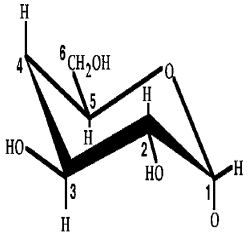
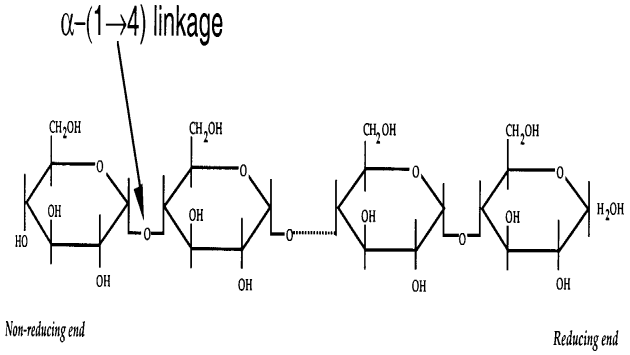
Self Assembly of Polysaccharides in Starch

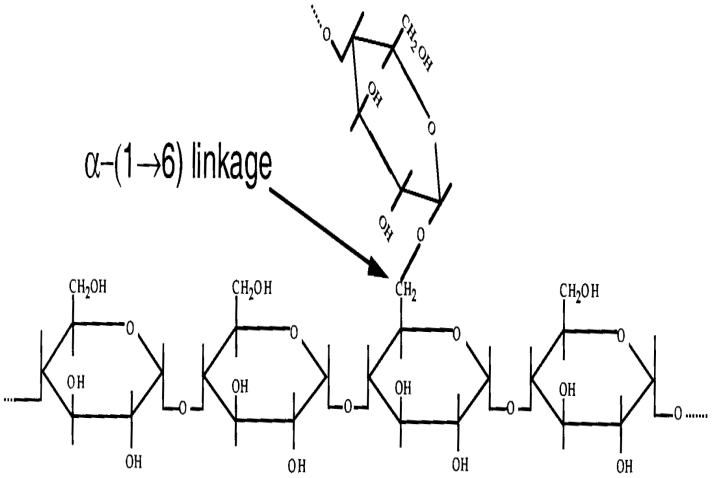
- **Wild type granules contain two main polysaccharides based on the glucose residue (plus other minor components)**



