Soft Matter Studies With Muons

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Overview

- The muon technique has been applied to a diverse range of soft matter / bio-physics problems
- Main methods used:
  - Low Field Repolarisation
    - broad estimation of hyperfine fields, muonium fractions
  - Avoided Level Crossing
    - structure, dynamics and reaction rate studies
  - Zero/ Longitudinal Low Field
    - electron transfer
  - High Transverse Field (PSI)
    - extract hyperfine couplings
- Science is well supported by Facility access panels but, esp. for bio-materials, it is underdeveloped area
  - Systematic studies, with speculative conclusions, underpin most published work
- However, advances in scientific computing should open up more complete investigations

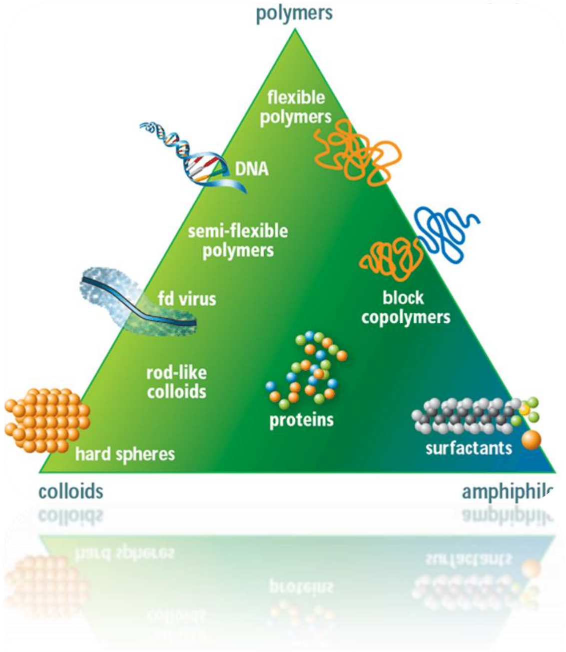
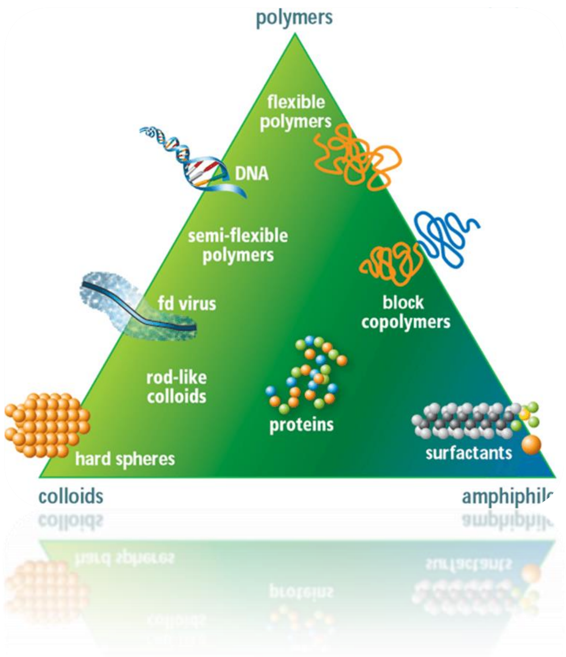


Image: Varrato, PhD Thesis, 'Routes to Novel Colloidal Gels', 2012

Select Topics

- Polymers
  - From conducting polymers (Pratt el al) and solar cell precursor materials (Morley et al) to organo-metallic compounds for use as green solvents (Romerosa Nievas et al)
- Proteins / DNA
  - Predominately **electron transfer studies** (Nagamine et al, 2001; Webster et al, 2000) underpinned by Risch-Kerr and Hartree-Fock calculations (Scheicher ,2006)
- Bio-compatible pharmacological compounds
  - Investigating whether **bio-compatible conductors** could be used in miniature power sources (Kilcoyne et al)
- Bio-magnetism
  - De-oxyhaemoglobin vs oxyhaemoglobin and the observed difference in spin relaxation due to haemoglobin magnetism. Possible future studies: oxygenation levels in various regions of the human brain



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Select Topics

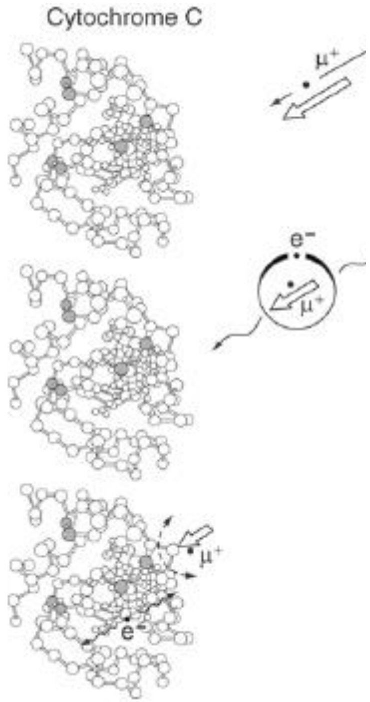
- Steroidal drug molecules in liposomes
  - To determine the location and orientation of a model hydrophobic drugs in a model multi-lamellar liposomal system suspended in deoxygenated H2O (Barker et al, 2006)
- Electrical conduction of melanin
  - The role of semi-conductivity and ion transport in the electrical conduction of melanin (Mostert et al, 2014)
- Radical Formation and Reaction Kinetics
  - Vitamin C and K (Jayasooriya et al) and green tea (Chass et al,) studies to investigate antioxidant behaviour in the body
- Elemental Analysis
  - Still in its infancy as a technique but an inventive application of the muon as a probe and a method sensitive to metal-ion cluster formation in tissues (Hillier et al)

