# NMR as an analytical tool to characterise dispersions

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## Outline

**Surface characterisation**
Relaxation NMR:
1. Polymers at surfaces
2. Competition

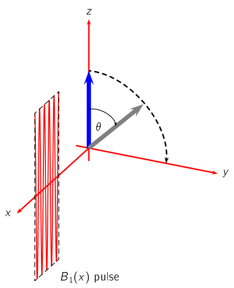
**Bulk characterisation**
Diffusion NMR:
1. Droplet size measurements
2. Cavity shape measurements

**Instrumentation**
Miniaturised NMR
1. Low power
2. Portable
3. Non-specialist



## Relaxation NMR

Direct measurement of concentrated dispersion




Rate for spin system to return to equilibrium:

- longitudinal relaxation ($R_1$)
- transverse relaxation ($R_2$)

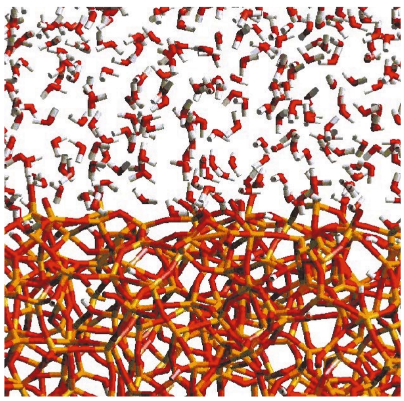
Influenced by
- local magnetic environment
- nuclei present
- correlation times (molecular motions)

Typical rates for solvent relaxation:

| | |
|---|---|
| water | $0.45\,s^{-1}$ |
| $SiO_2$ | $3\,s^{-1}$ (dispersion) |
| glycerol | $20\,s^{-1}$ |
| $CuSO_4$ | $100\,s^{-1}$ (10 mM) |



## Molecular mobility and surfaces



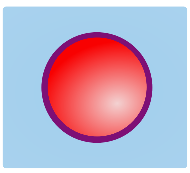
Warne, Allan & Cosgrove, Phys. Chem. Chem. Phys., 2000, 2, 3663

Molecular mobility
- rotational and translational correlation times
- surface chemistry

Two limits for behaviour
- fast exchange (one average rate)
- slow exchange (two rates)

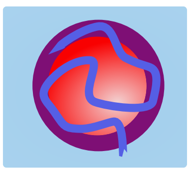


## Solvent relaxation



- Relaxation of near-surface water much faster than bulk water
- Fast-exchange limit
- Population-average measured:

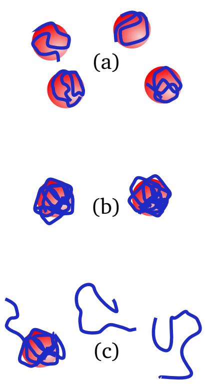
$$R_{\text{average}} = \phi_{\text{surface}}\, R_{\text{surface}} + (1 - \phi_{\text{surface}})\, R_{\text{bulk}}$$

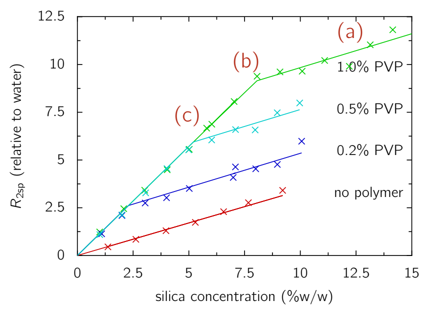


- Adsorbed polymer increases average rate of relaxation
- Molecular motions restricted
  ⇒ correlation times longer
  ⇒ relaxation more efficient
- More molecules in near-surface layer ($\phi_{\text{surface}}$ increases)



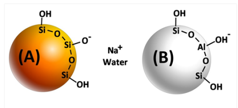
## Measuring polymer coverage on nanoparticles

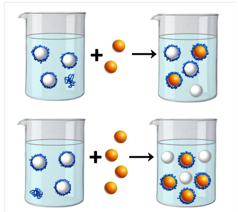


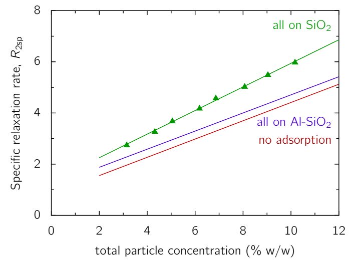

poly(vinyl pyrrolidone) + $SiO_2$ (diameter 15 nm)

## Competition between surfaces



$SiO_2$ particles and Al-modified particles ($\sim 2$at%Al)

