Clays and Microrheology

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Geoff Maitland at Schlumberger - Colloid Physics

- I first met Geoff when he was at Schlumberger
- A large DTI grant on Colloid Physics was awarded to Cambridge, Bristol and Imperial involving Unilever, Schlumberger, ICI and Zeneca.
- This ran from 1992 -7
- Thereafter I held a series of studentships and other links while he remained there.

Environmental Scanning Electron Microscopy (ESEM)

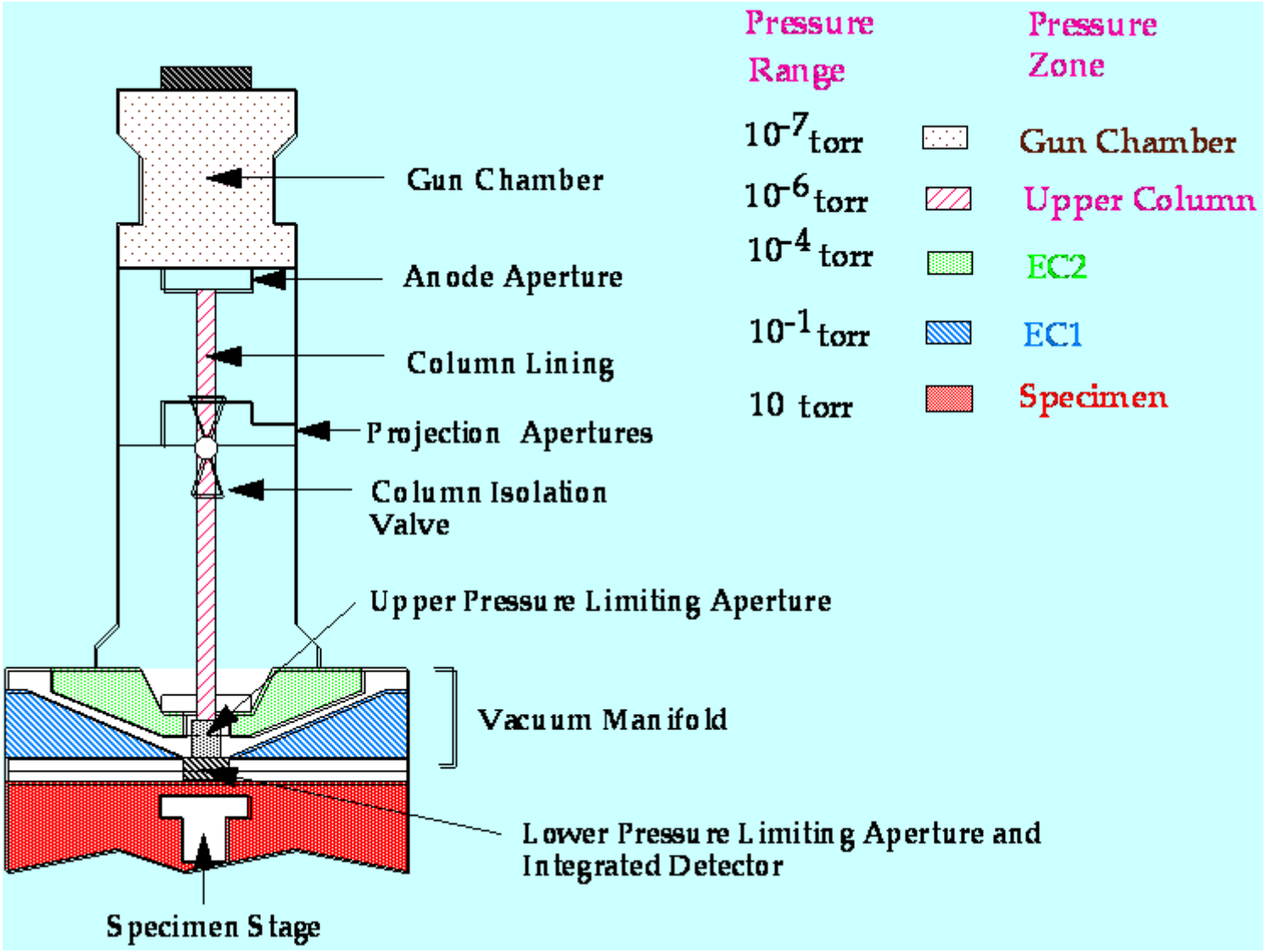
- The colloid grant was set up to study generic problems in colloids, which could be relevant to the range of industries involved.
- At that time a new kind of microscope was just hitting the market, targetted at being able to image wet systems – the ESEM – and this seemed an ideal instrument to purchase under the grant (which had the luxury of about £1M capital attached, at 1992 prices).
- It turned out to be a lot more challenging than I'd expected, because the instrument manufacturers were fairly naïve.
- So, things got off to a slow start, but within the 5 years of the grant, we were able to work well with Schlumberger, notably on the hydration of cement (and its components).
- Much of the time was, however, spent in understanding what the instrument was and wasn't able to do!
  (The manufacturers certainly didn't understand)

Difficult Sample Types for Conventional SEM

- Insulators: a coating needs to be applied. FEG instruments have significantly improved the situation.
- Wet and hydrated samples: problem usually overcome by sophisticated routes for sample preparation eg cryo.
  These risk introducing artefacts during sample preparation.
- Study of in situ reactions - very difficult, some scope with special environmental chambers.

- ESEM can cope with all these types of problems!

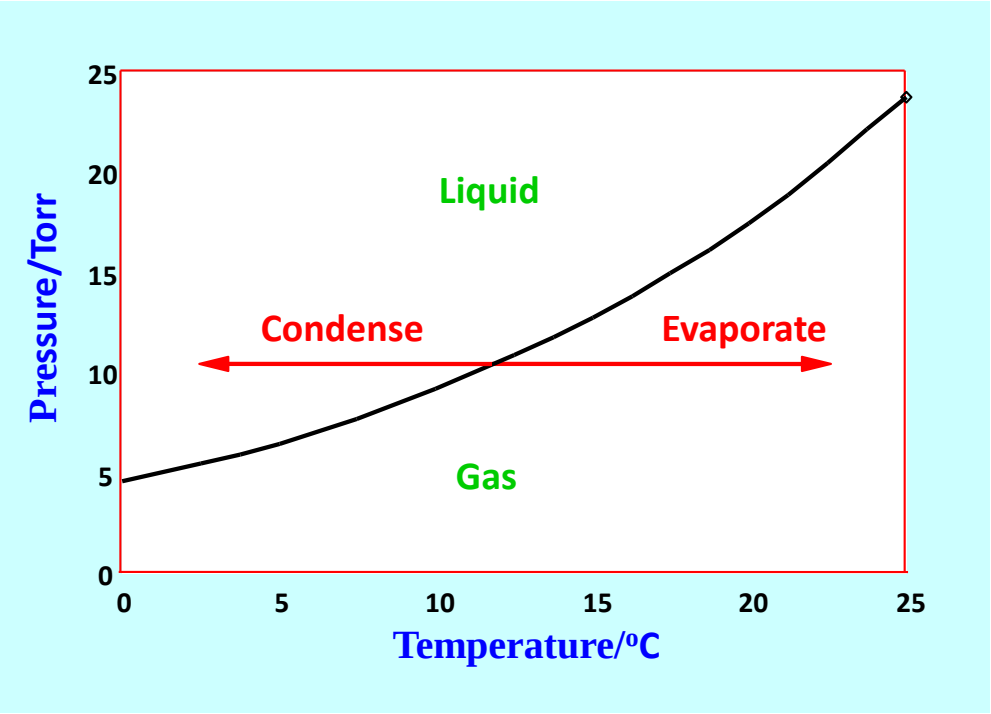
Basic Design of ESEM



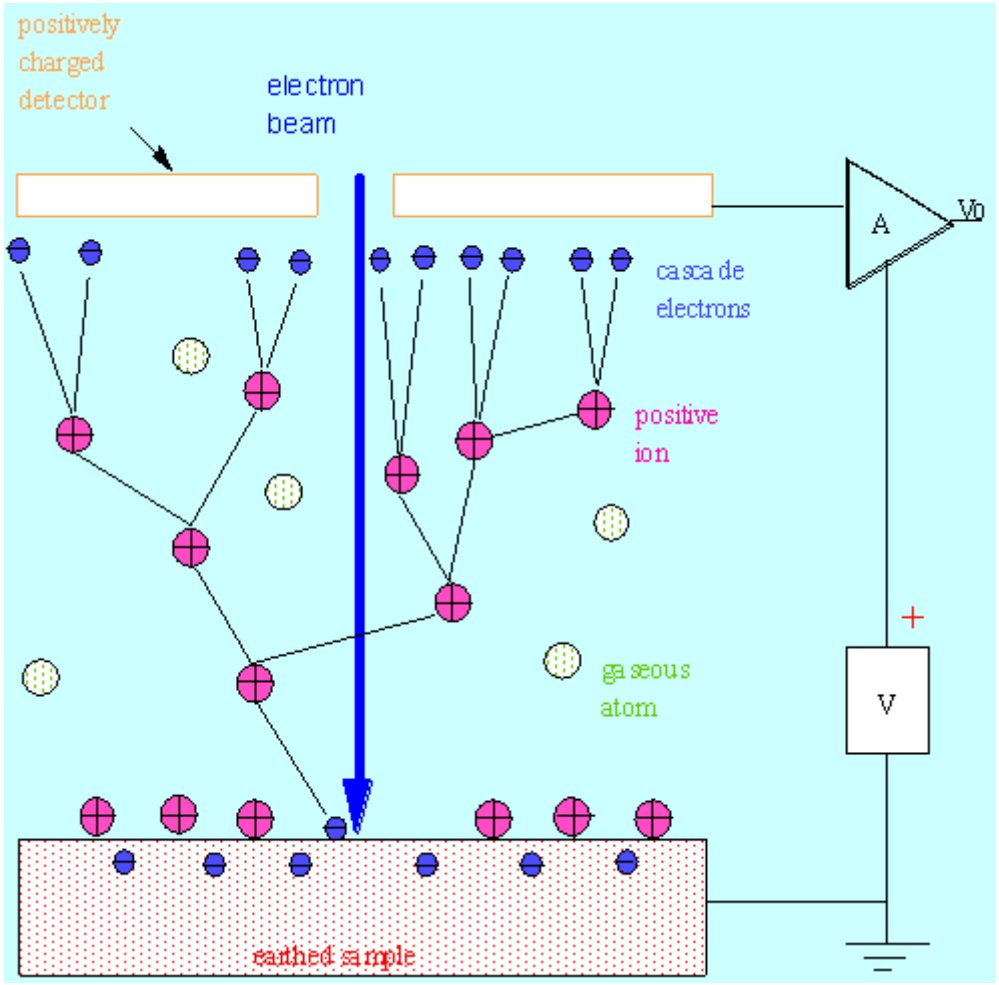
ESEM compared with other Low Vacuum SEM's (LVSEM's)

Most LVSEM's cannot operate with SVP of water vapour in the sample chamber, severely limiting the ability to image hydrated samples.