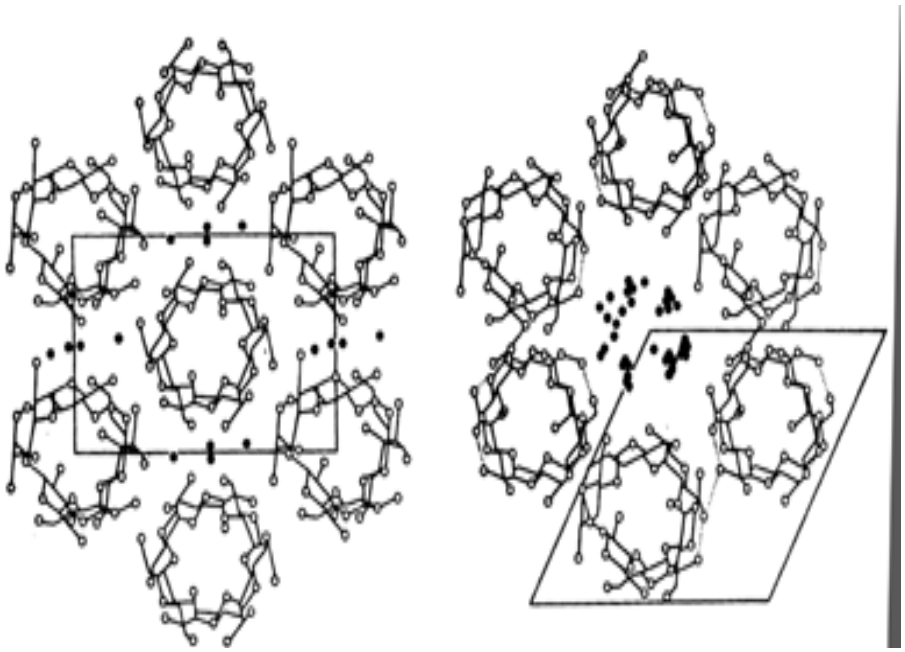
- **essentially linear amylose**



- **branched amylopectin**



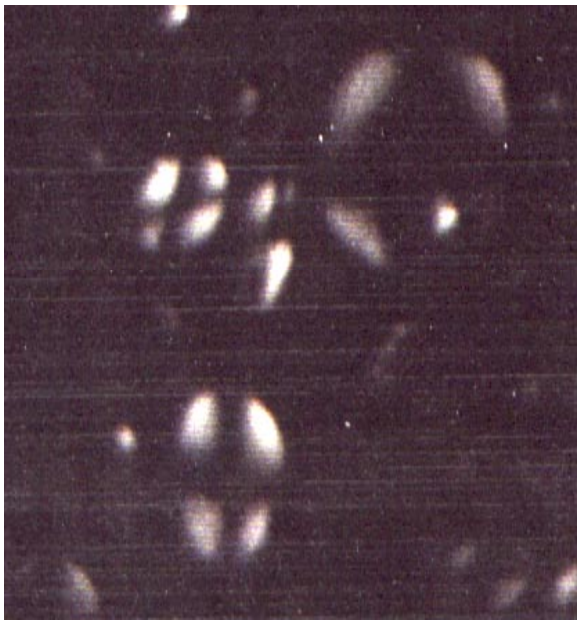
- **Both are very high molecular weight polymers, and their proportions, degree of branching and MW are species dependent.**
- **Waxy mutants (which may be natural!) have no amylose.**
- WAXS shows different polymorphs according to species



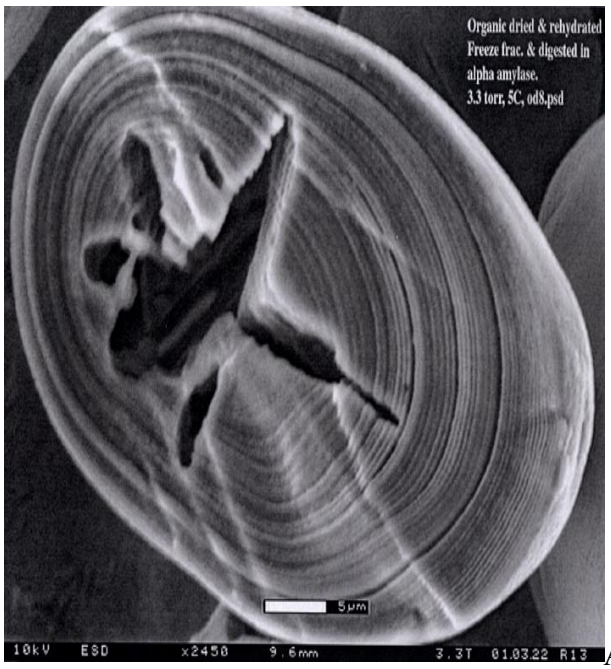
A type (cereals) **B type (potato)**

- **It is the branched amylopectin which forms the crystals.**

Macroscopic Granule Structure

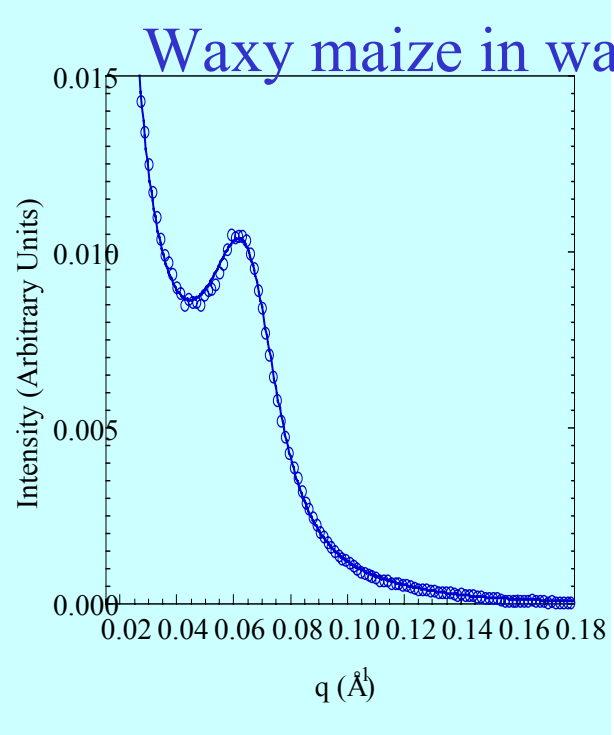


- Granule size is species dependent, in range 5-80μm.
- Birefringent - typically show a Maltese cross structure implying radial orientation of the amylopectin crystals.