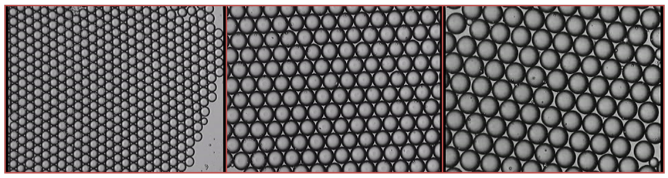





## Characterising emulsions

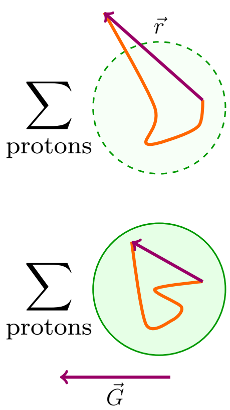
**Droplets**
- size
- internal structure
- shape, deformation
- volume fraction

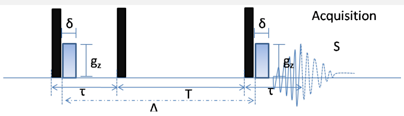
**Approach**
- $Q$-space NMR
- measurements of diffusion
- phase correlation technique
- strong analogy to scattering



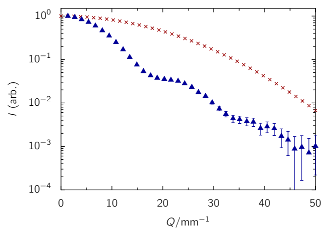


## Diffusion NMR measurements



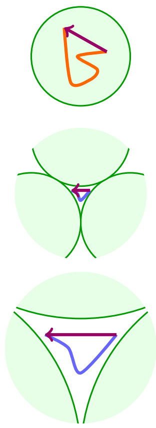



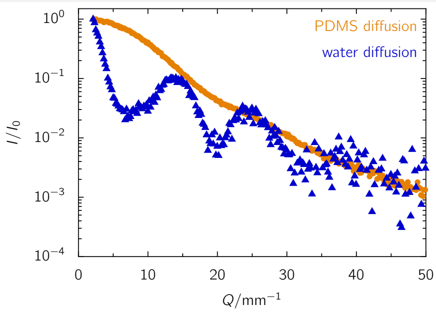

$$\Delta\phi = \gamma\delta\vec{G}\cdot\vec{r}$$

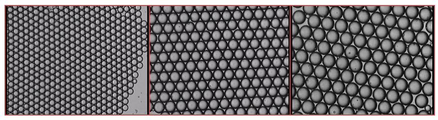





## Shapes and "scattering patterns"

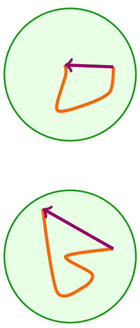


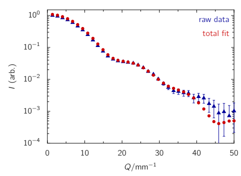


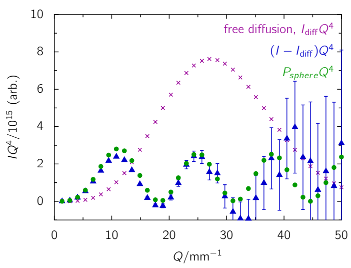





## Fitting the data – a Porod plot analysis



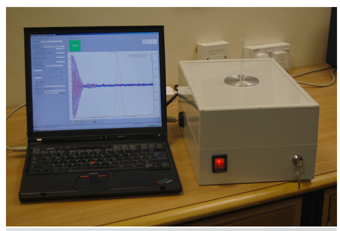


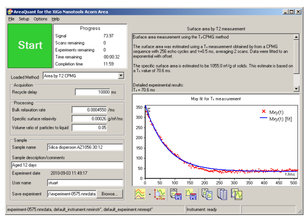






## Miniature 13 MHz NMR

**Requirements:**
- Small, portable
- Low power (< 50 W)
- USB connection
- Doesn't need an NMR expert






## Conclusions

### Polymers at surfaces

- Saturation of surface can be measured by NMR
- PVP will leave Al—$SiO_2$ surface and migrate to $SiO_2$ surface

### Emulsions

- Drop sizing with NMR is straightforward
- Diffusion paths give shape of droplet

⇒ see also:

1. "Competition at the nanoparticle surface: one polymer, two surfactants, many possibilities"
   Beatrice Cattoz PC5
2. "A highly monodisperse O/W emulsion by NMR diffusometry and relaxation technique"
   Panithi Wiroonpochit C14
3. "Growth and shrinking of Pluronic micelles in Pluronic-flurbiprofen solutions: variation of pH"
   Shirin Alexander C23

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