Even in the ESEM one has to work at sub-ambient temperatures via a Peltier chip controlled stage.



Role of the Ions - Cascade Amplification

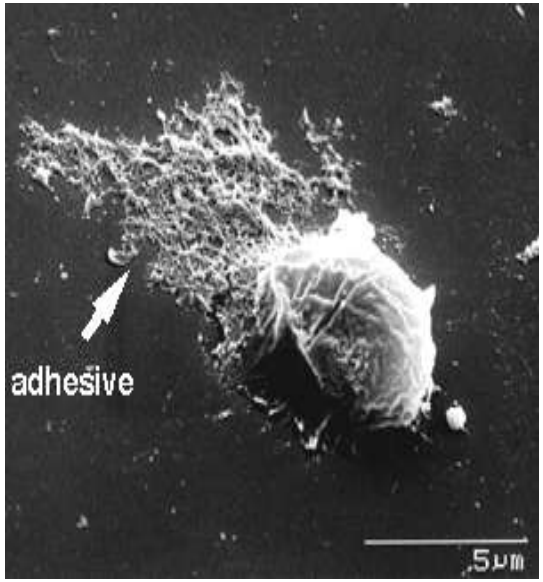


- Secondary electrons can ionise gas molecules, producing a cascade of daughter electrons.
- Positive ions may drift back towards the sample surface.
- These help to compensate the build up of charge, and remove the need for conductive coatings on insulators.
- However their role is still not completely understood.

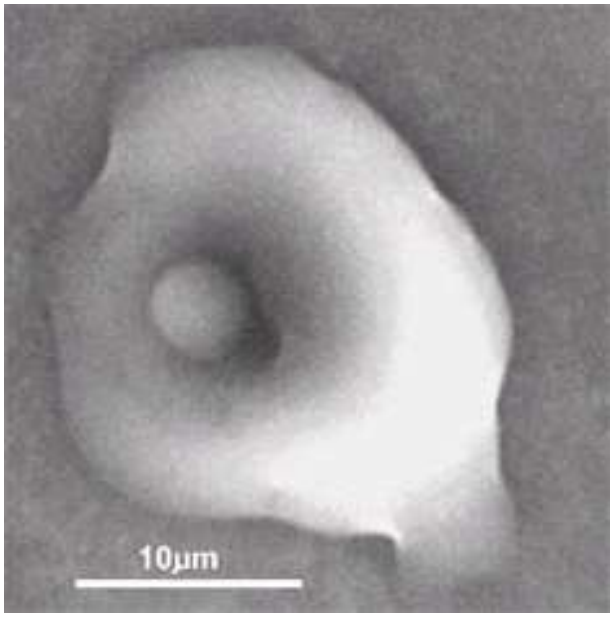
Impact of Removal of the Vacuum Conditions

- The range of samples that can be imaged is enormously extended.
- Hydrated samples can be imaged in their native state.
- And the level of hydration can also be altered.
- Even liquid dispersions can be imaged.
- Biological samples can also often be imaged without fixing, drying etc.
- All this substantially reduces the risk of artefacts being introduced.
- The presence of the gas also reduces the usual problem of charging of insulators.
- Thus they no longer need to be coated, avoiding covering up fine surface detail.

Avoiding Artefacts: Example - *Enteromorpha* Spores



Conventional SEM of fixed and dried spore of *Enteromorpha;* adhesive pad looks fibrillar.

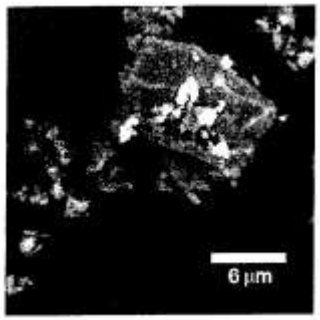


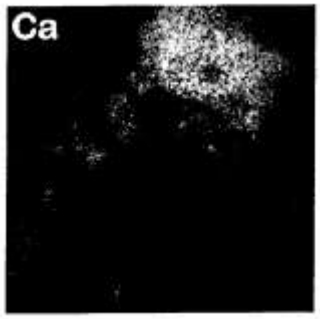
Hydrated spore, showing that adhesive pad is not really fibrillar, but appears to be structureless.

Prof Jim Callow, University of Birmingham

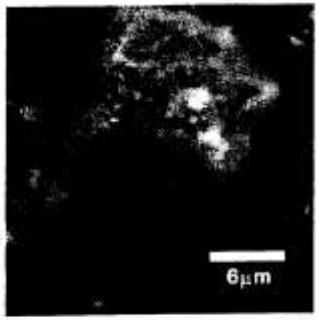
JA Callow, MP Osborne, ME Callow, F Baker and AM Donald – 2003. Coll and Surf B 27 315-21.

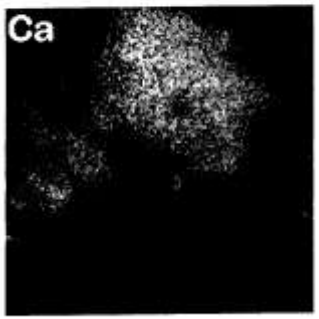
Elemental Distributions - EDX Maps





Dry C_3S



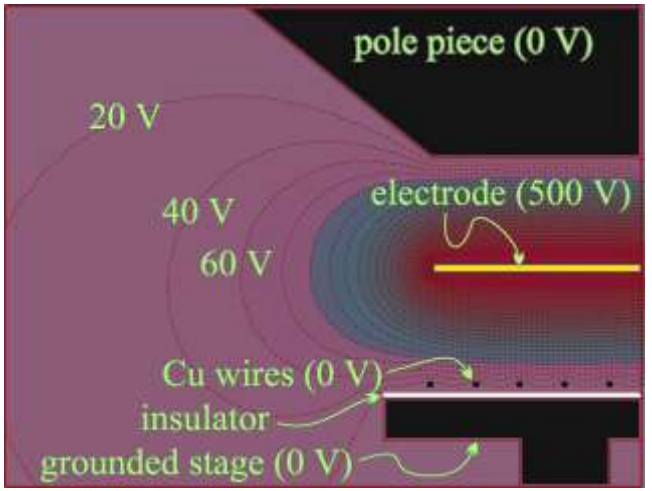


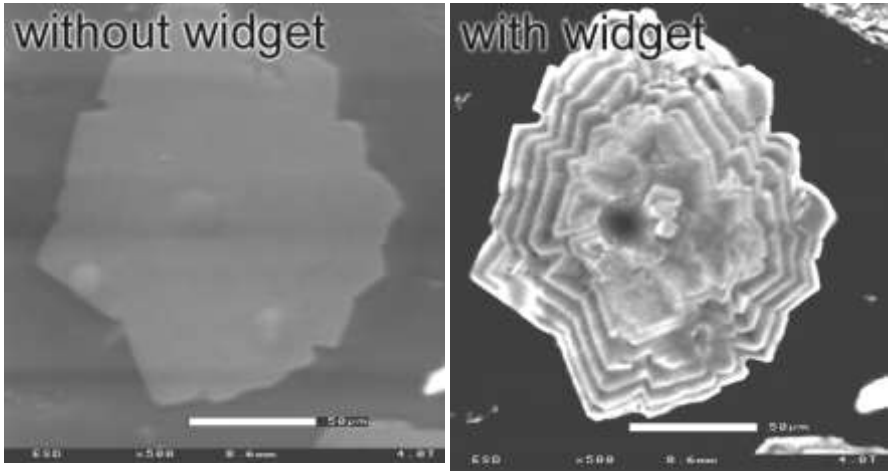
Hydrated

- It is in EDX mode that the presence of the skirt is most deleterious.
- It is less of a problem for maps.
- However, in point mode, X-rays from far away in the skirt can be most misleading, and make quantification all but impossible.

Effects of SE-ion Recombination on SE Contrast

- Emitted secondary electrons can interact with ions.
- Their field can enhance emission BUT also
- Combination of ions with SE's can reduce collected signal.
- By introducing a "widget" – a device placed above the sample to pick up the ions –contrast can be significantly enhanced for many specimen types (insulators).