- However micrographs of etched granules show a concentric ring structure.

Small Angle Scattering



- **The full scattering pattern can be modelled in terms of a 3 phase model:**

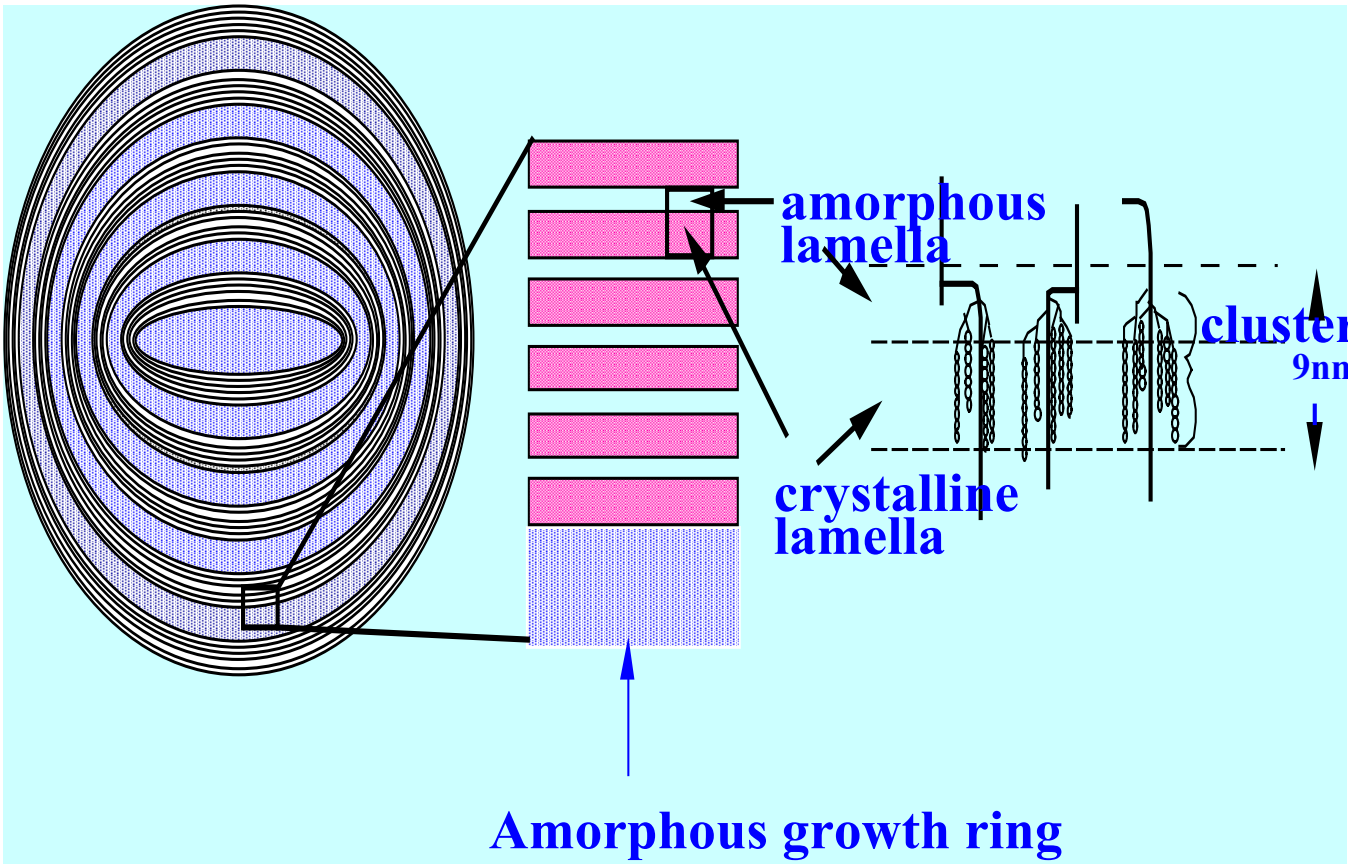
- **Amorphous growth ring - large periodicity giving rise to the upturn in scattering at low q.**

