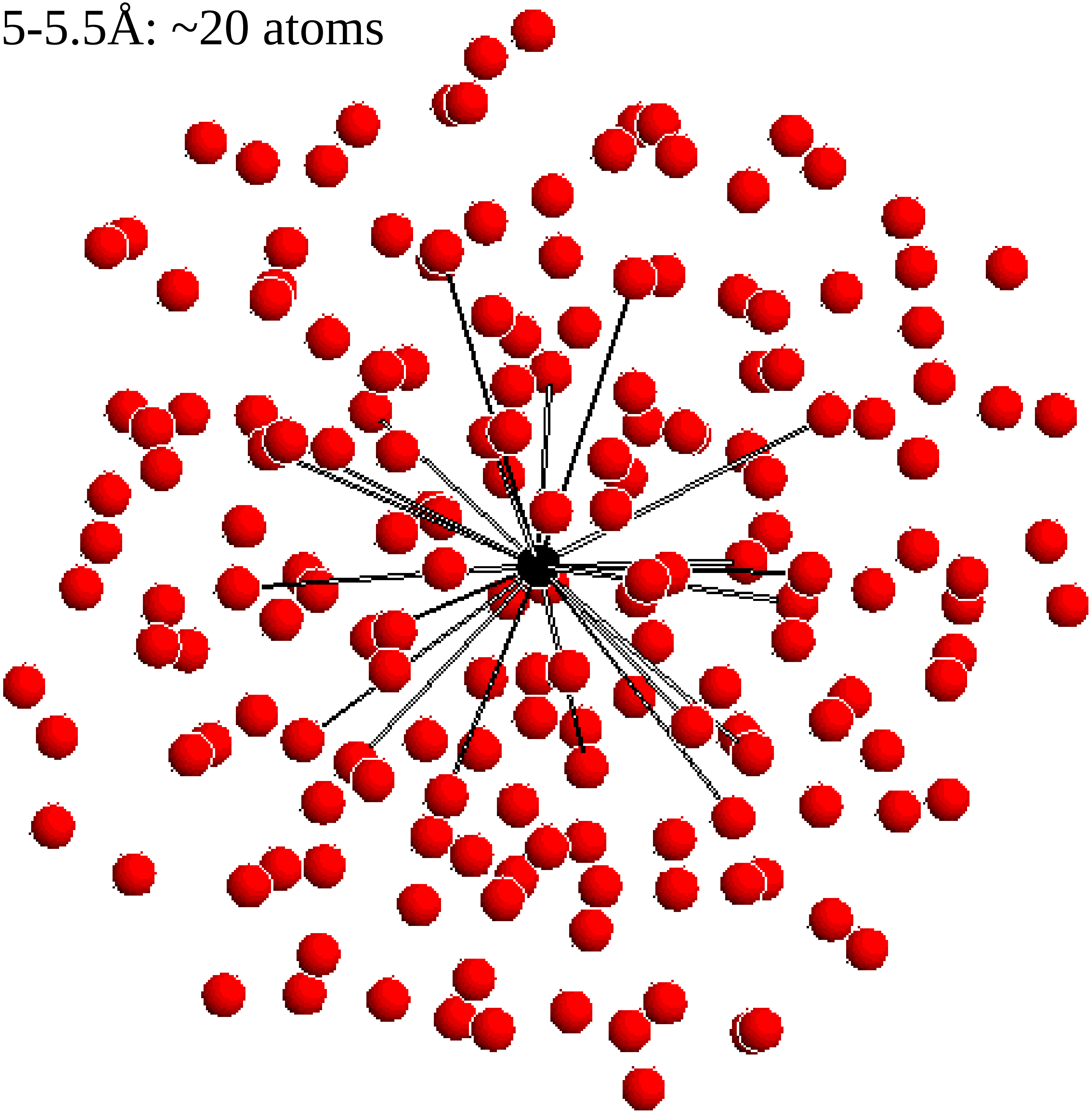
2.5 - 3.5 Å: 12 atoms



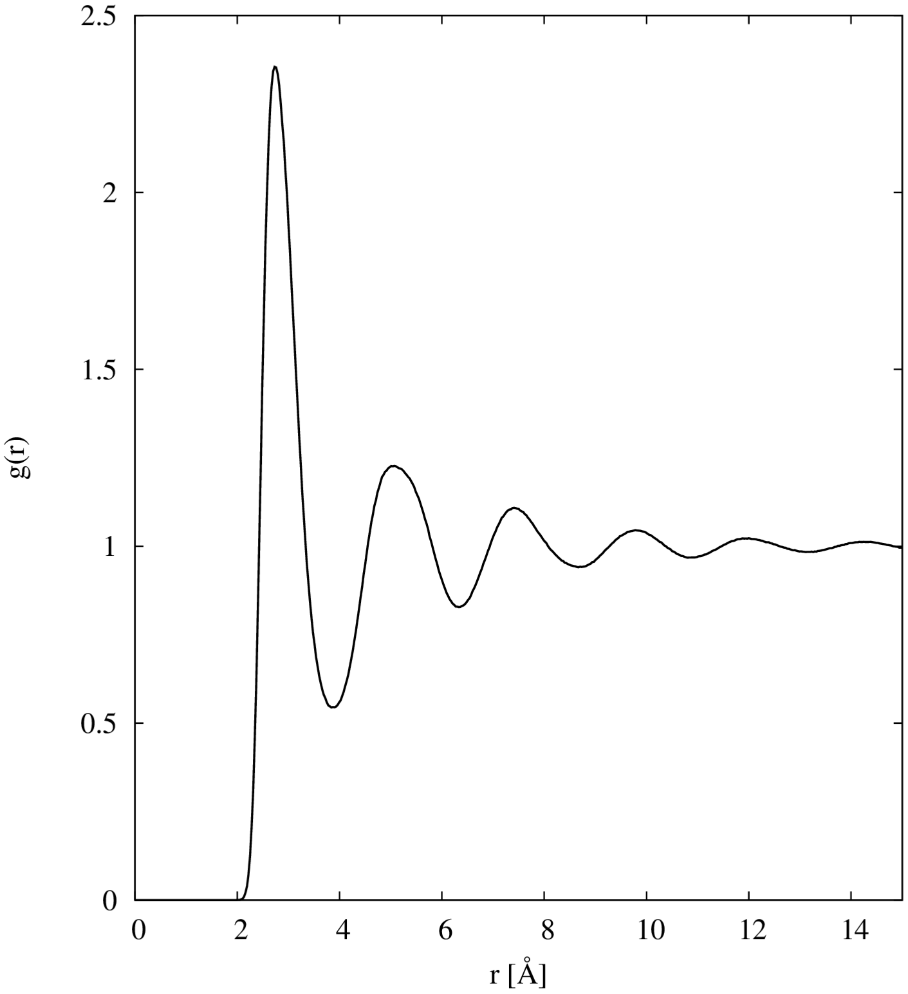
3.5 - 4.5 Å: 8 atoms



4.5-5.5Å: ~20 atoms



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

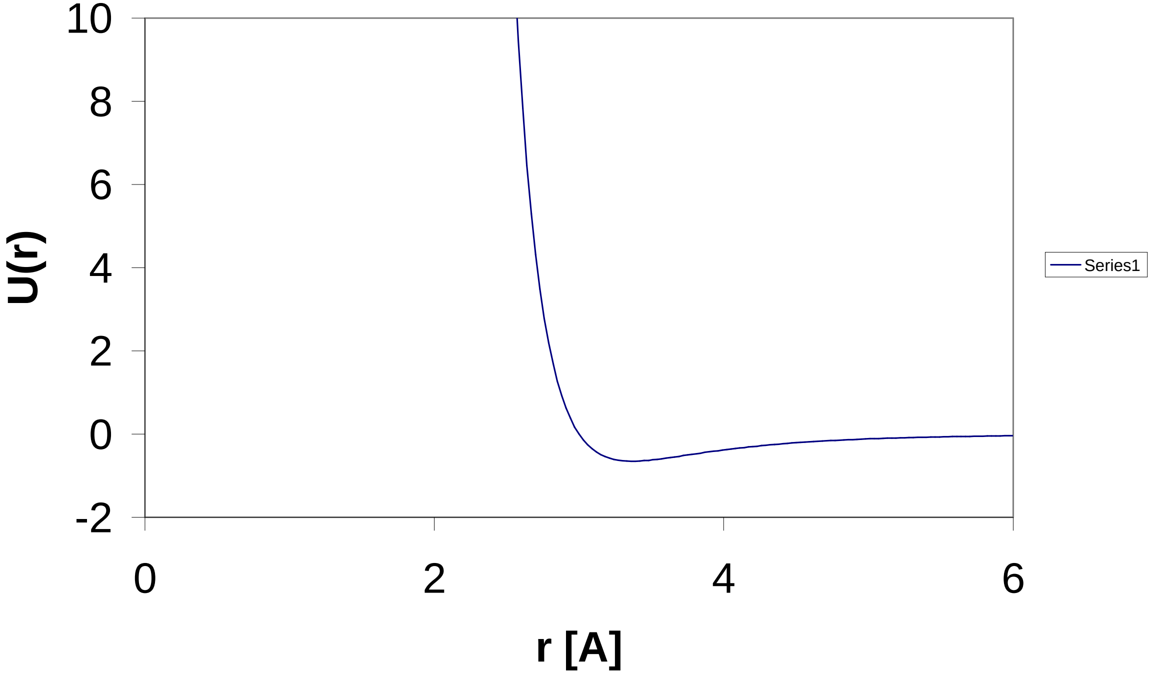


What is this radial distribution function, g(r), telling us?

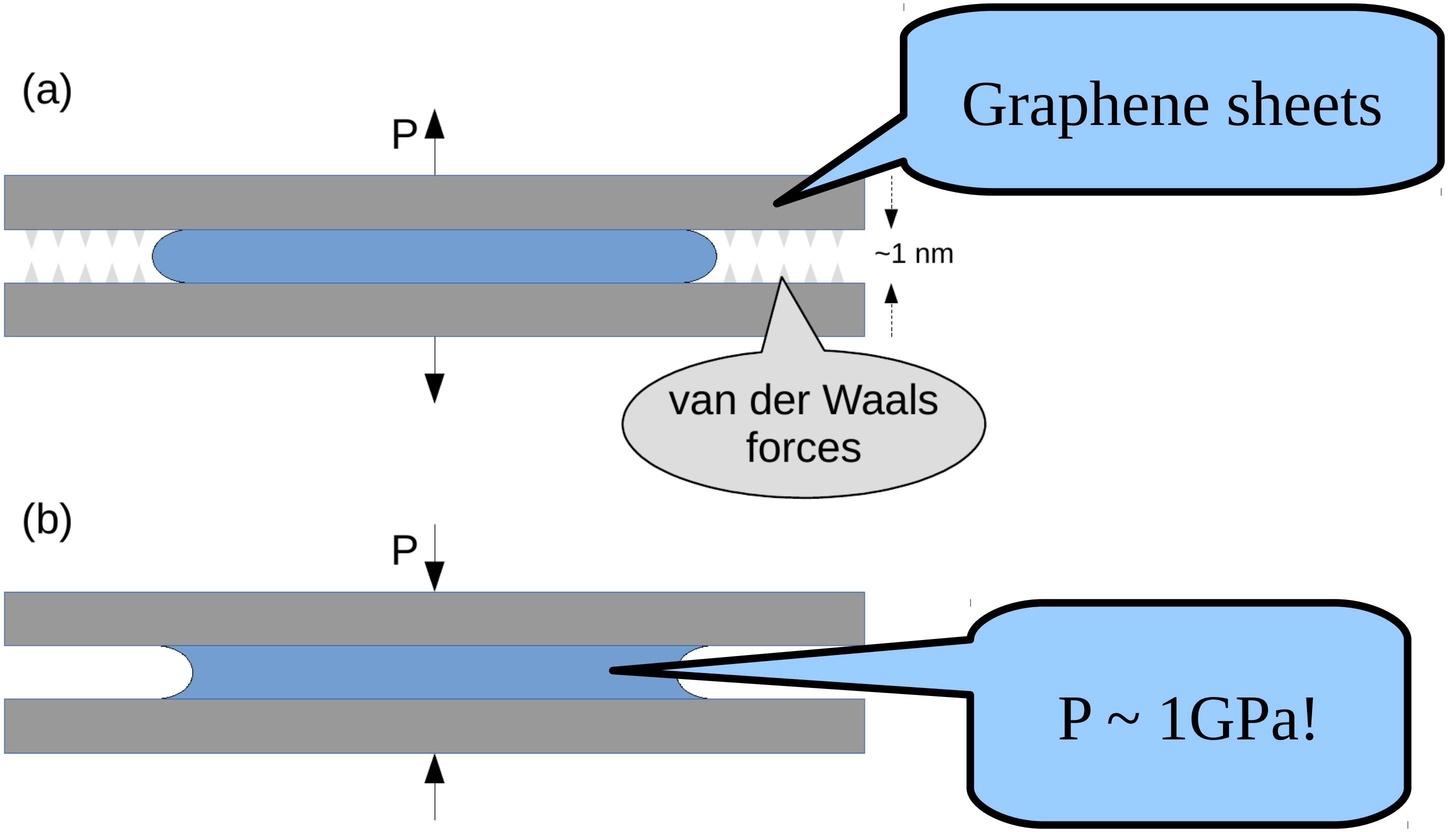
- It tells us about the nearest-neighbour numbers and distances;
- It tells us about the hardness of the atomic core repulsion;
- It tells us about the attractiveness each atom has for its neighbours;
- In other words it tells us about the local potential energy environment of an atom in the material.