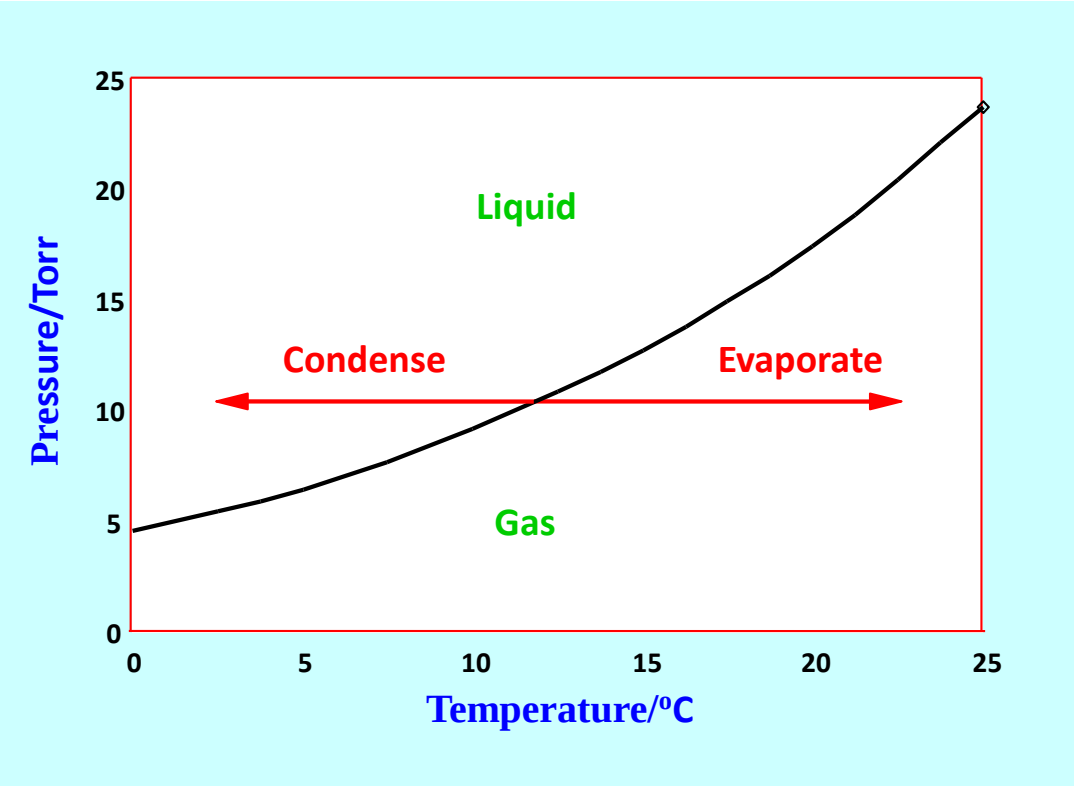




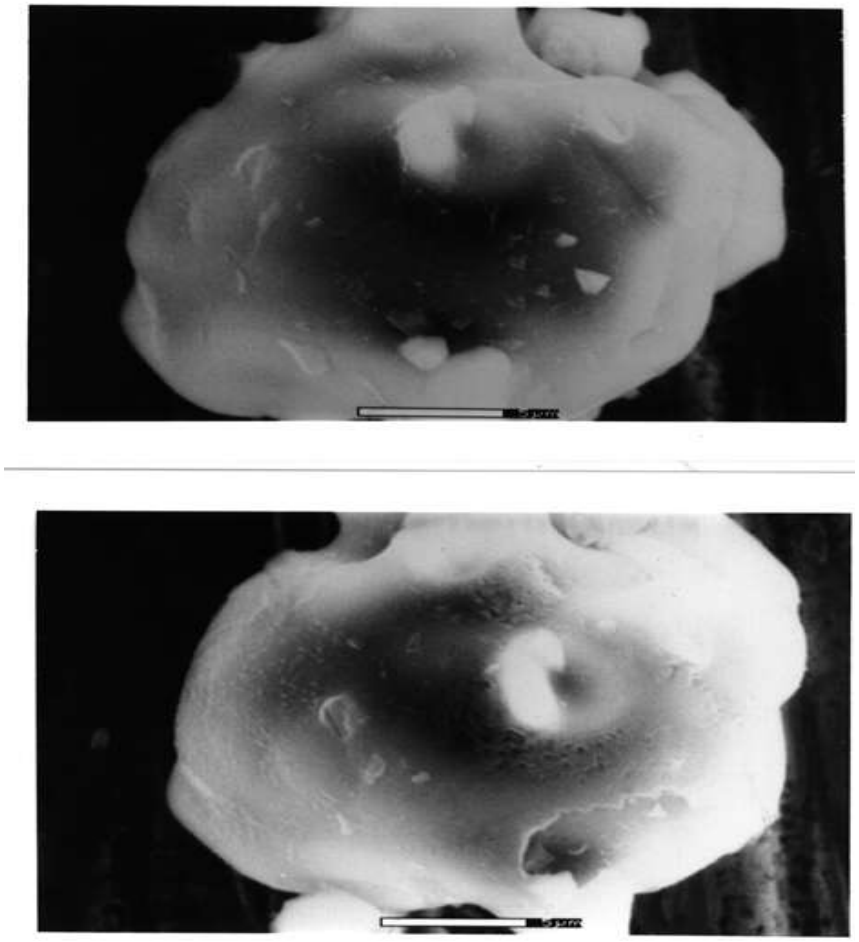
Gibbsite [20 kV, 4 torr, 3.1 mm, 2.1 fr./sec]

Dynamic Experiments in the ESEM

- Dynamic experiments can be carried out by changing the vapour pressure.
- This allows you to cross the line from condensation to evaporation (or conversely).
- Hence drying films (as in paint) or hydrating powders (as with cement and its constituents) can readily be carried out.
- In principle this can also be done by changing the temperature; in practice this is much less controllable.



In situ Chemical Reactions- Hydration of Cement and its Components

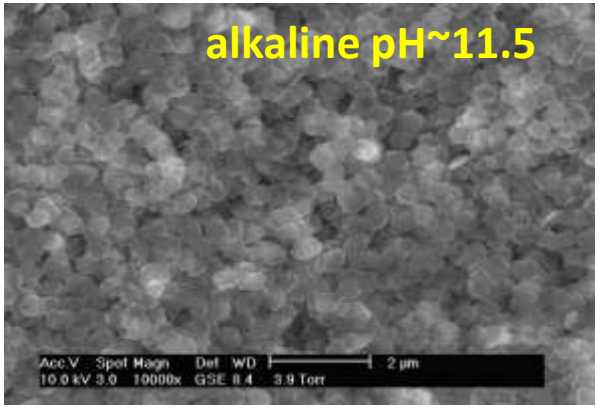


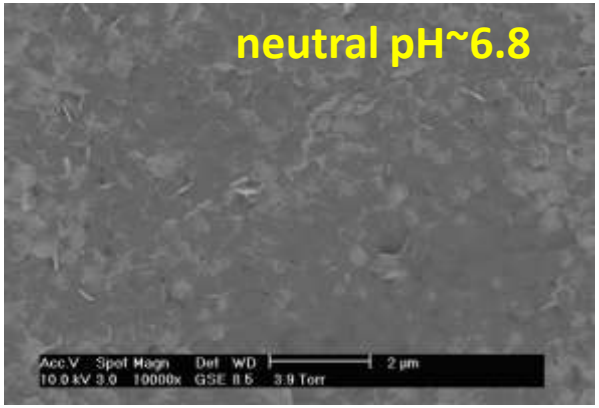
- Hydration of C_3S (calcium trisilicate) shows the formation of a semi-permeable membrane, previously hypothesised to exist to explain the dormancy period observed by calorimetry.
- After only 1 minute exposure to water, this membrane can be seen covering an individual particle.

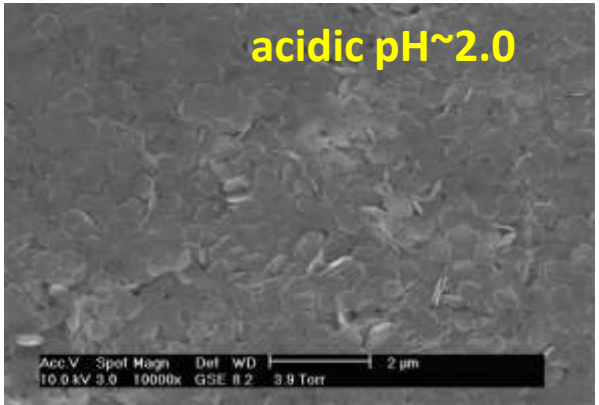
P Meredith, AM Donald and K Luke - 1995 - J Mat Sci. 30 1921-1930.

Packing in Synthetic Gibbsite

- Synthetic gibbsite came from Henk Lekkerkerker's group
- Surface structure was studied by allowing evaporation of water from dispersions with different pH
- This has permitted inference to be made about platelet interactions under different conditions.