- **Crystalline lamellae - the crystals comprise double helical regions formed from the neighbouring side chain branches of amylopectin.**

- **Amorphous lamellae - sandwiched between the crystalline lamellae where the amylopectin branch points sit.**

Basic Starch Granule Structure

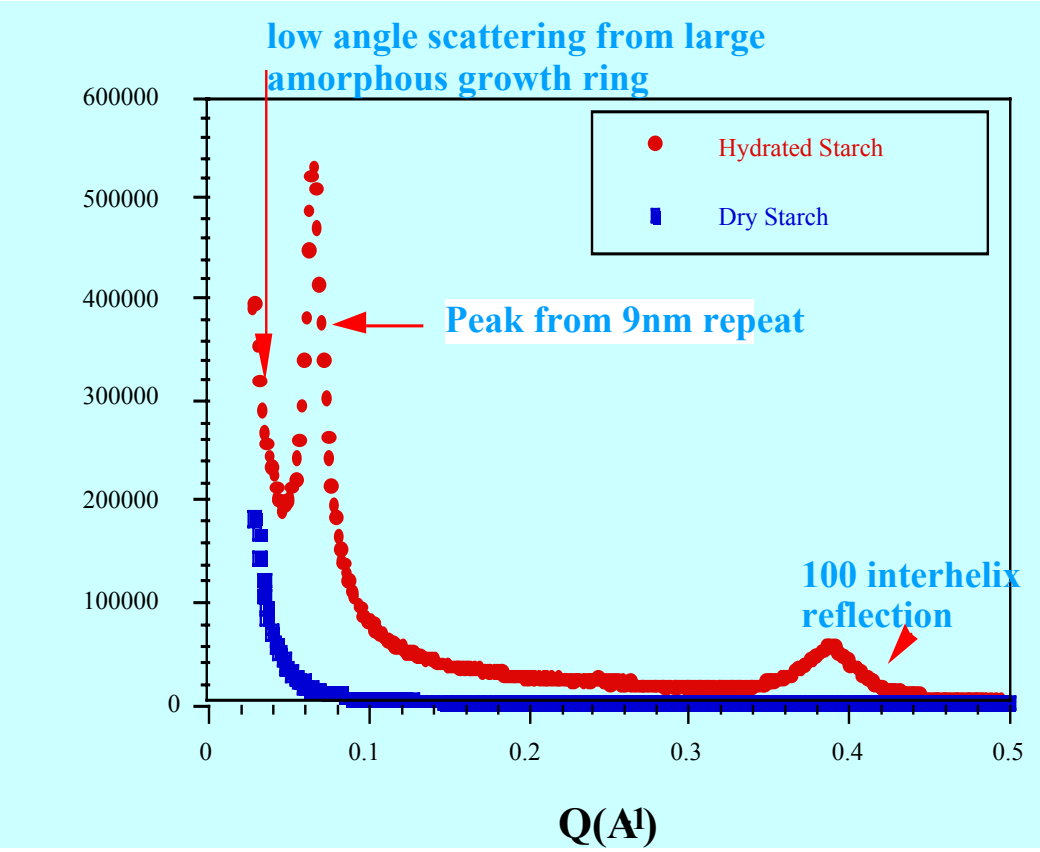
Must incorporate these various different elements of structure.



Summary of the Model

- **This model is derived from small angle scattering data.**
- **In it it is the amylopectin - the branched polysaccharide in starch - which is involved in the crystalline lamellae**
- **The amylose is presumed to sit in the amorphous regions.**
- **This is based on the fact that way mutants show the same kind of crystallinity.**
- **However, the amylose may also interact with the amylopectin, and current work on mutants is exploring this.**
- **Understanding of why the granule lays down alternate amorphous and semicrystalline rings is still poor.**

Small angle X-ray data as a function of water content



- The strong peak at 9nm - arising from the semicrystalline stack - is only present when the starch is hydrated.
- Its disappearance coincides with the disappearance of the interhelix peak.