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.



Diversion: Van der Waals forces can give large effects!

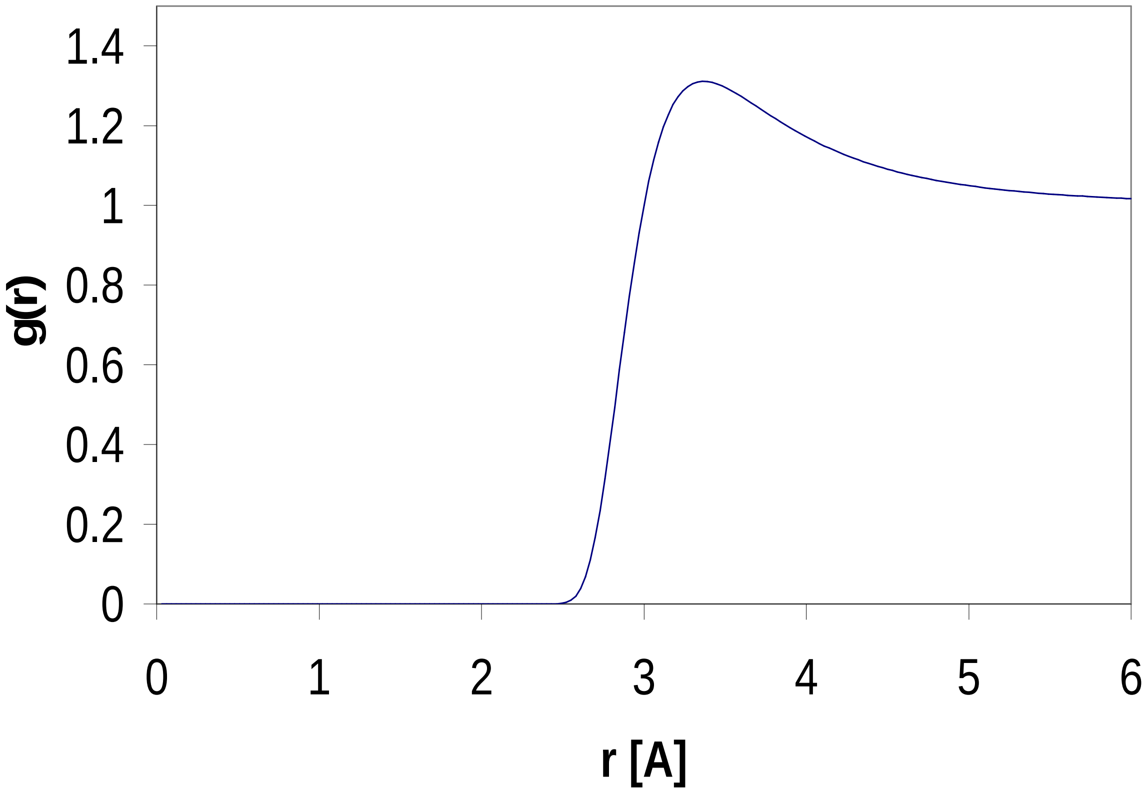


P ~ 1GPa!

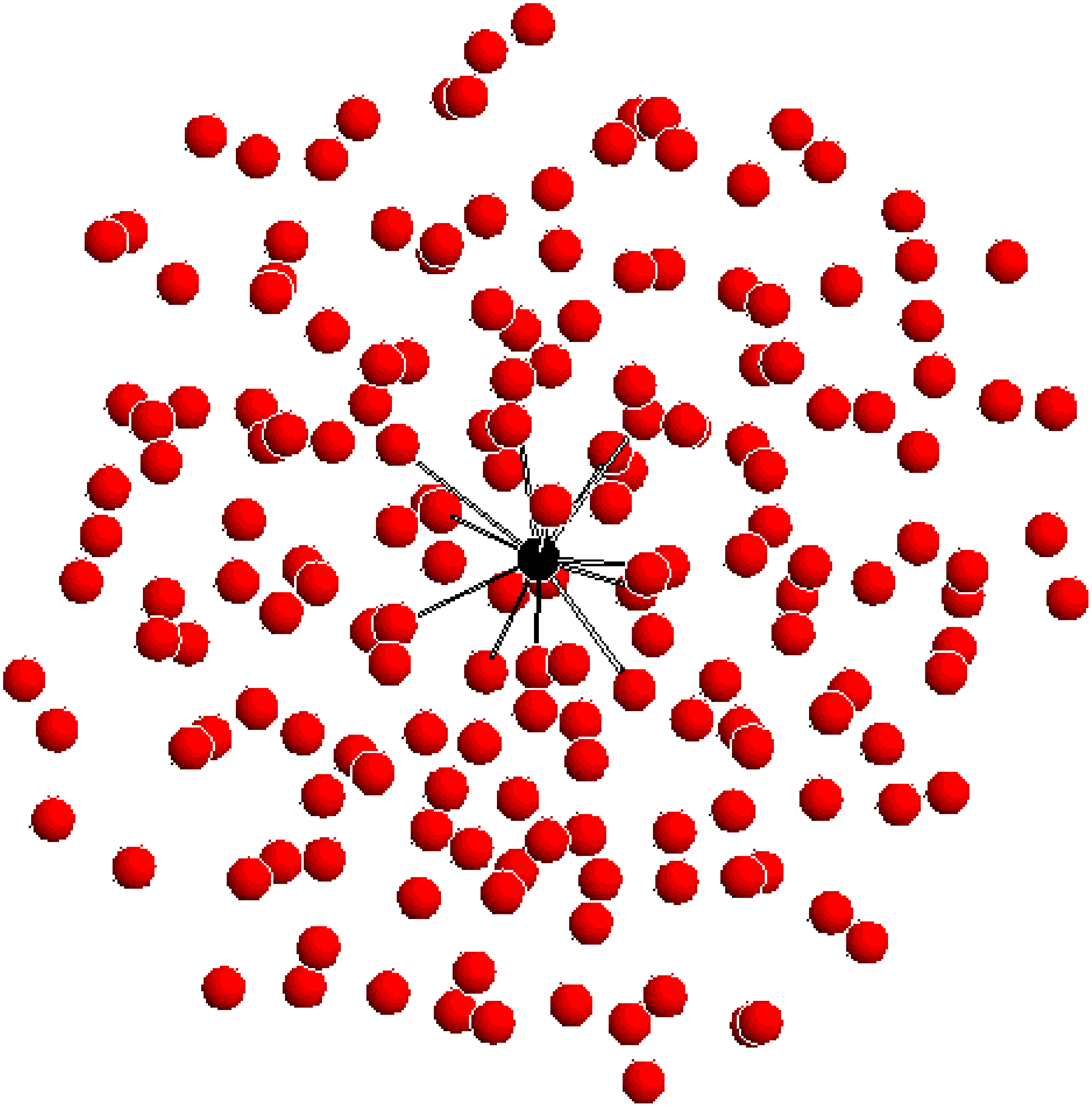
Corresponding g(r):

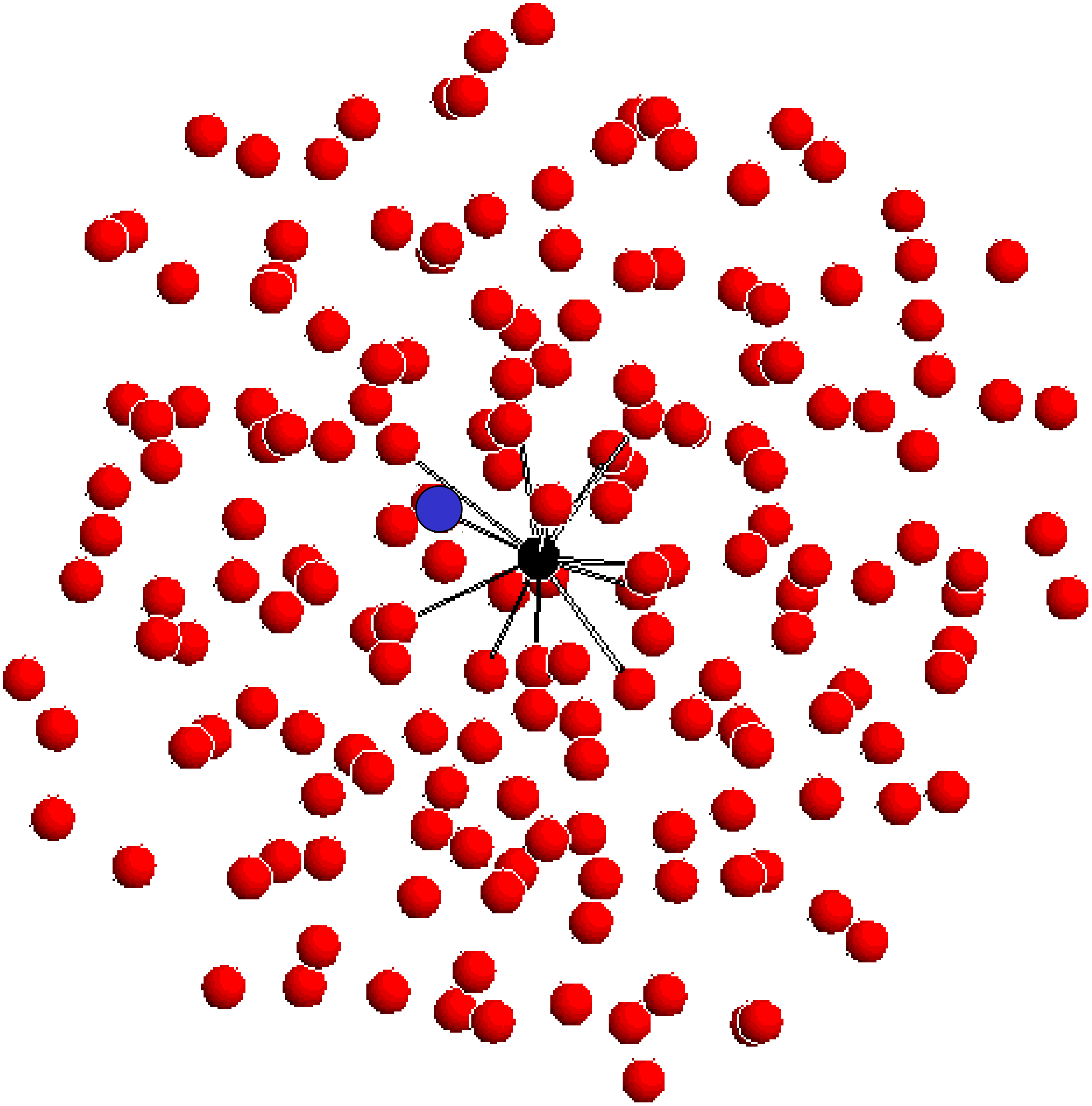
- At zero density, formally exact result:

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



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

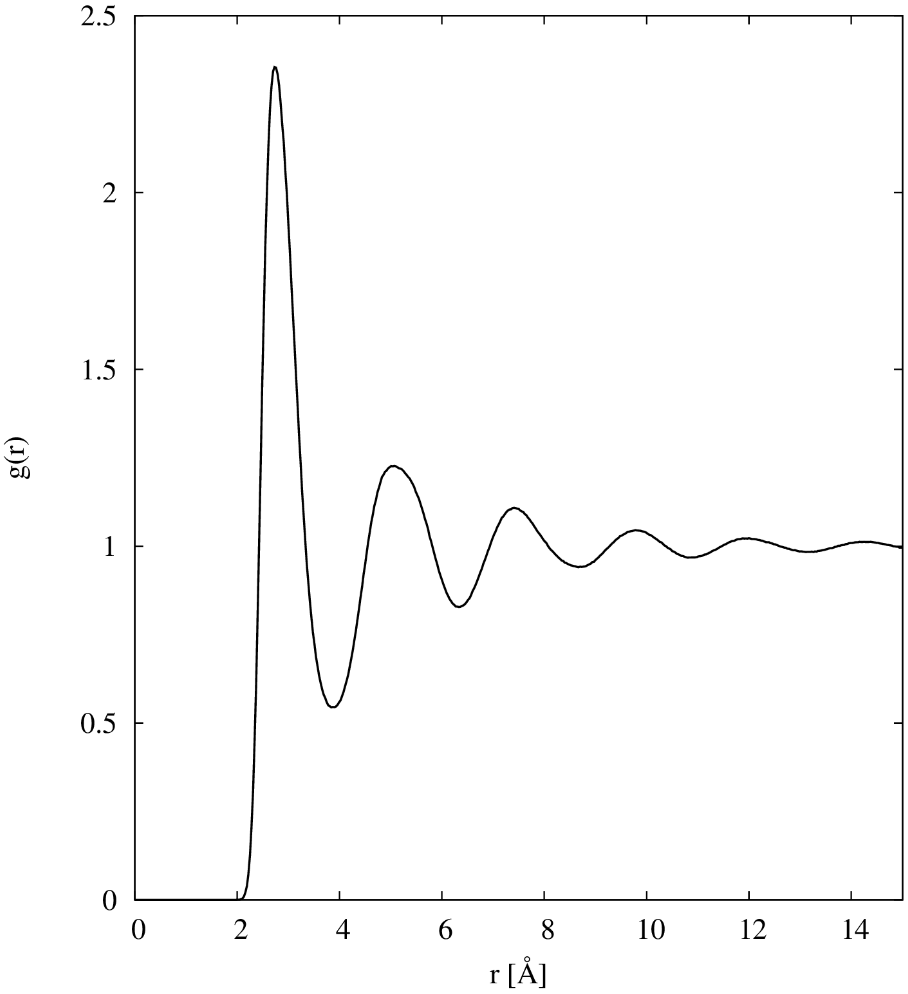




Effect of many body correlations

Many body correlations give rise to the oscillations...

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



How do we measure $g(r)$?

You can’t measure *g(r)*!

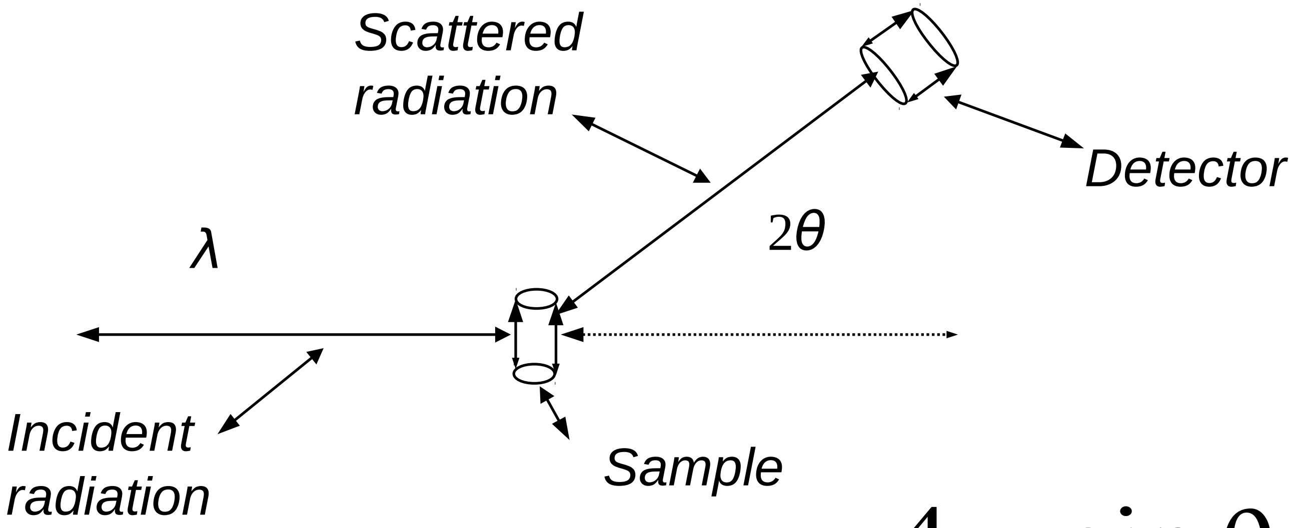
Instead you have to use a diffractometer to do the atom counting.

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

(Actually a differential scattering cross section)

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

Diffraction from disordered materials - a simple experiment in principle:



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

Diffraction from disordered materials
- a simple experiment in principle:

“Neutron scattering length” or
“electron form factor”

Scattering amplitude: $A(Q)=\sum_i b_i \exp\left(i\vec{Q}\cdot\vec{r}_i\right)$

Scattered intensity [per atom]:-

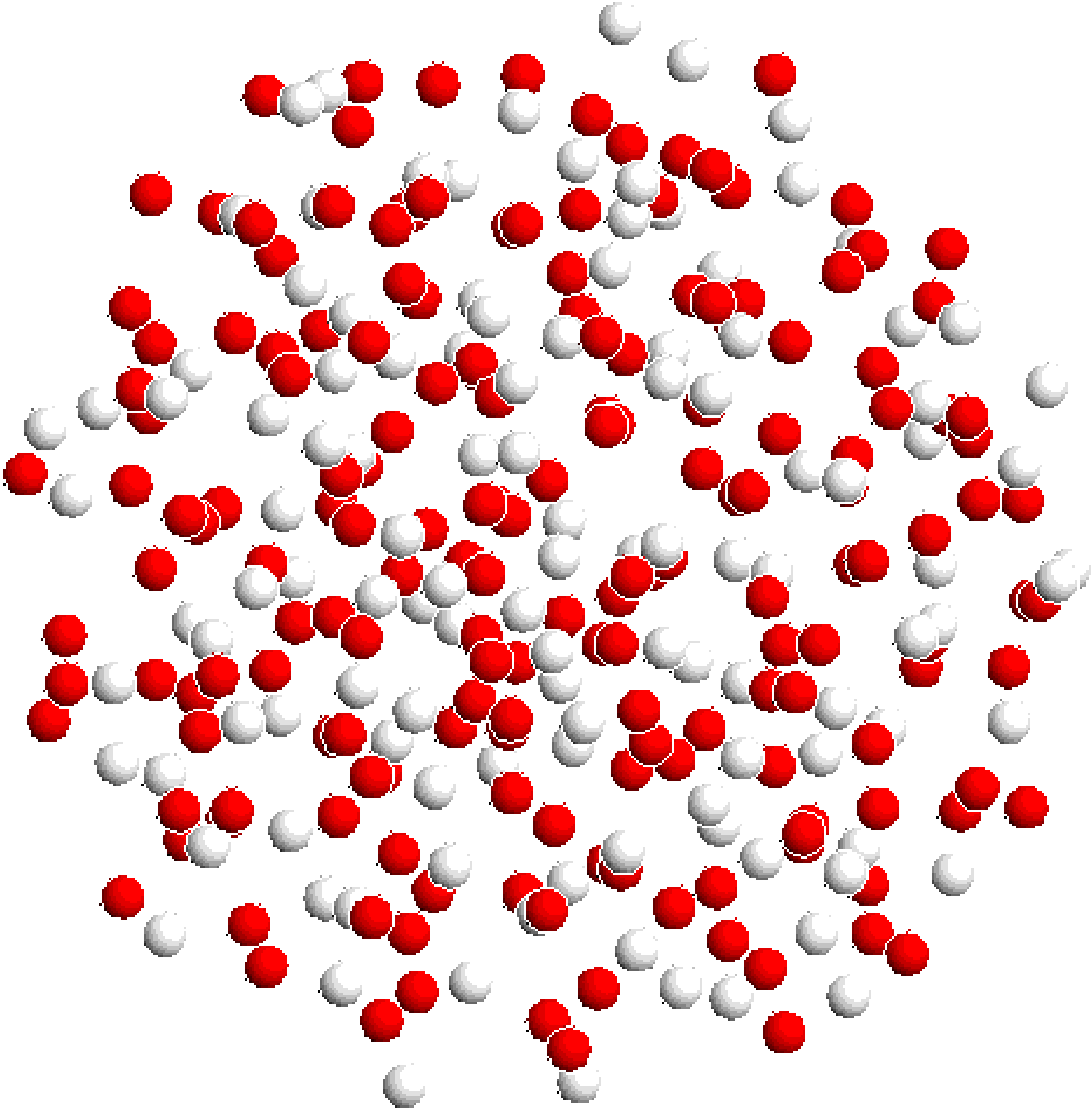
$$I(Q) = \frac{|A(Q)A(Q)|}{N} = \frac{\sum_{i,j} b_i b_j \exp i\vec{Q}\cdot(\vec{r}_i-\vec{r}_j)}{N}$$

$$= \frac{\sum_i b_i^2}{N} + \frac{\sum_{i,j\neq i} b_i b_j \exp i\vec{Q}\cdot(\vec{r}_i-\vec{r}_j)}{N}$$