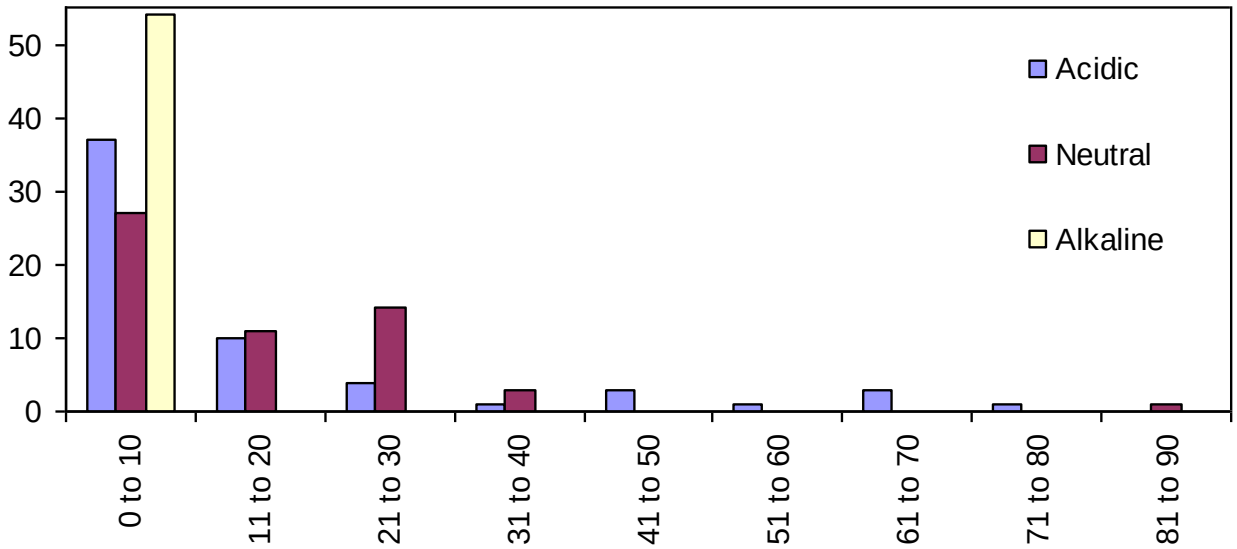






HA Houghton and AM Donald – 2008. Scanning 30 223-7

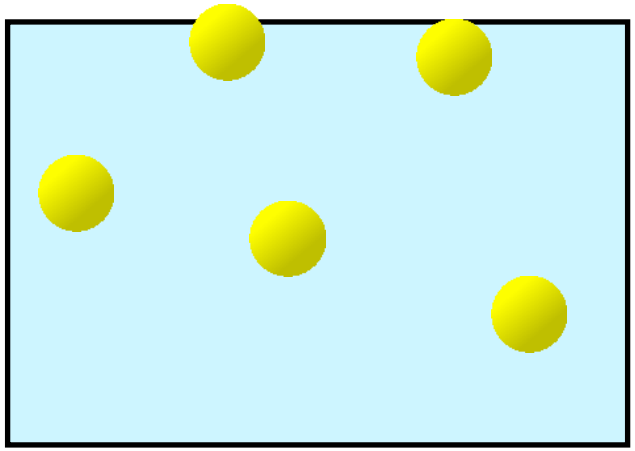
Clays – Gibbsite (synthetic)

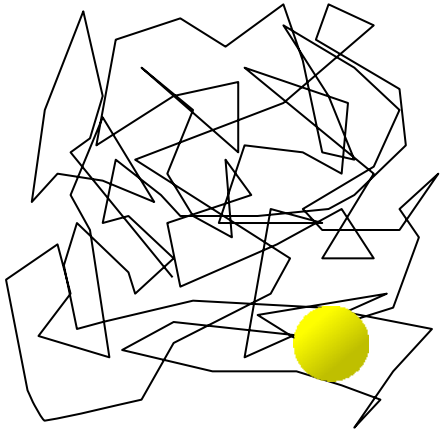


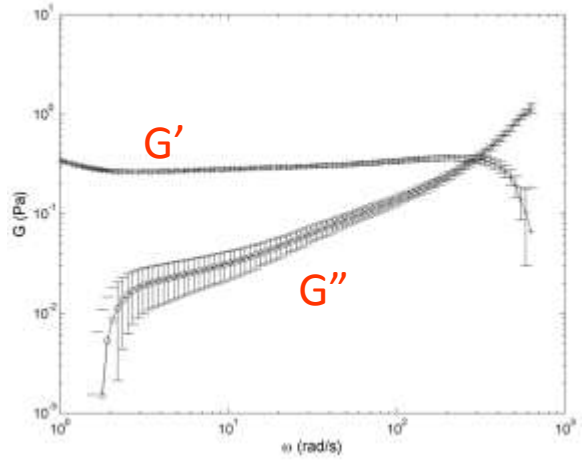
- In the alkaline sample relatively few plates stand edge on, as compared with the acidic and neutral samples.
- This can be quantified by counting number of edge-on plates in each sample type (9 fields of view, separated by 200μm).
- Given charge on face and edges of gibbsite, expect edge-face interactions to dominate for pH < 10.
- Drying tends to cause plates to come together edge-to-face, but less so at alkaline.

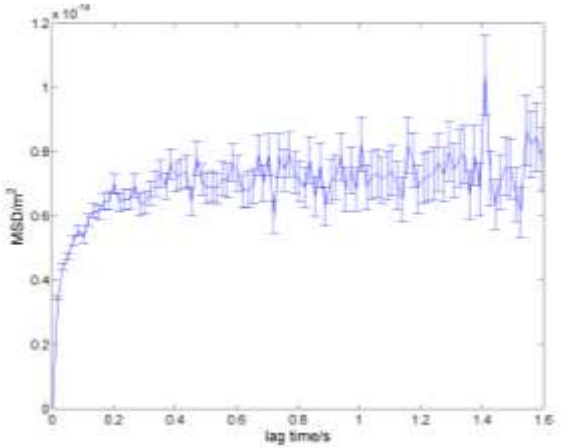
HA Houghton and AM Donald – 2008. Scanning 30 223-7

Microrheology – a Means to Study Local Viscoelastic Properties: Particle Tracking