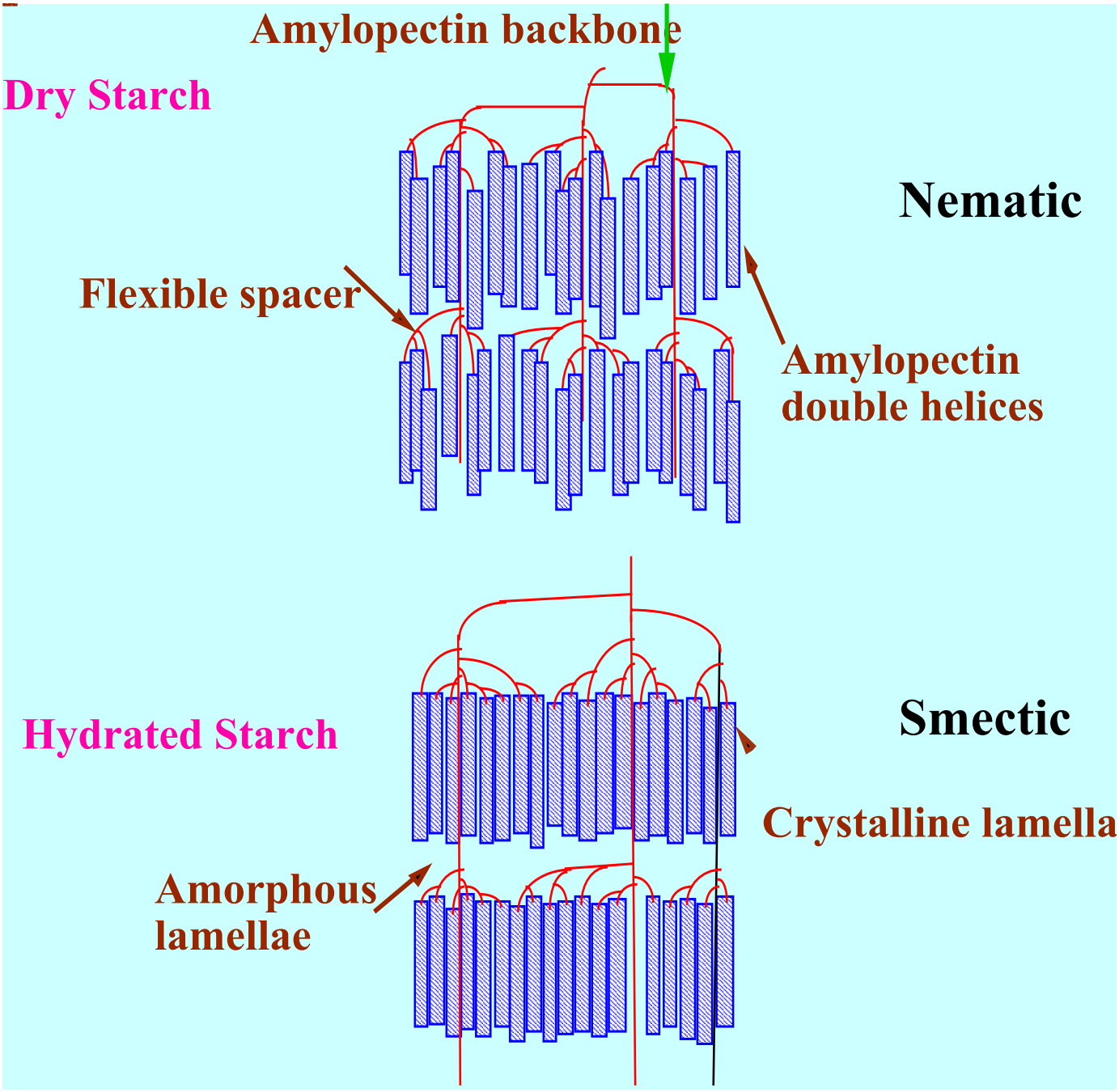
Why do the peaks disappear - and simultaneously?

- Originally it was thought the 9nm peak disappeared due to a 'loss of contrast'.

- But the fact that the 100 interhelix peak disappears simultaneously indicates there is a structural change occurring.
- There is a loss of long range correlation as dehydration occurs.