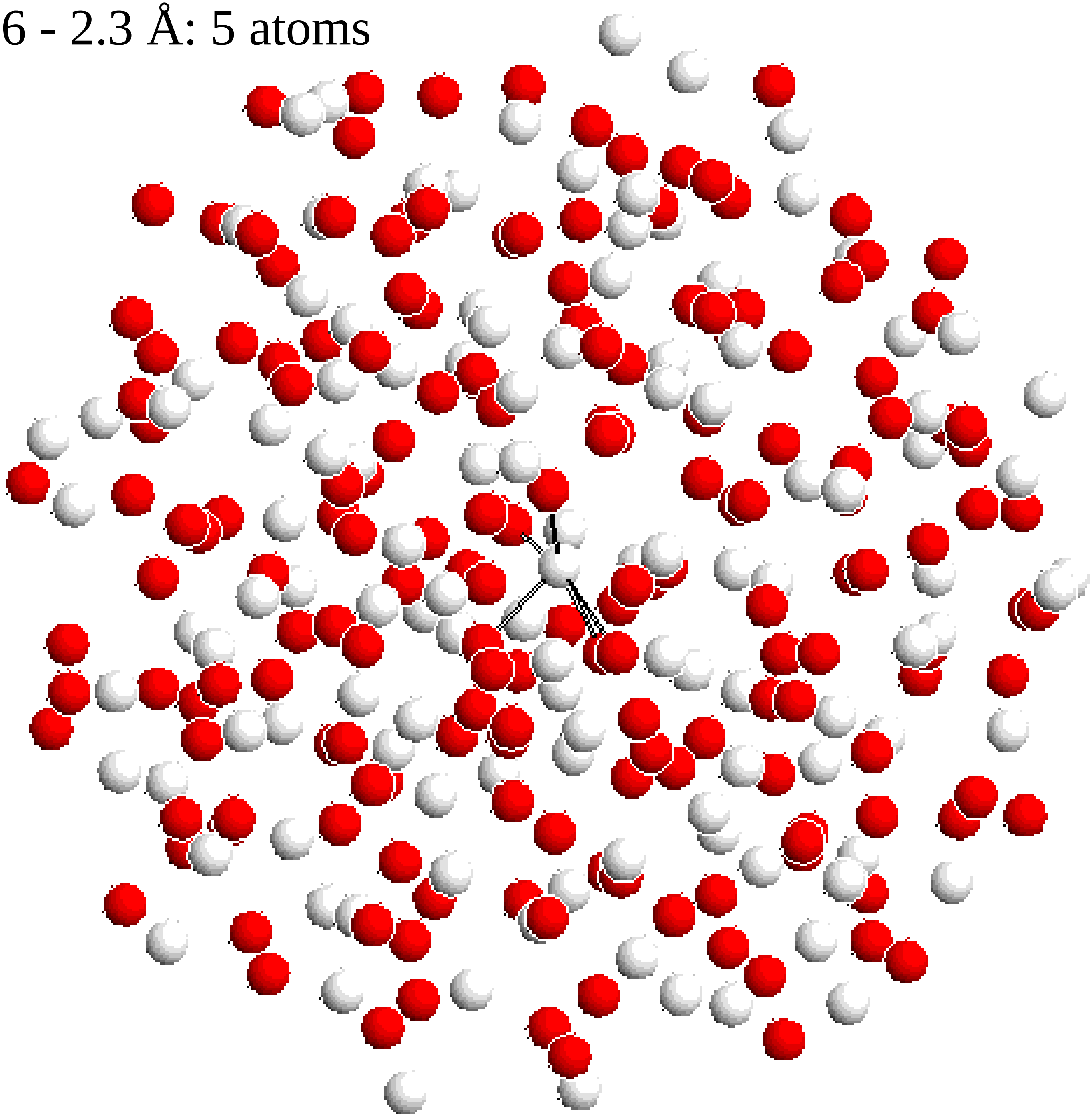
“Single atom” or
“self” term

“Distinct” or
“interference” term

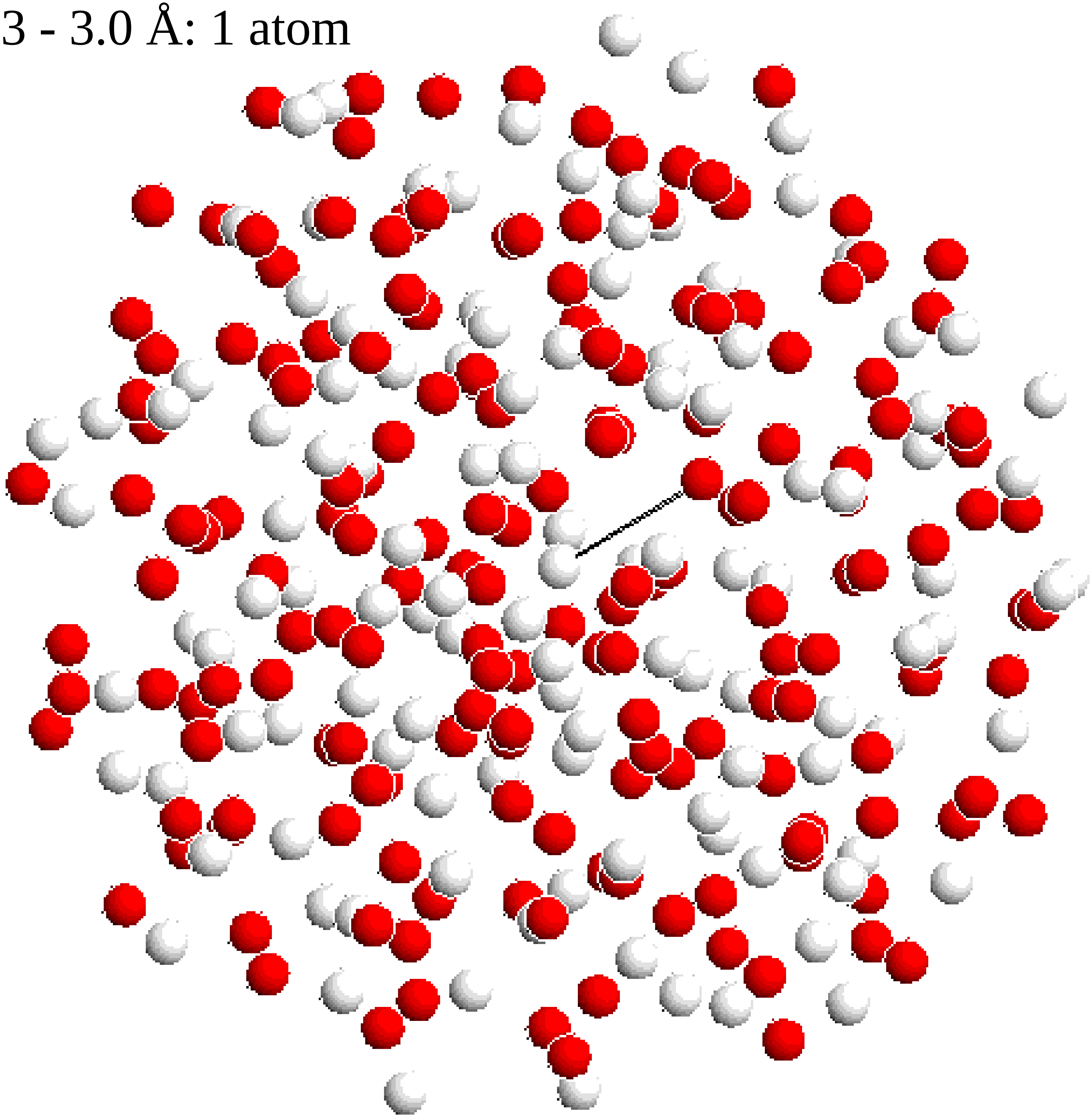
Now consider a 2-component system, Al_2O_3:



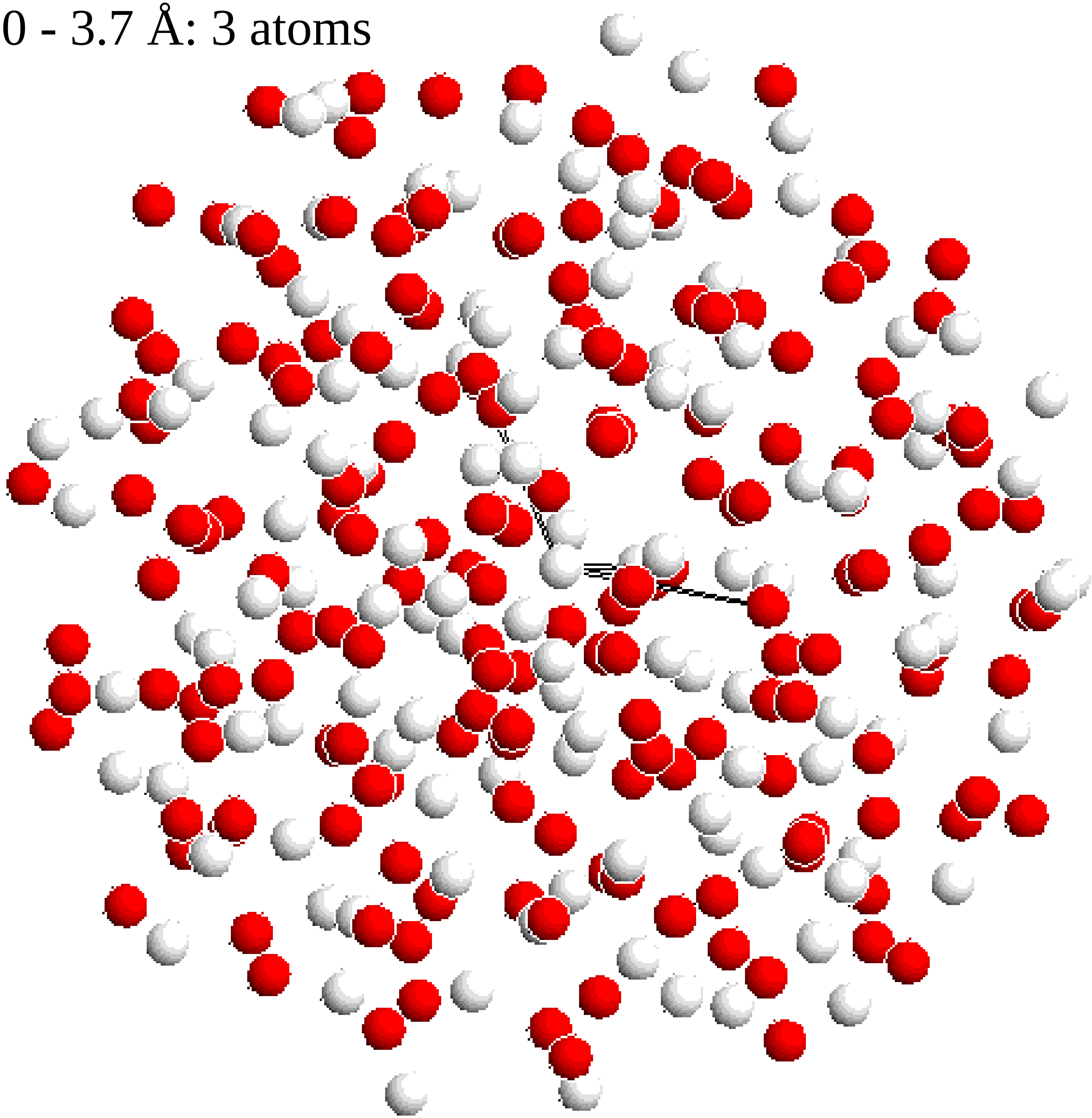
1.6 - 2.3 Å: 5 atoms



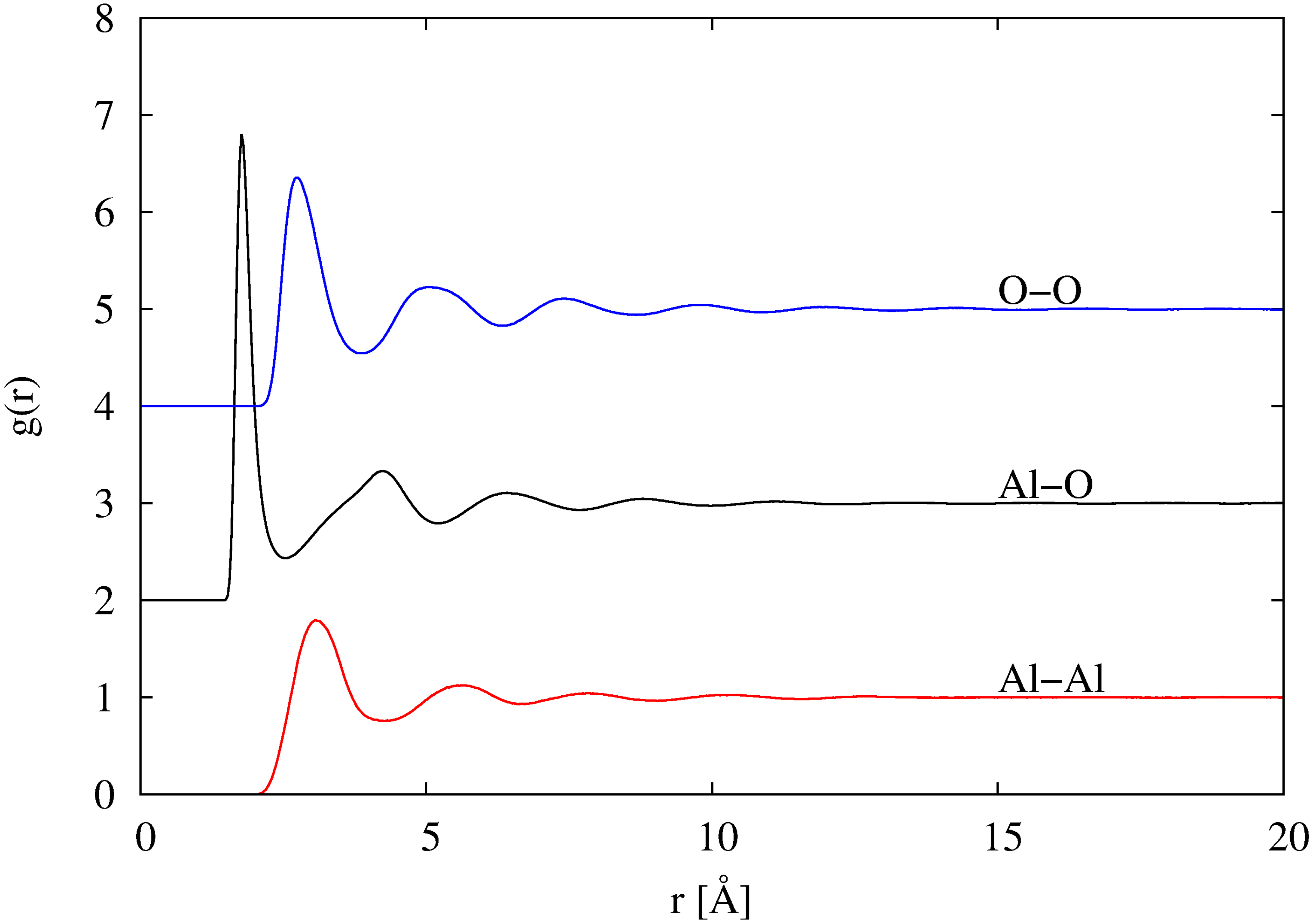
2.3 - 3.0 Å: 1 atom



3.0 - 3.7 Å: 3 atoms



Partial *g(r)*'s for Al_2O_3



The “distinct” structure factor:

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

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

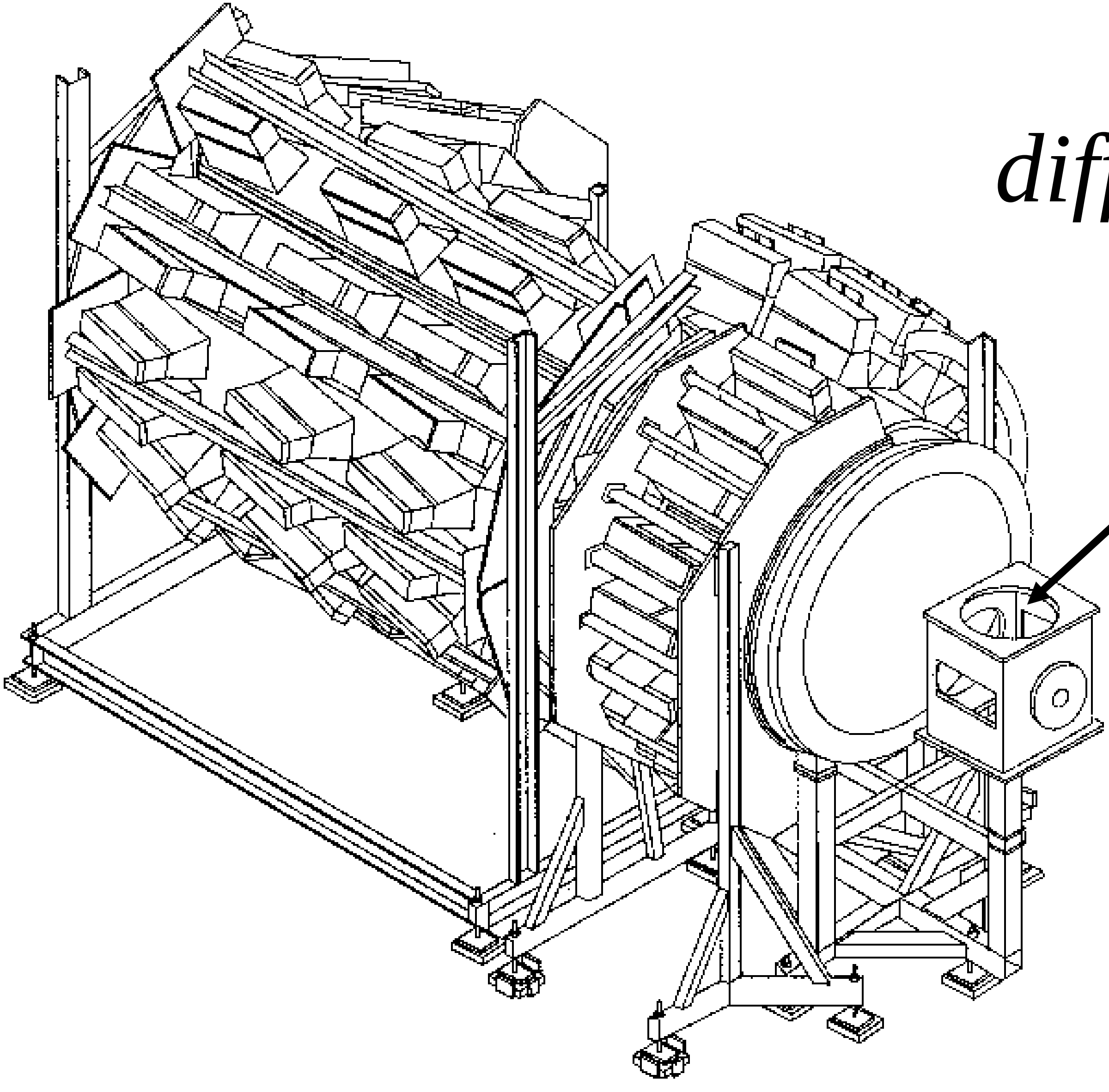
$$F(Q)=\sum_{\alpha,\beta\geq\alpha}\left(2-\delta_{\alpha\beta}\right)\,c_{\alpha}c_{\beta}b_{\alpha}b_{\beta}\left\{4\pi\rho\int r^{2}\,2\left(g_{\alpha\beta}(r)-1\right)\frac{\sin Qr}{Qr}\,dr\right\}$$

Atomic fraction of component “α”

The atom scattering factor or “form factor”

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

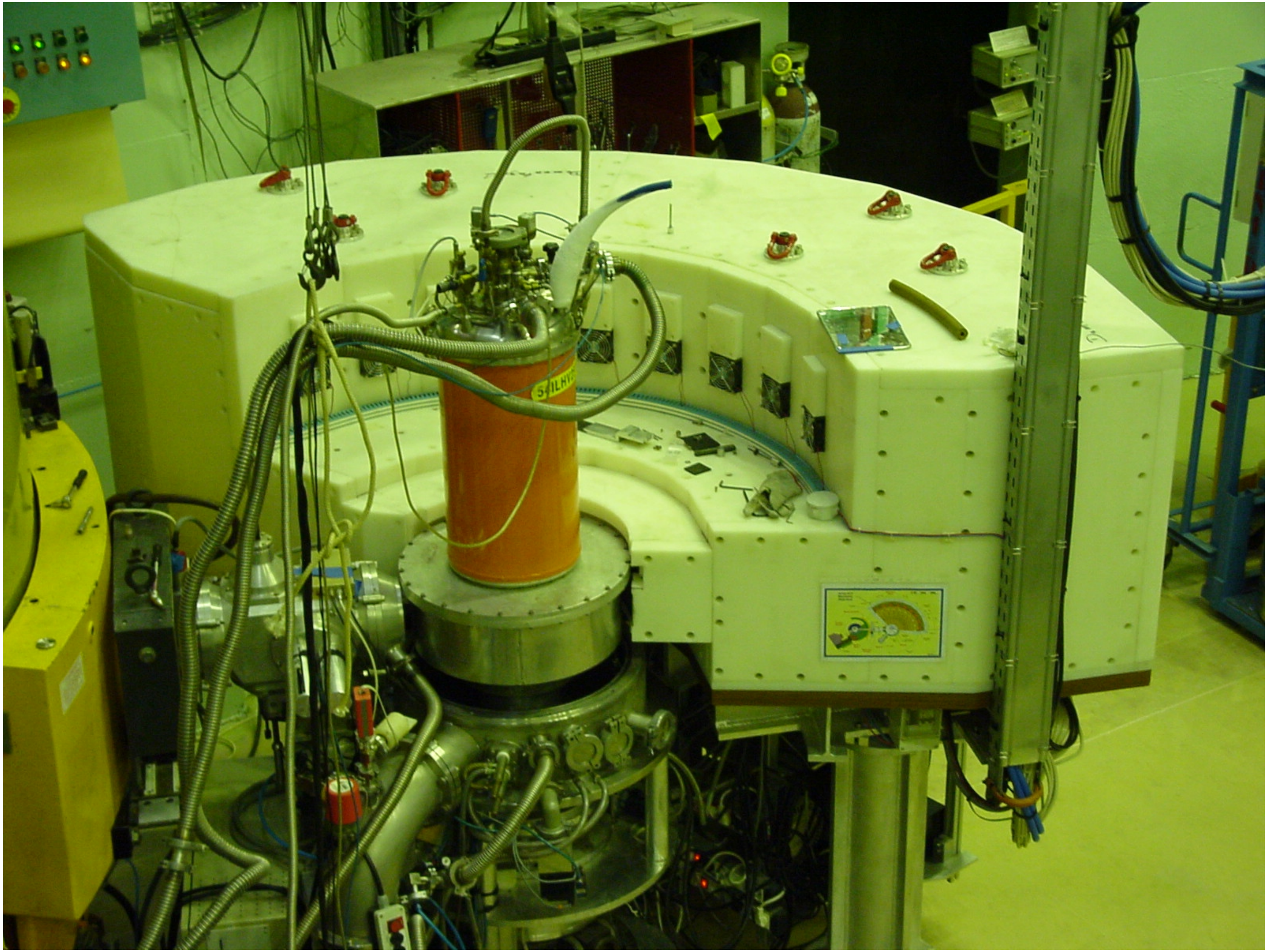
ISIS SANDALS (*liquids diffractometer*)