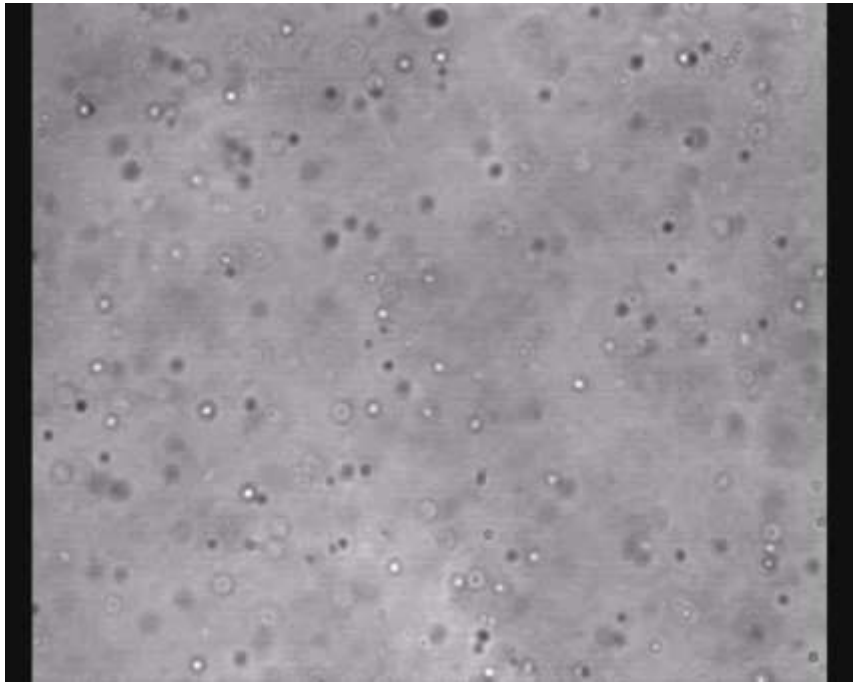


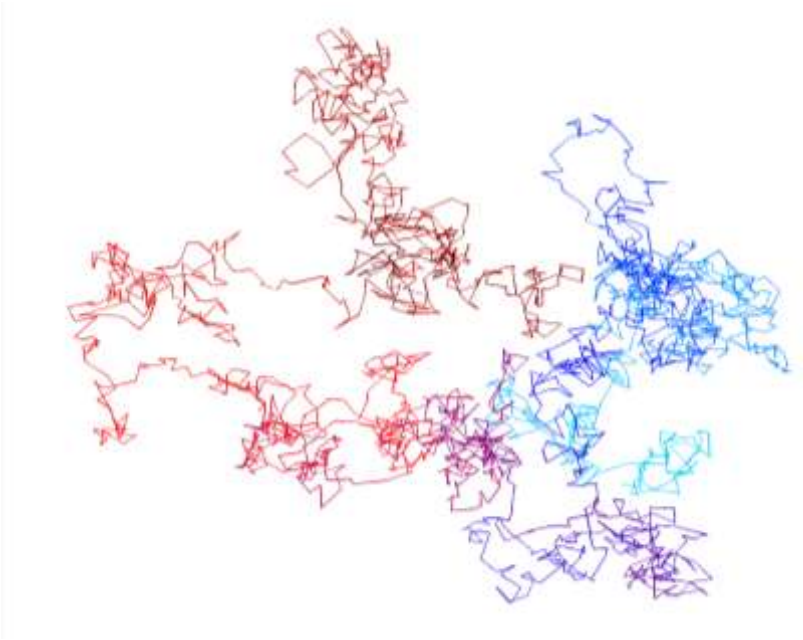




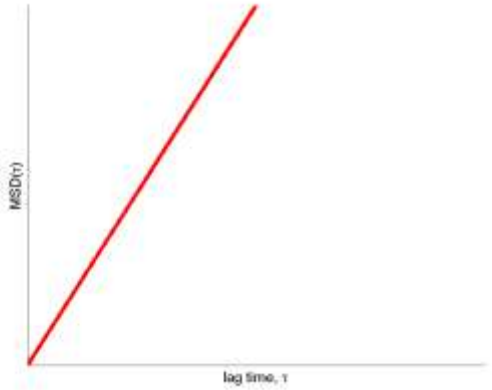


Example – Viscous Fluid

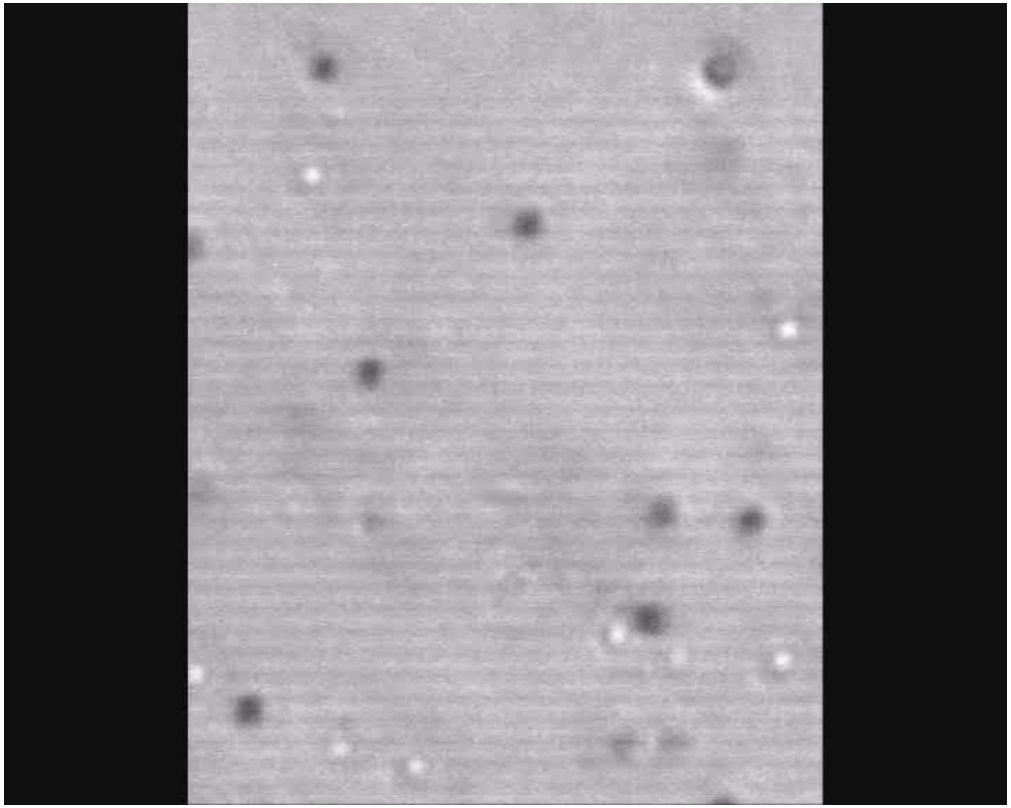


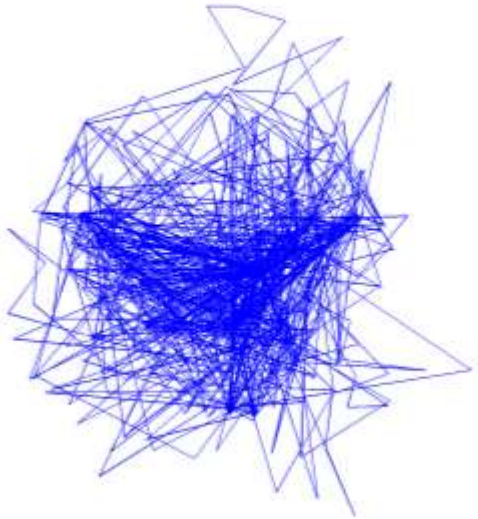


Mean squared displacement (MSD) is linear with time

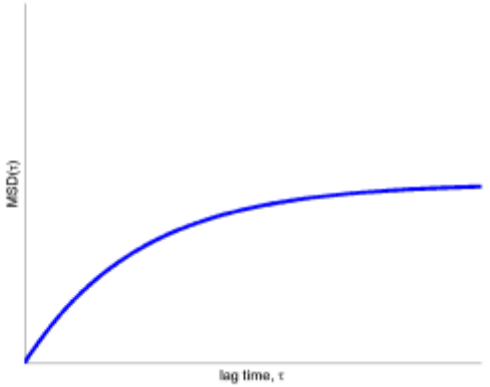


Example – Weak Gel

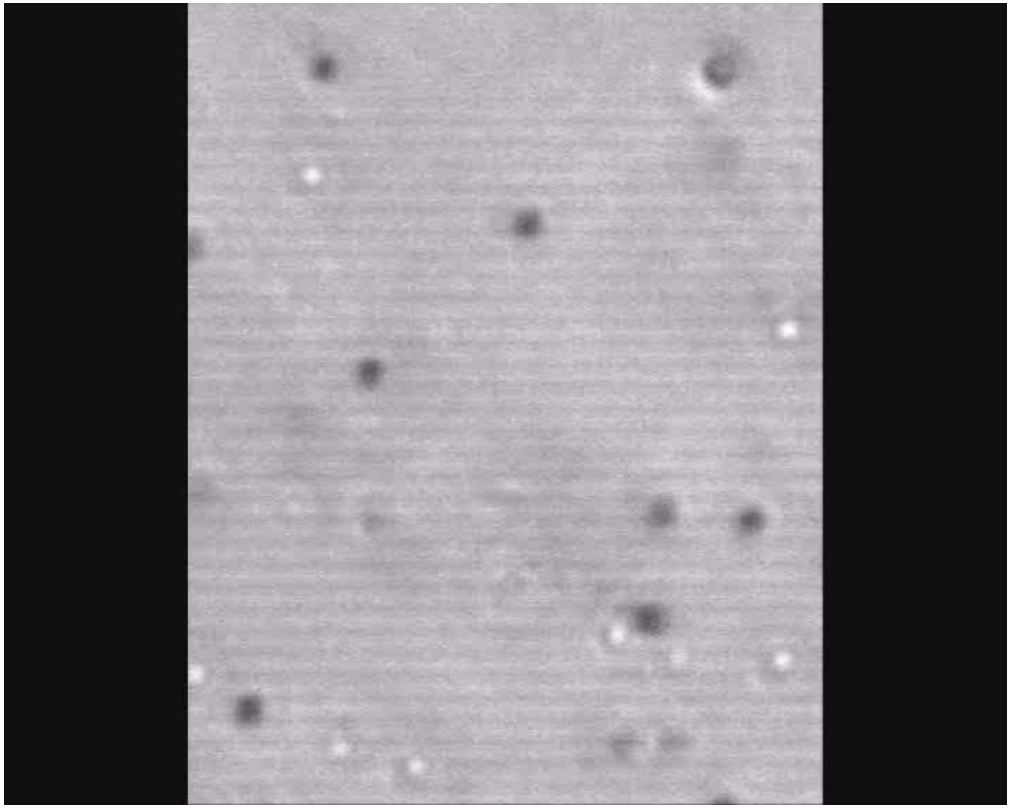


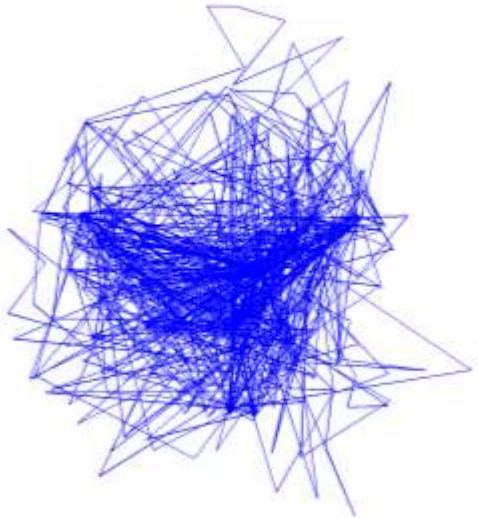


MSD increases initially, but once the displacement exceeds the ‘mesh’ size, it plateaus



Example – Weak Gel





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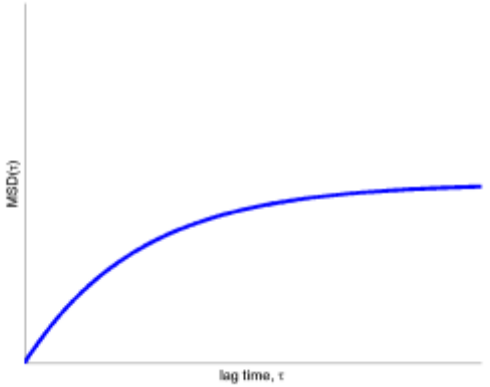
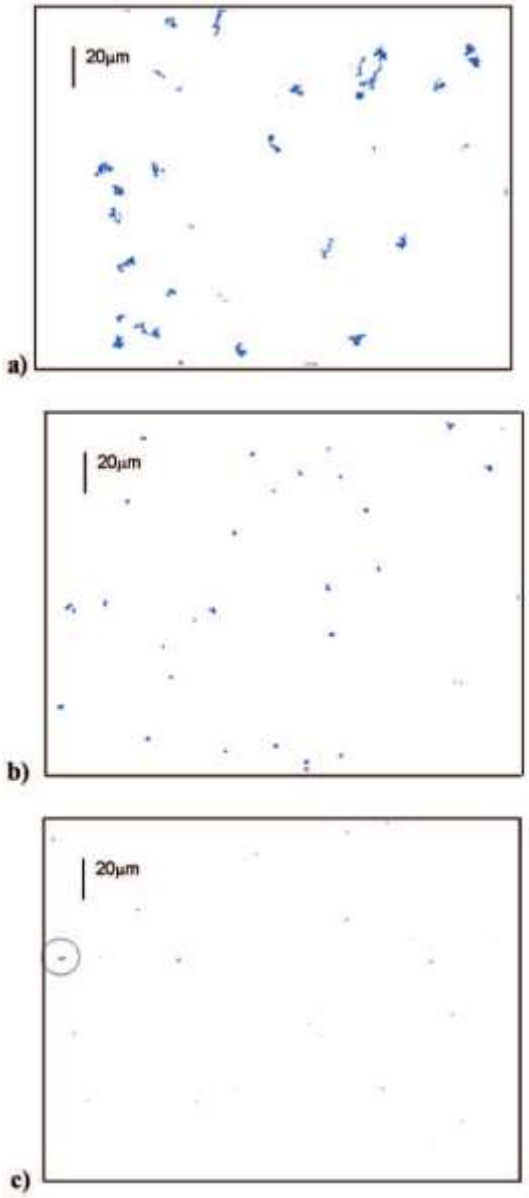