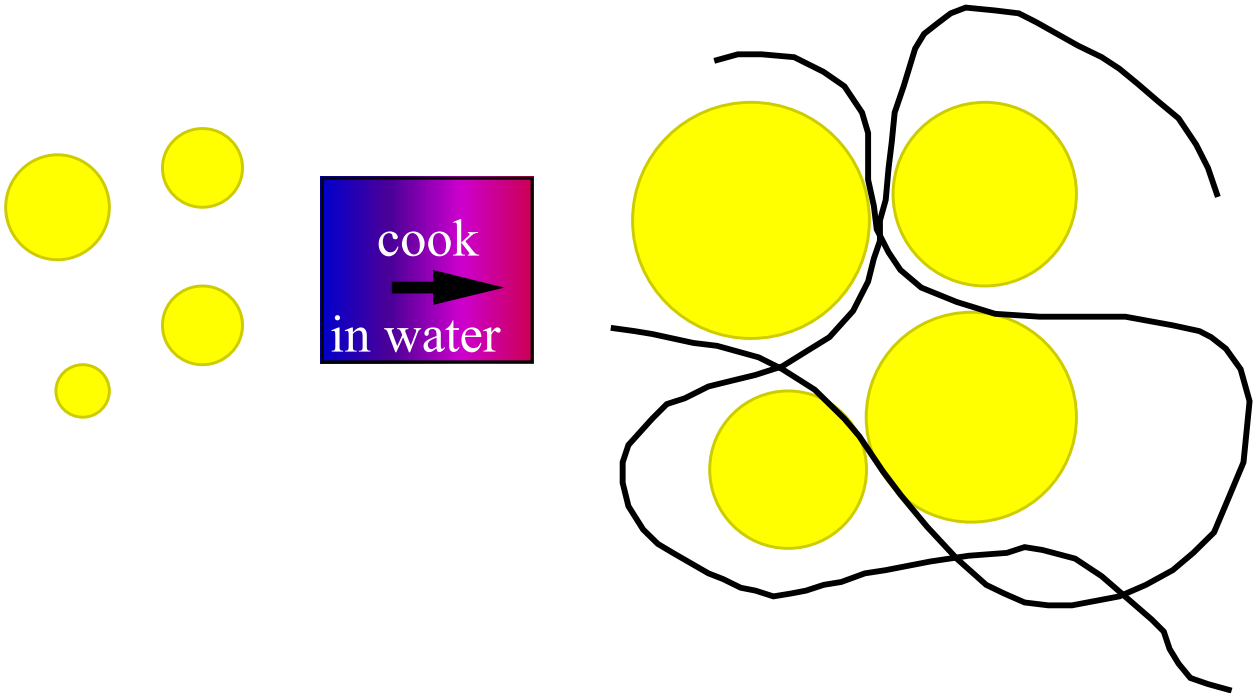
- We have rationalised this within the framework of liquid crystalline side chain polymers.

Amylopectin as a Side Chain Liquid Crystalline Polymer



AM Donald

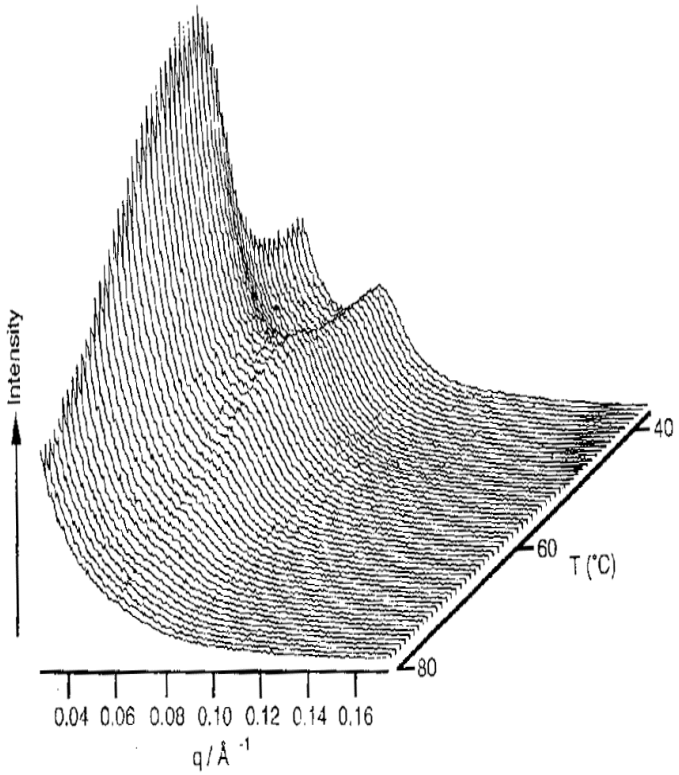
Cooking Starch - Gelatinisation



- **When starch granules are cooked in water two main events occur:**
- **The granules swell**
- **Amylose leaches out.**

These two events lead to a thickening of the solution ie the viscosity increases.
The amylose chains in solution are entangled - so this pushes up the viscosity steeply.