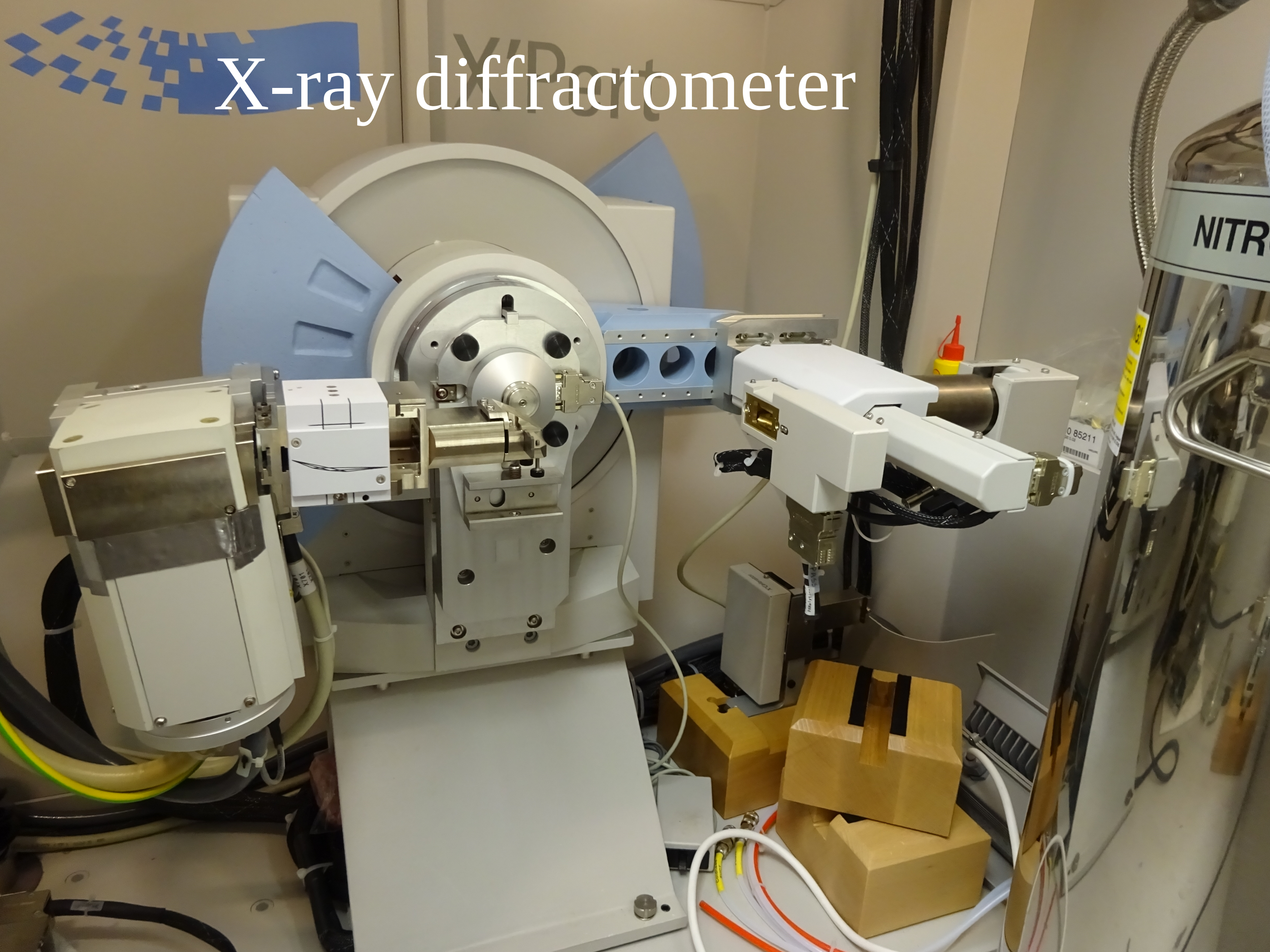
Sample position

Incident neutron beam

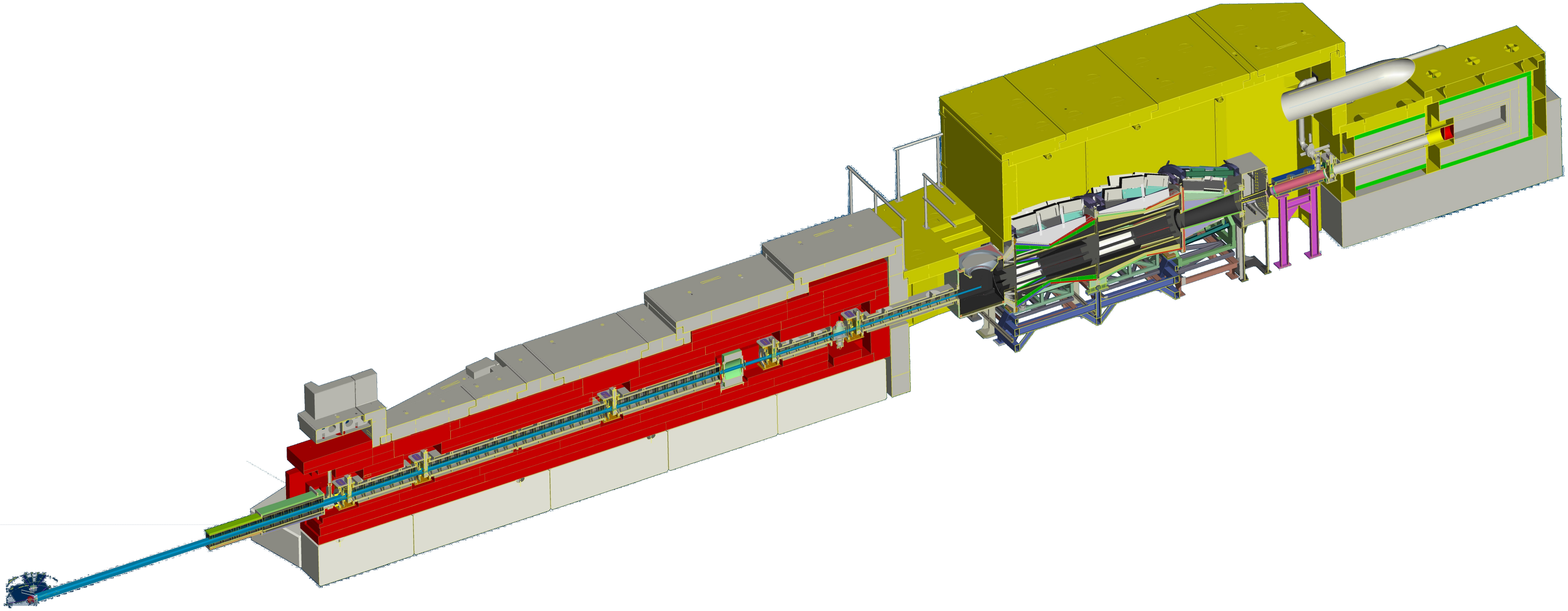
ILL – D4C



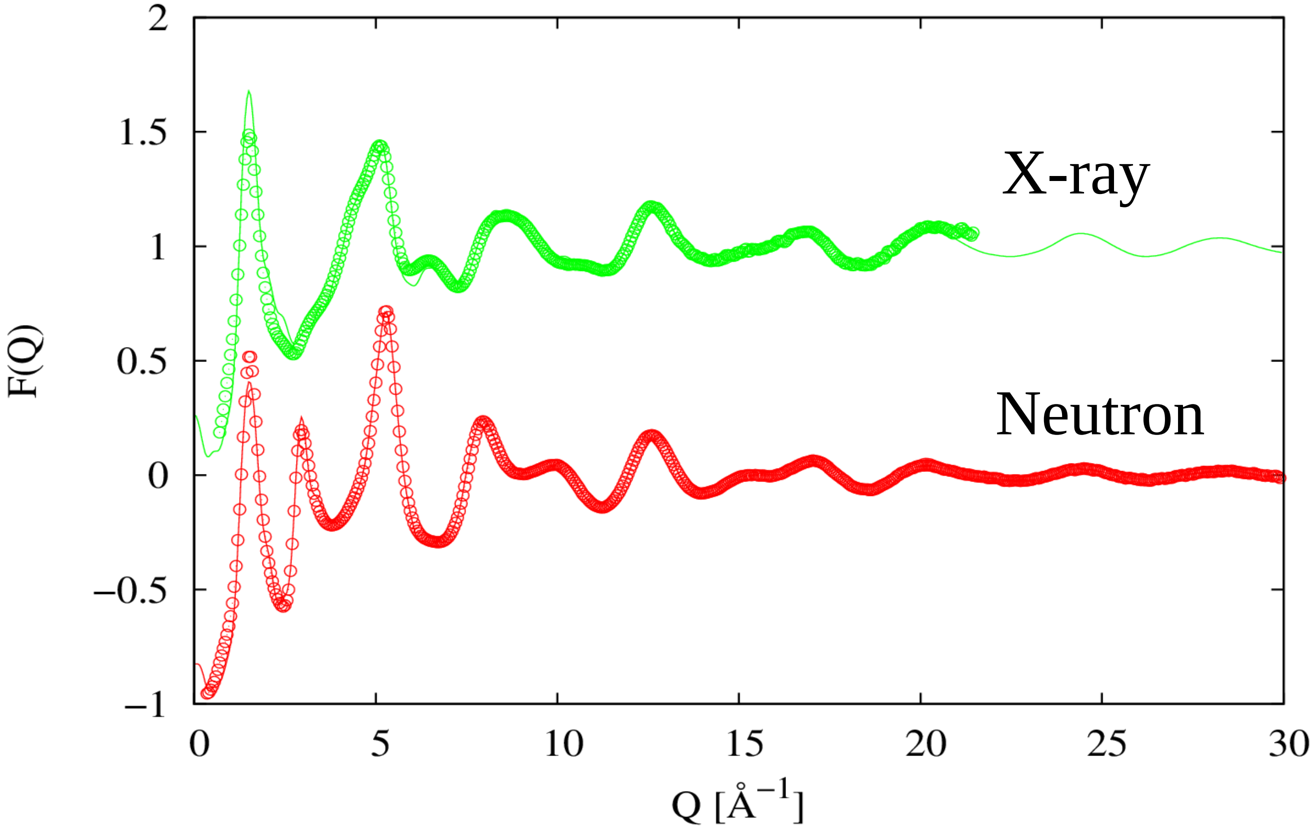
X-ray diffractometer



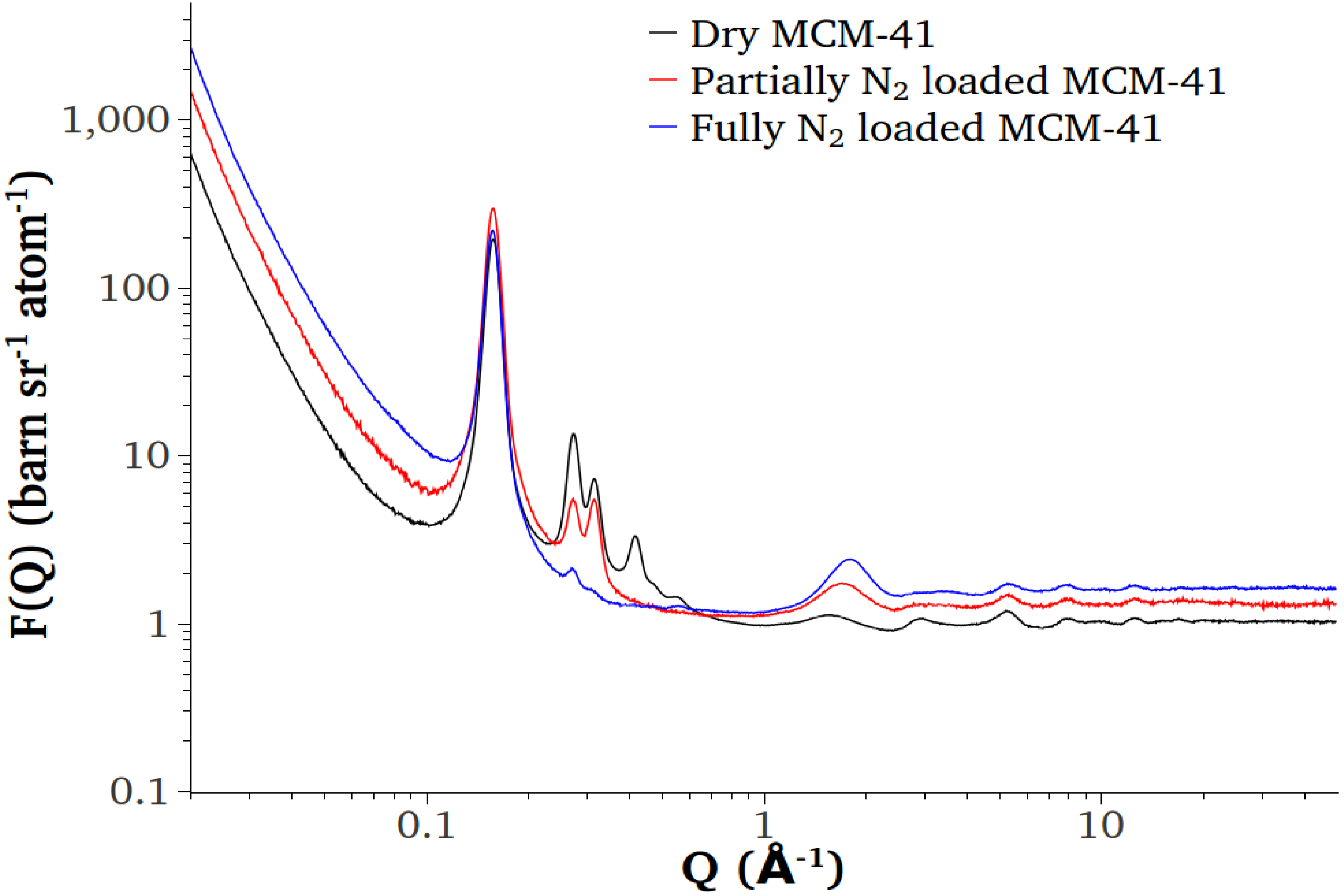
Now... NIMROD



... gives some data:



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 :-

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

  – "Instantaneous structure" averaged over positions
- This must be carefully distinguished from the **elastic** 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

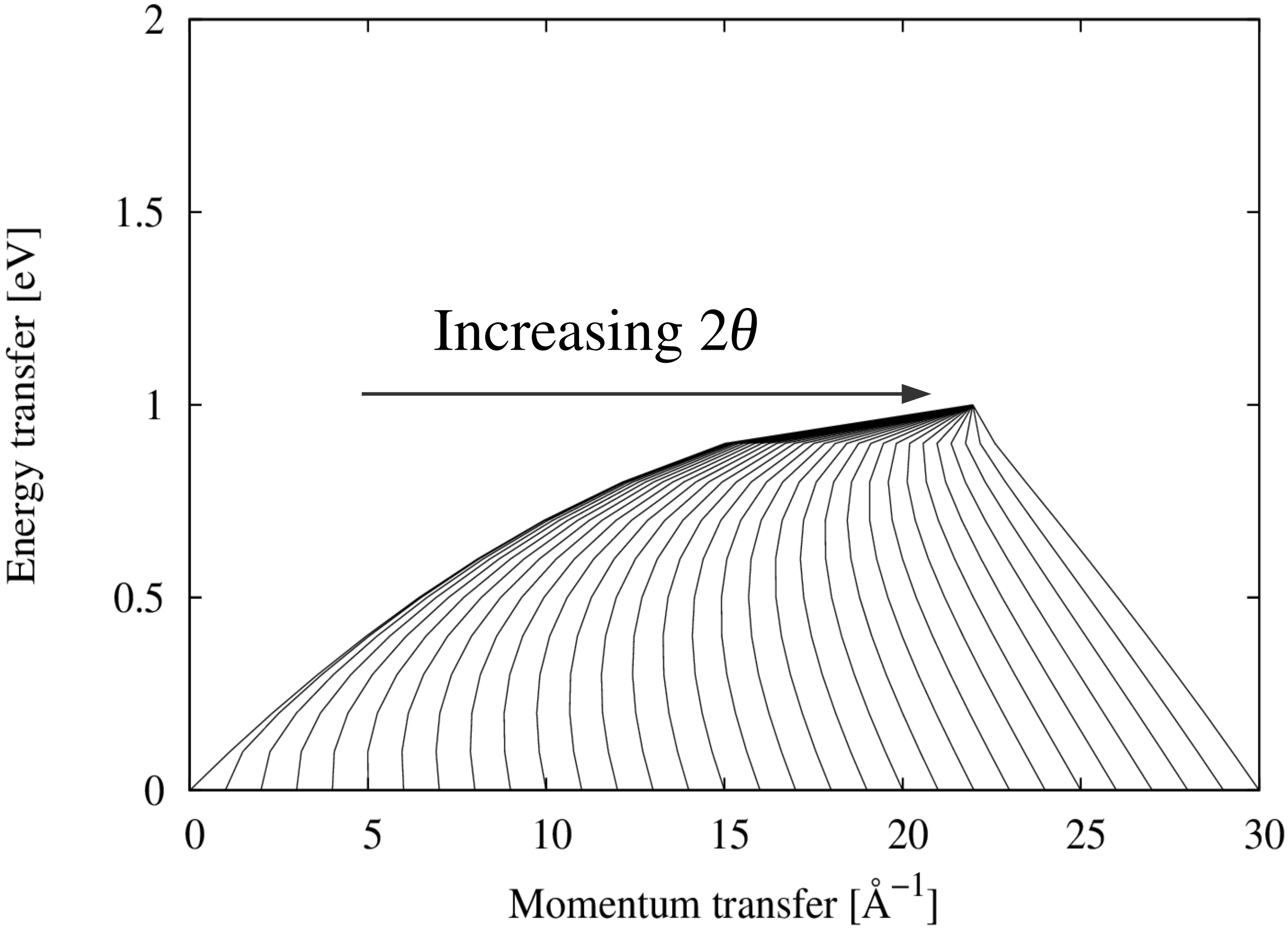
- Kinematics of neutron scattering:-

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

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

- 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):-

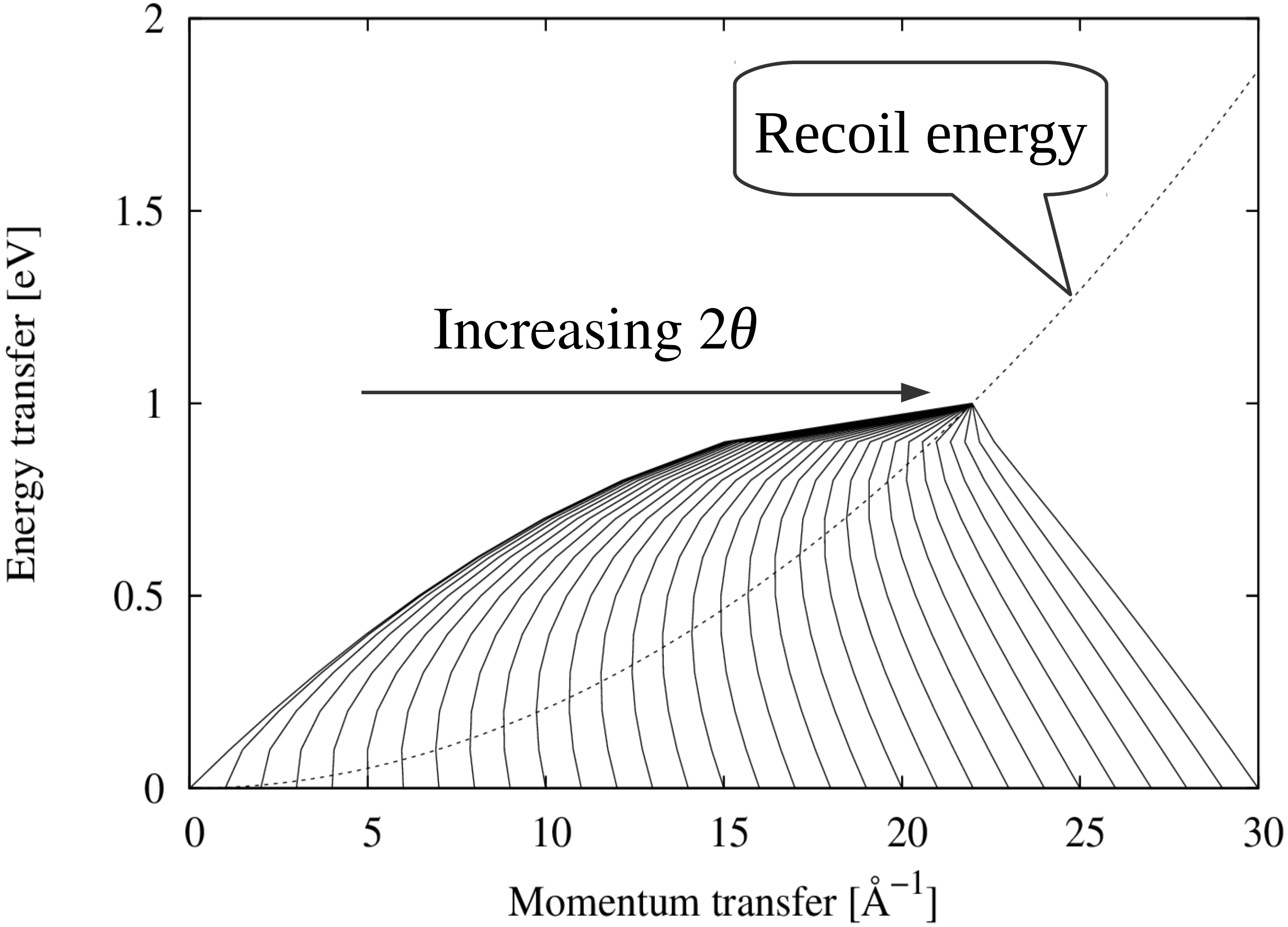
$$\int_Q \epsilon S_d(Q,\epsilon)\, d\epsilon = 0$$

- For self scattering:-

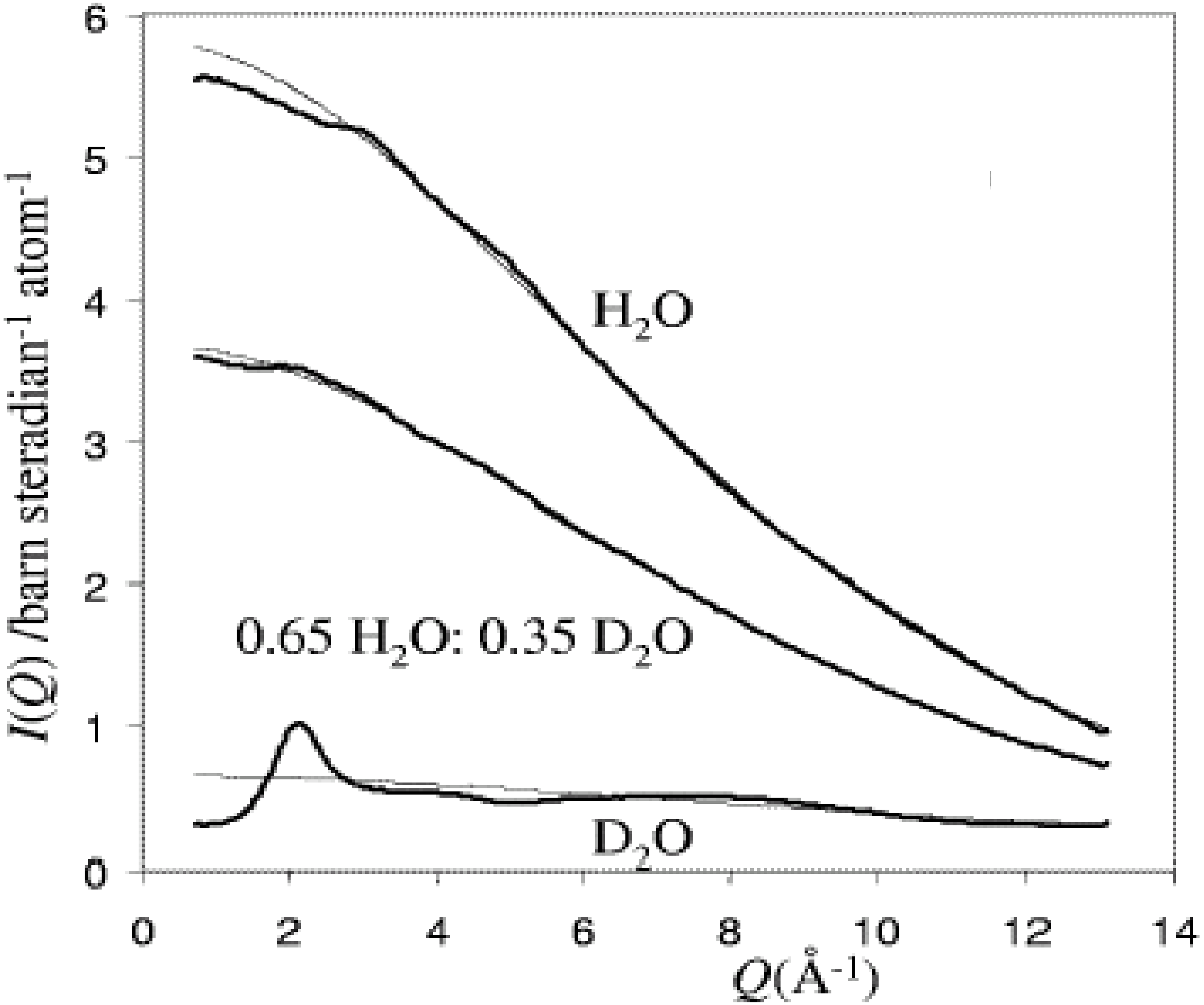
$$\int_Q \epsilon S_s(Q,\epsilon)\, d\epsilon = \frac{\hbar^2 Q^2}{2\mathrm{M}}$$