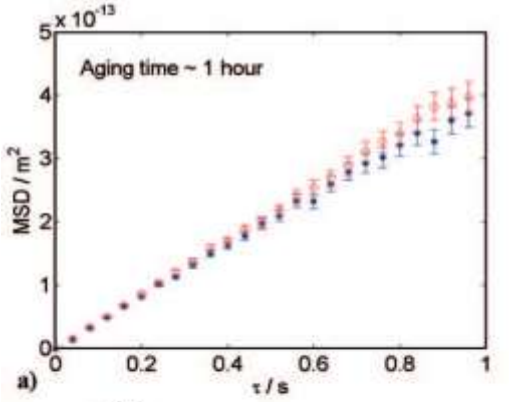
Time Evolution of Hectorite

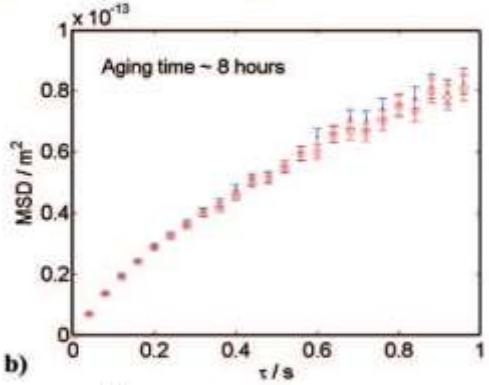


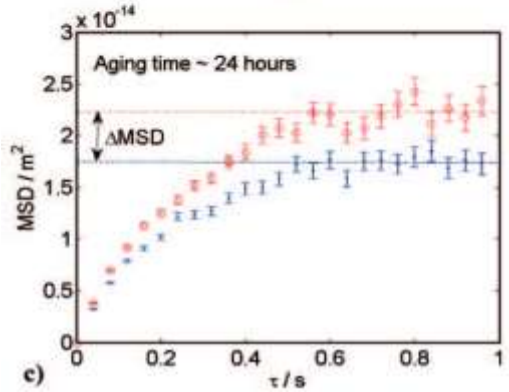
- Lines on these plots indicate the paths of tracked particles in hectorite (ρ = 1.0008 g/cm^3) over the course of a one-minute video recorded at ageing times of approximately a) 1 hour, b) 8 hours and c) 24 hours.
- Each plot represents the camera field of view.
- As the sample ages the tracer particle motion is significantly reduced.
- The circle in c) highlights a tracer particle displaying more motion than other particles.

HA Houghton, IA Hasnain and AM Donald, - 2008. EPJE 25 119-127.

Development of MSD in Hectorite

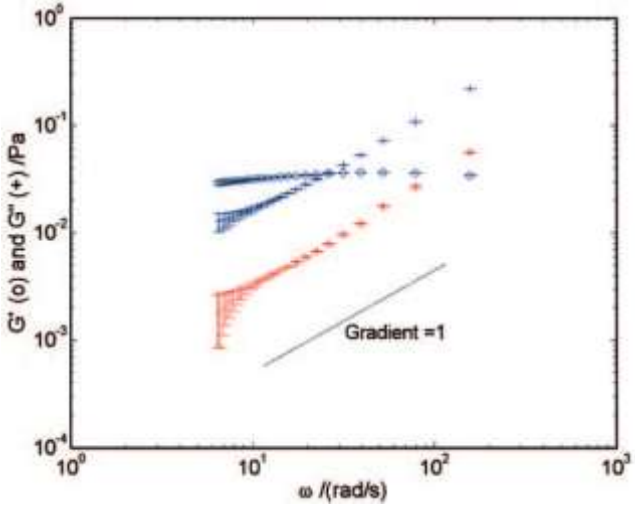






- The one dimensional MSD is plotted as a function of lag time (ρ = 1.0008 g/cm^3)
- For each lag time the MSD is plotted for the two perpendicular directions corresponding to the maximum (red) and minimum (blue) displacement axes found.

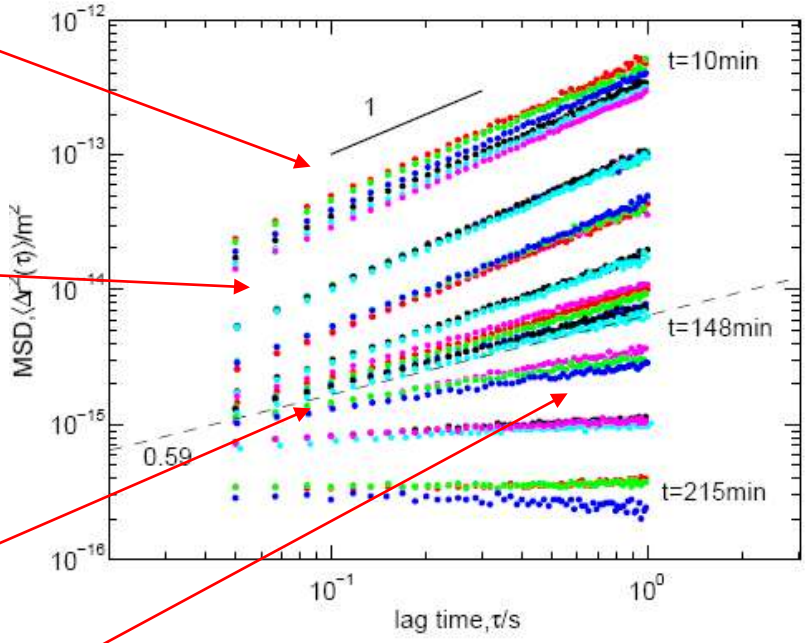
Viscoelastic moduli calculated from Generalised Stokes Einstein equation for sample after 20 minutes (upper two curves) and 24 hours ageing (lower); the plots are for *G* ( ) and *G* (+).



HA Houghton, IA Hasnain and AM Donald, - 2008. EPJE 25 119-127.

Pushing the Analysis Further: Using Beta Lactoglobuilin Gelation as Model

- At early times have a viscous fluid: $\left\langle \Delta r^2(\tau) \right\rangle = A\tau$
- As incubation proceeds, at short times MSD becomes sub-diffusive, but diffusive at longer t because there is a high frequency elastic component which can rapidly relax
- At longer times reach a point when MSD sub-diffusive for all t
- This is the gel point.
- Beyond this start to develop a plateau as particles become 'caged' in the viscoelastic solid.