Using Scattering to study Gelatinisation



- **At a synchrotron (Daresbury) simultaneous SAXS/WAXS/DSC experiments can be carried out.**
- **Changes occuring during gelatinisation can therefore be followed.**
- **9nm peak does not shift in position – swelling of the semicrystalline stack cannot be occurring.**
- **But there is a large increase in low q scattering, consistent with changes in the amorphous growth ring.**

Complementarity of SAXS with SANS

X-rays

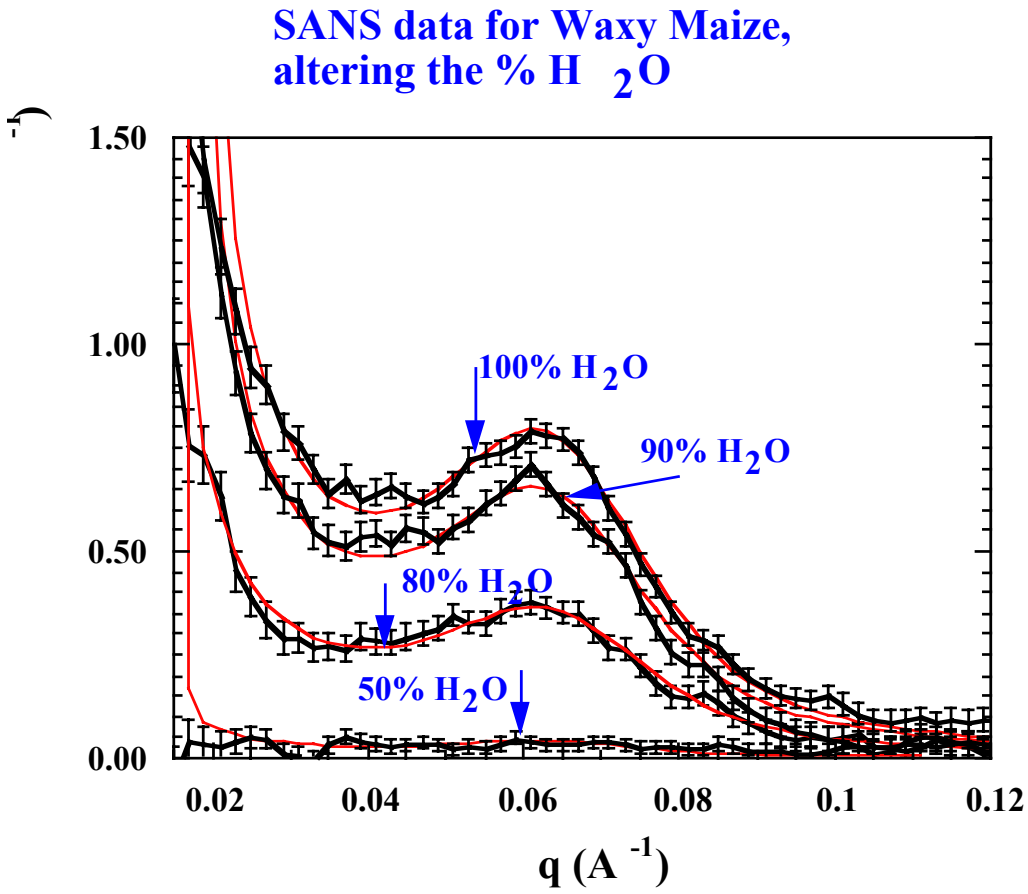
- **X-rays scatter off electron density differences.**
- **These may arise from packing considerations (eg crystal/amorphous regions), or from atomic number differences.**

Neutrons

- **Neutrons scatter from differences in scattering length density.**
- **The differences between hydrogen and deuterium are particularly useful to exploit, and will give larger effects than simple differences in packing.**