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

Fixed incident energy plot
E_i = 1eV



Reactor data



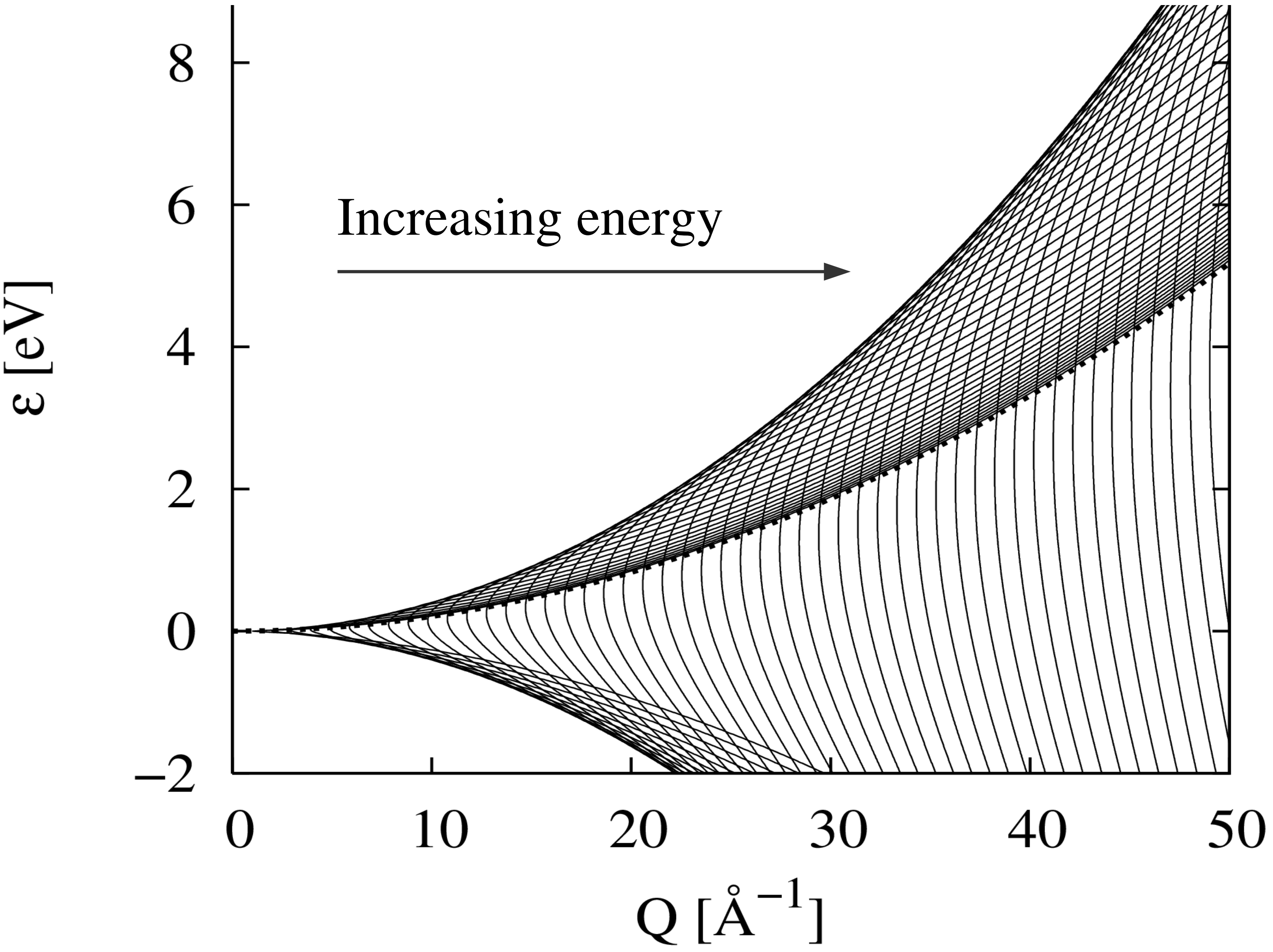
Time of Flight diffraction

- 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:

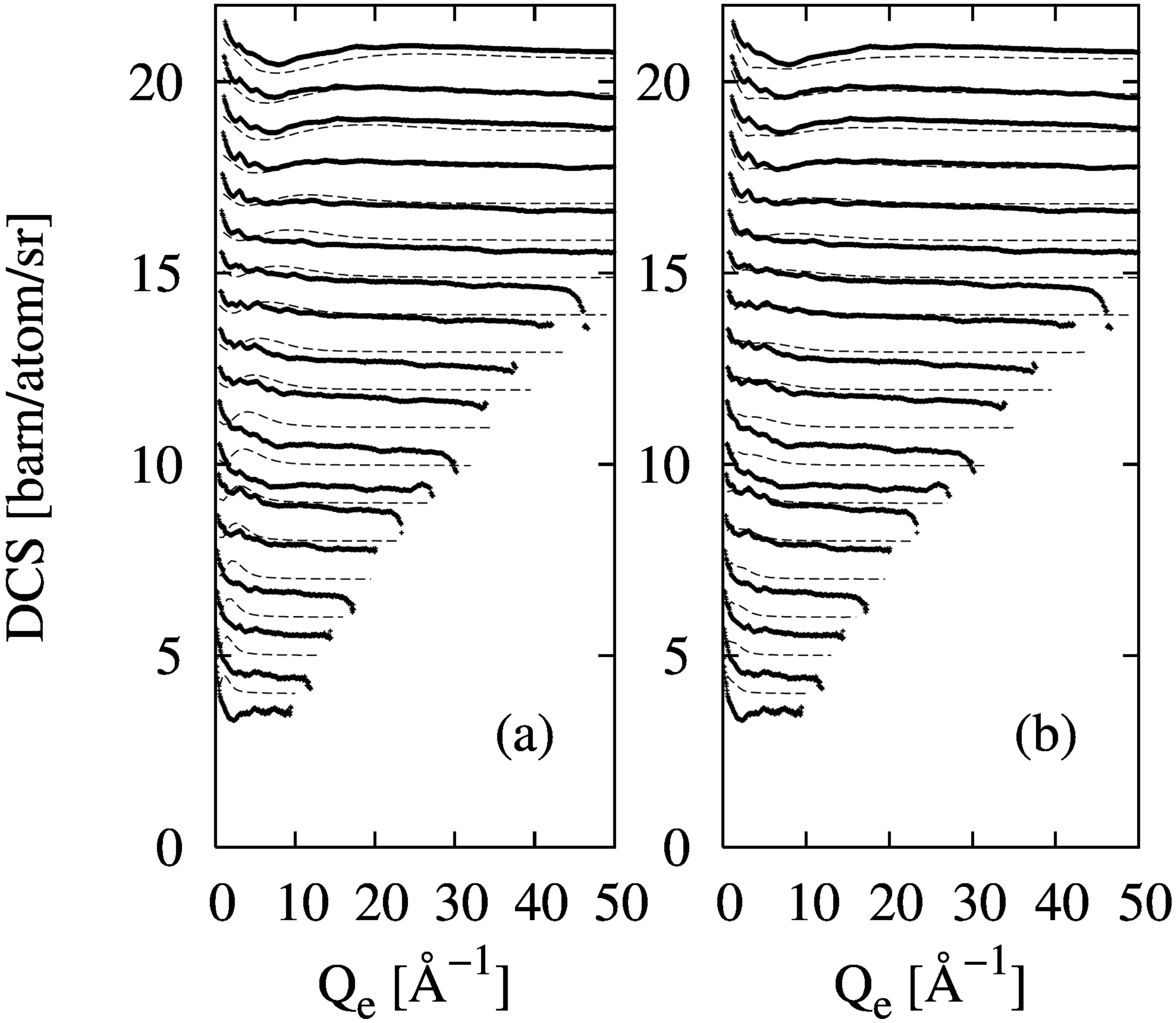
$$\frac{(1+R)}{k_e} = \frac{1}{k_i} + \frac{R}{k_f}, \quad k_e = \frac{Q_e}{2\sin\theta}$$

Constant time-of-flight plots:

$2\theta = 30°$



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.

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

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

$$
\begin{aligned}
d(r) &= \frac{1}{2\pi^2\rho}\int_0^\infty Q^2 F_d(Q)\frac{\sin Qr}{Qr}\,dQ \\
&= \sum_{\alpha,\beta\geq\alpha}\left(2-\delta_{\alpha\beta}\right)c_\alpha c_\beta b_\alpha b_\beta\left(g_{\alpha\beta}(r)-1\right)
\end{aligned}
$$

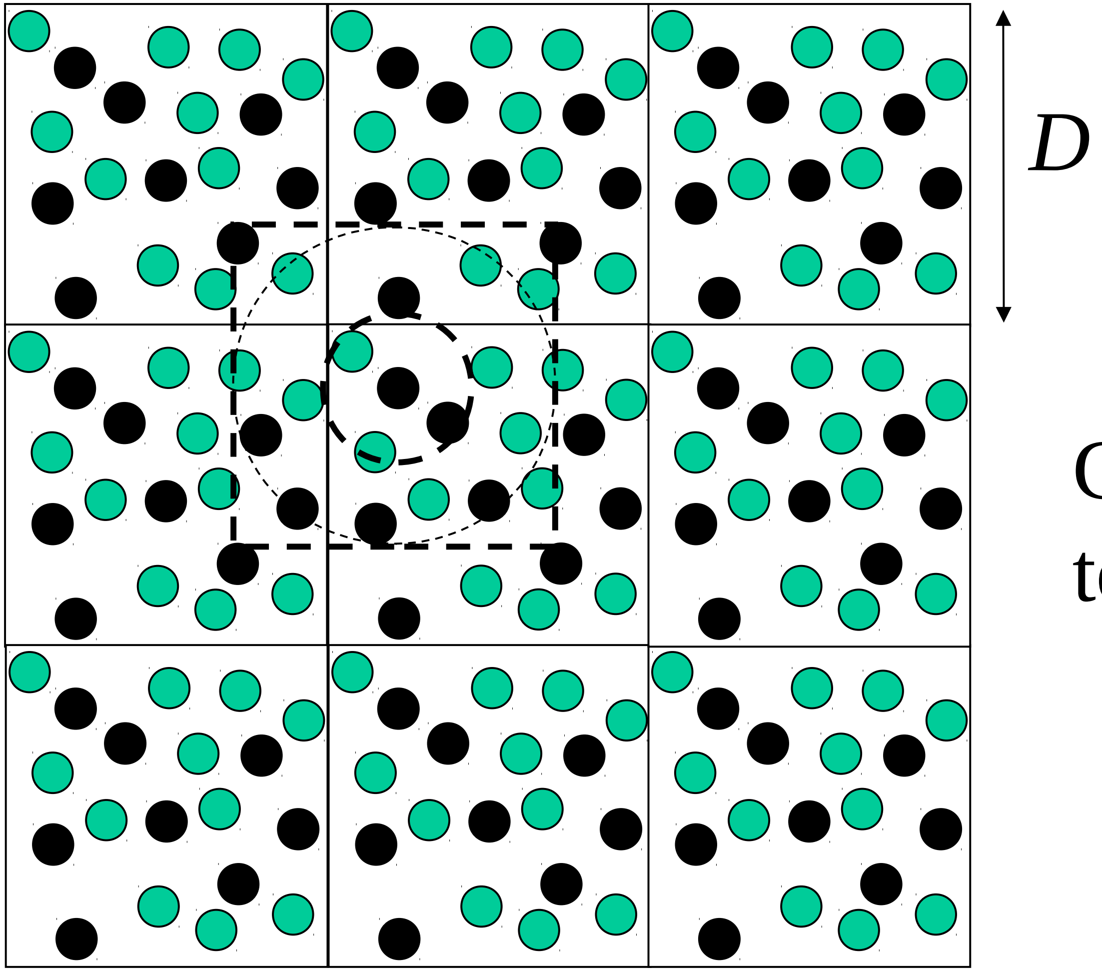
This approach has many limitations...

- 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 ±δ.
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

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

- *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:

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

- 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

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

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

Summary of Lecture

- 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.