So we can use these to work out the gel time

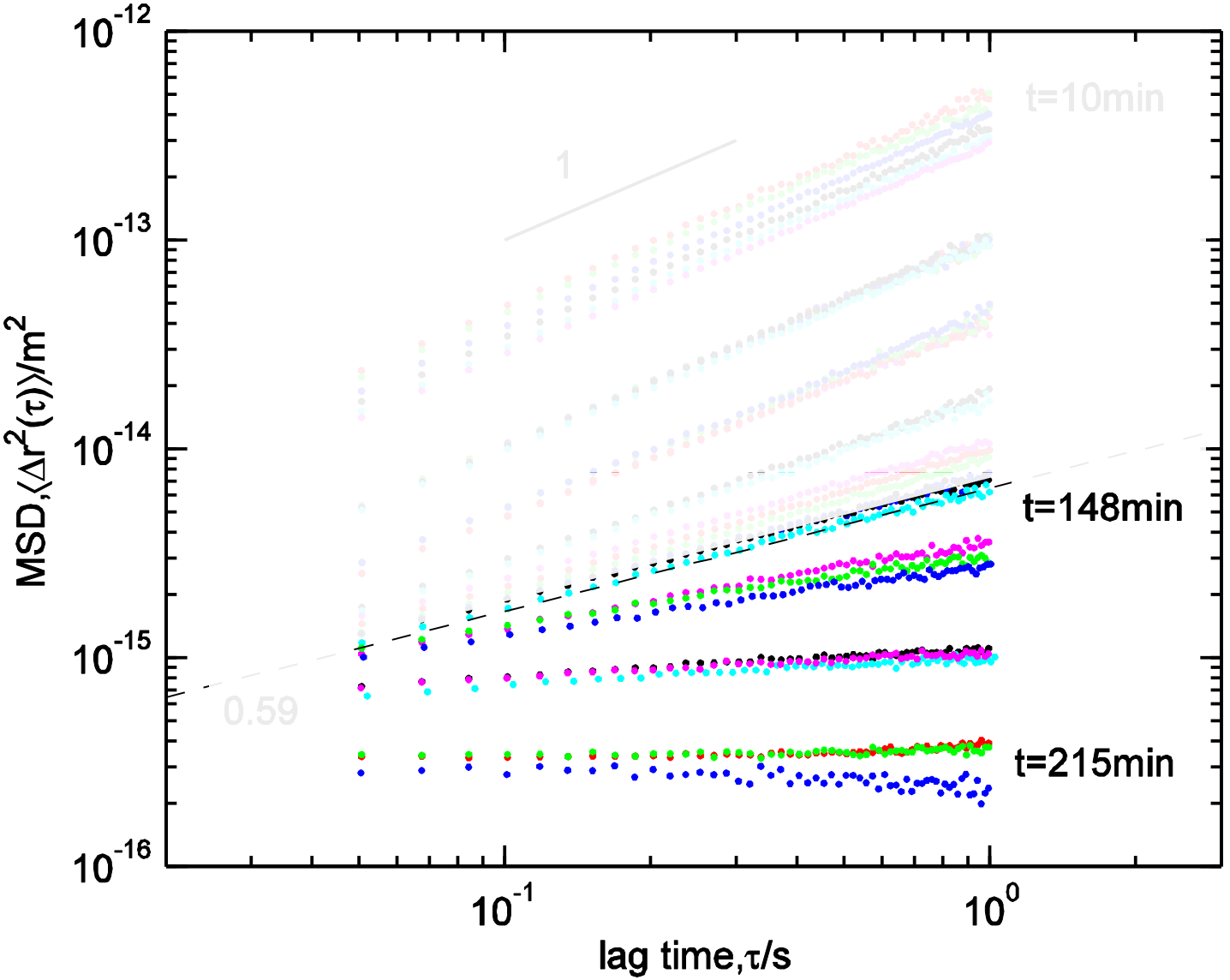
Constructing a Master Curve

- In conventional rheology, master curves can be constructed by using time-temperature superposition, so that data over limited ranges can be used to reveal the behaviour over much wider conditions.
- The same can be done with microrheology, by shifting according to lag time t and mean square displacement MSD (Larsen and Furst 2008).
- This shows different behaviour before and post gelation.
- At the gel point there is self-similar fractal scaling of the network, and the presence of relaxation mechanisms over all time scales leads to critical power scaling

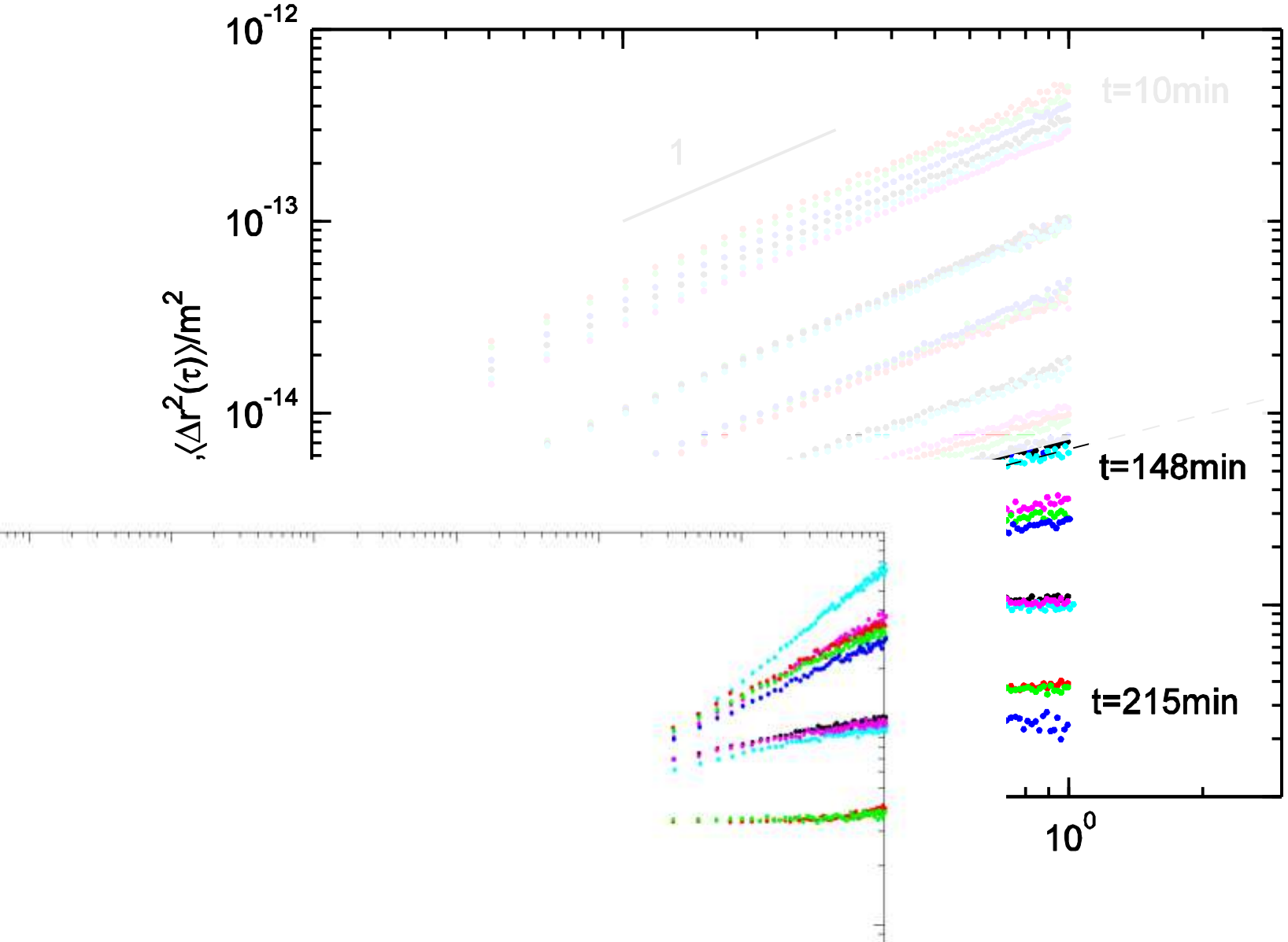
$$\left\langle \Delta r^2(\tau) \right\rangle = \tau^n$$

- Experimentally we find for the alcohol-induced gels that n=0.59, slightly below that predicted in Rouse theory (2/3).