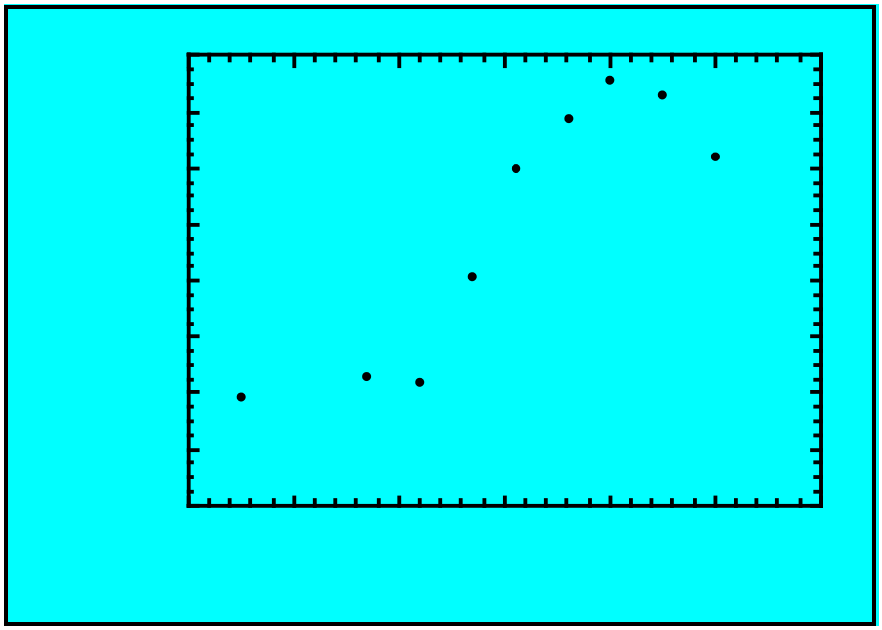
Thus the two methods are sensitive to different aspects of the structure of a sample, and by combining data from the two approaches complementary information can be obtained.

Contrast Variation SANS

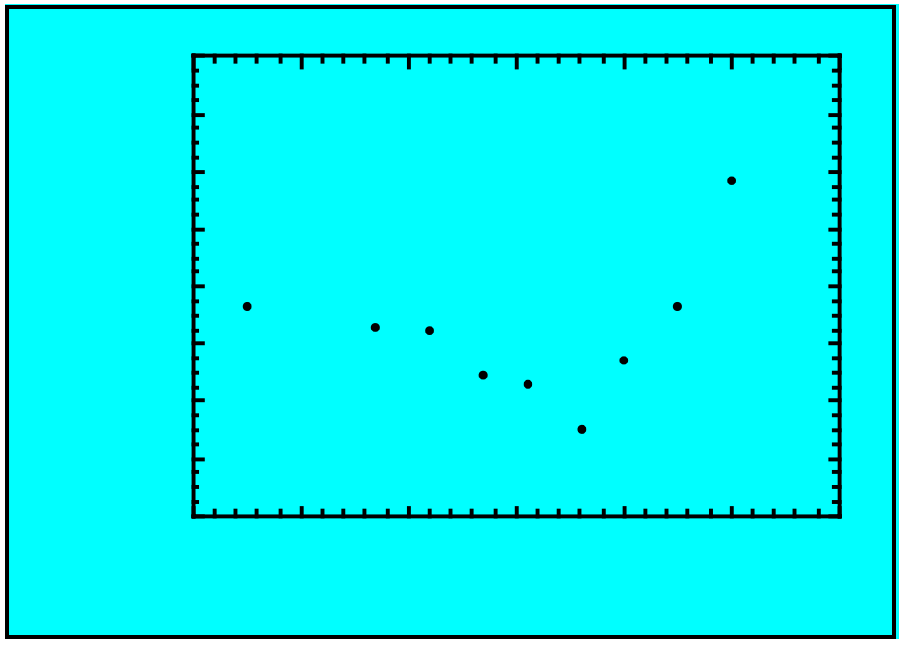


- **By soaking the granules in water with different levels of heavy water, an additional parameter becomes available to fit the scattering curves.**
- **This enables us to quantify the amount of water in different regions of the granule.**

SANS on waxy maize during gelatinisation



Amorphous growth ring shows water uptake well below peak in gelatinisation temperature.



Conversely , crystalline lamellae show little change inititially followed by disruption at higher temperatures.