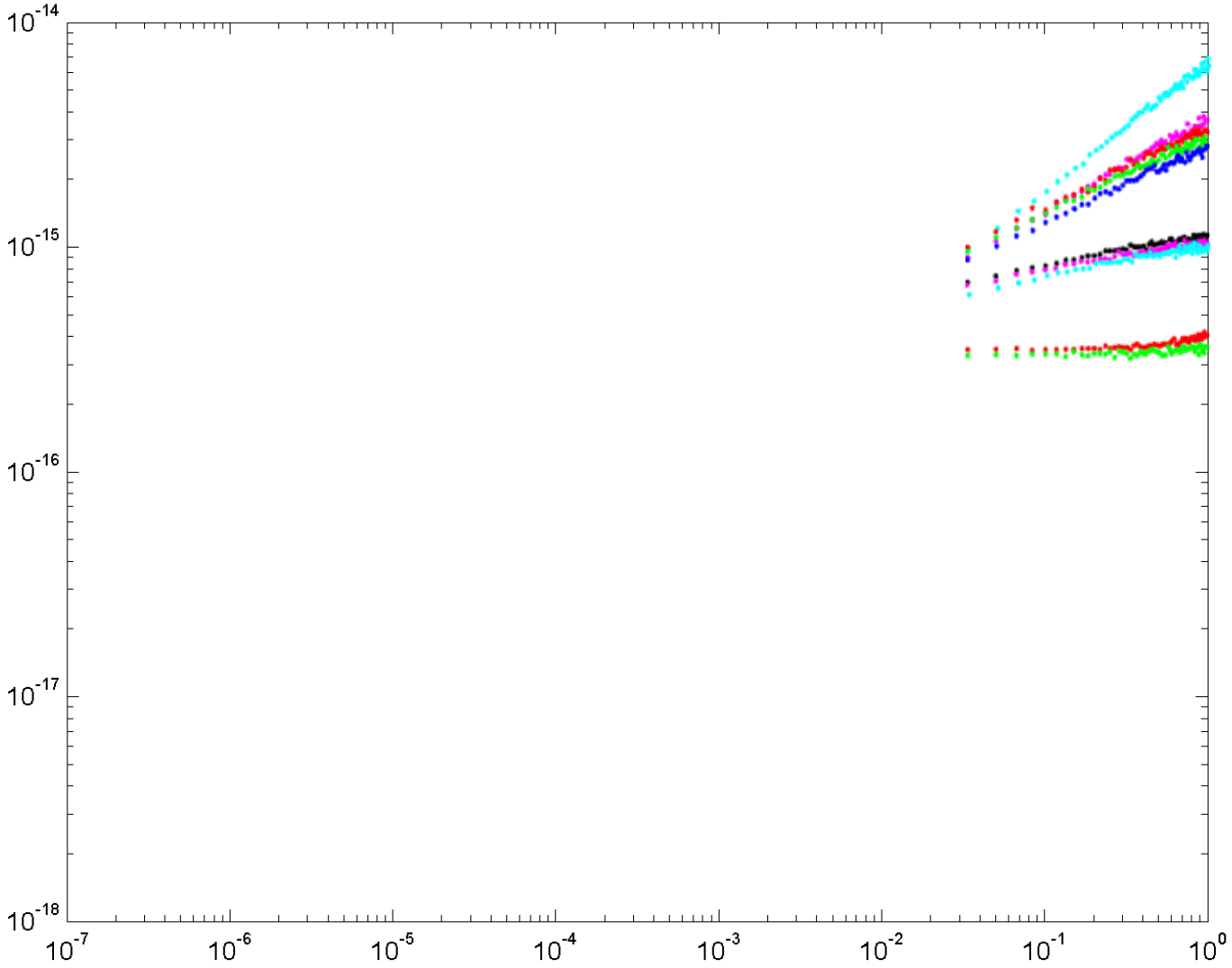
The Sol-Gel Transition



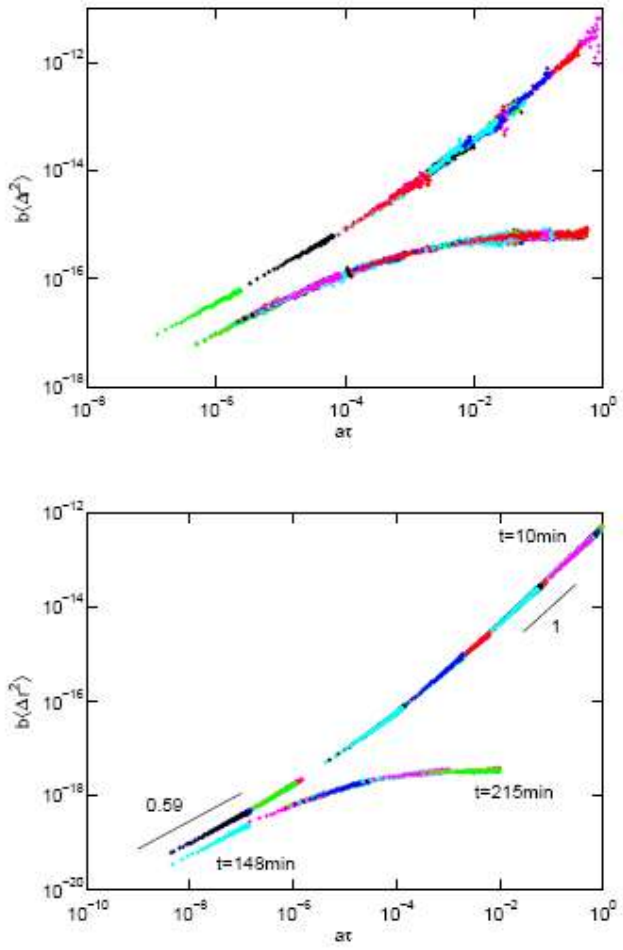
Master Curve Behaviour



Master Curve Behaviour



Comparison of Master Curves for Heat-set and Alcohol- induced Gels



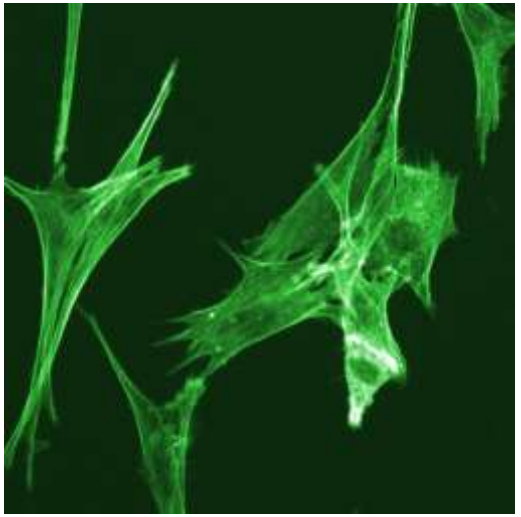
- Heatset gels have a critical exponent of 0.62 and a critical concentration of ~3%, lower than that found by extrapolation of bulk rheology.
- Alcohol induced gels have a slightly lower critical exponent of 0.59 and a critical concentration of ~4%.
- In both cases the critical exponent is lower than Rouse theory predicts, and this has been found for other systems too.

AM Corrigan and AM Donald – 2009. Langmuir 25, 8599-8605.
AM Corrigan and AM Donald – 2010. Soft Matter 6 4105-4111

Probing Cell Contents

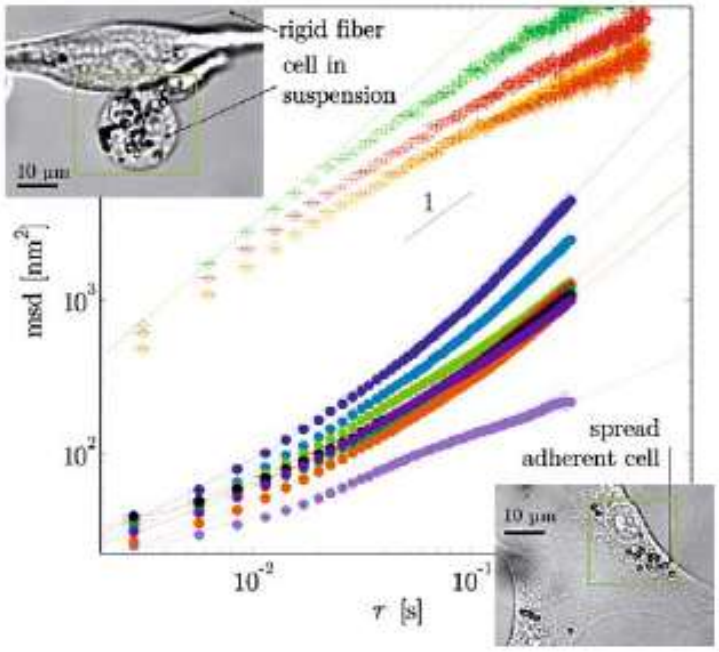
- Mammalian cells are very complex structures.
- The cytoplasm contains many polymers, many of which are involved with the ‘cytoskeleton’, the internal framework for the cell.
- These polymers, particularly actin, are ‘active’ in that they can rapidly remodel to allow the cell to change shape, move, adhere to surfaces etc.

Actin labelled with FITC-phalloidin; in adherent cells these will form stress fibres



- Consequently, the cytoplasm is likely to be both dynamic and heterogeneous, and microrheology provides an excellent tool to probe the behaviour.

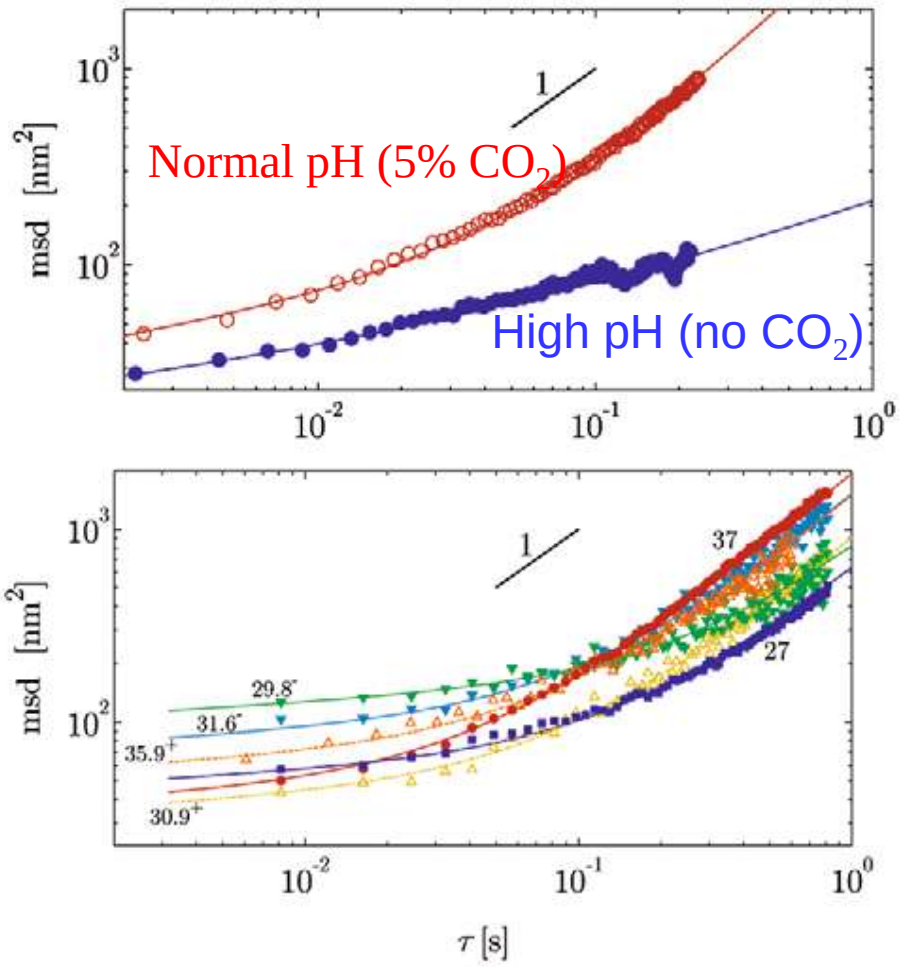
Microrheology Inside Cells



- We have been working with the 3T3 cell line, which are immortal fibroblasts.
- They rapidly take up the probe particles spontaneously, so we can follow their motion inside cells.
- We find very different responses for free cells and cells which are attached to a substrate.
- The suspended cell is much softer.
- We can also look at the anisotropy and heterogeneity of motion of the individual particles.

C Picard and AM Donald – 2009. EPJE 30, 127-34.

Effect of Stress on Cells



- We have also used the approach to see how cells respond to stress:
  - By altering the pH of the environment
  - By changing the temperature.
- The changes are found to be rapid and substantial.
- Any deviation from physiological conditions appears to stiffen the cell (but this is reversible).

Data from a cycle comprising a temperature drop of 10 C over 4 minutes from the physiological value of 37 C, a period of stabilisation of 20 min at a temperature of 27 C and a 4 min temperature increase back to 37 C.

C Picard and AM Donald – 2009. EPJE 30, 127-34.

Conclusions

- ESEM offers many opportunities for studying aqueous dispersions such as clays.
- But it cannot be used without careful thought and optimisation of conditions.
- Microrheology is a powerful tool for studying gelling systems
- It can also be used to explore heterogeneity in such systems
- It can provide a useful comparator with bulk rheology, particularly for weak gels.
- And its use can be extended to look inside mammalian cells.