Electron transfer as probed by μ^+SR

- Electron transfer in macro-molecules is the most important mechanism for many biological phenomena
  - Energy consumption and storage
  - Photo-synthesis and respiration
- Experimentally, most information on electron transfer is determined using macroscopic methods
- Muons have proven extremely useful for probing **LOCAL** e^- transfer in conducting polymers …
  - Francis Pratt (ISIS), Stephen Blundell (Oxford) *et al*
- … extended to bio-materials (DNA, cytochrome etc)
  - Nagamine *et al,* Kilcoyne *et al*

Electron transfer as probed by μ^+SR

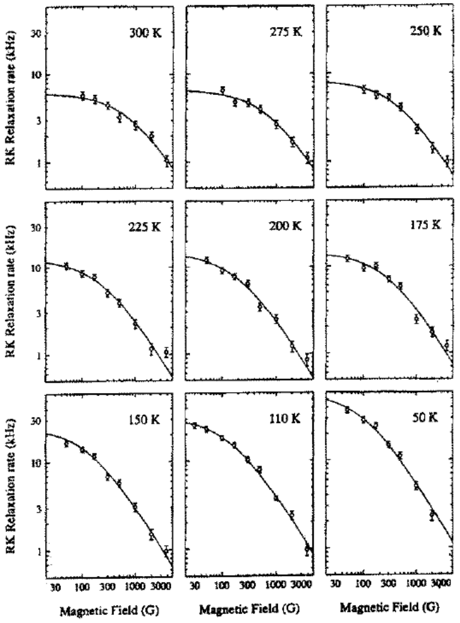
- Positive muons are implanted into the sample and the muon picks up and electron to form a neutral atomic state called muonium
- The muonium thermalizes and chemically binds to a molecule in the bio-material
- Then, depending on the nature of the molecule, the electron brought in by the μ^+ can:
    - localise to form a radical state or
    - move linearly along the molecule
- If the latter, then μ^+ spin relaxation occurs via the interaction between μ^+ and moving e^-



K Nagamine et al, J. Phys Conds Mat, 16, 2004

Signatures of the electron transfer process

- Beauty of this method is that implanted μ^+ is both electron donor and the probe of said electron's behaviour
- Two key parameters can be extracted:
  - the rate at which the electron is moving can be determined from the spin relaxation rate, λ_μ
  - the dimensionality of the motion (1D, 2D, 3D) from the external field dependence of the relaxation rate
    - 1D : $\lambda_\mu \propto (B_{ext})^{-1/2}$
    - 2D : $\lambda_\mu \propto (\log (B_{ext}))^{-1}$
    - 3D : λ_μ shows no B_{ext} dependence



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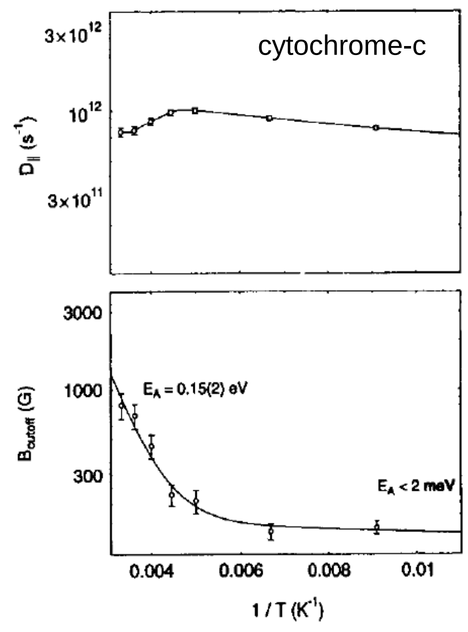
- In cytochrome-c the e^- transfer process exhibits two different modes. Inflexion point aligns with onset of molecular dynamics as seen by neutrons



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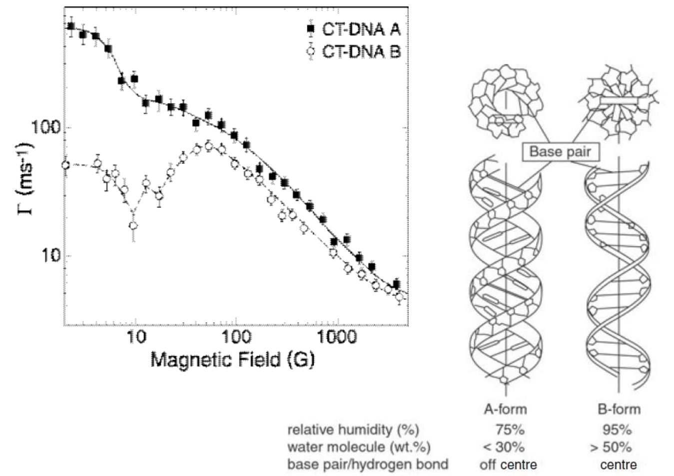
- A and B base pair forms of DNA ?
  - Isao's talk: Weds 21st, 14:50



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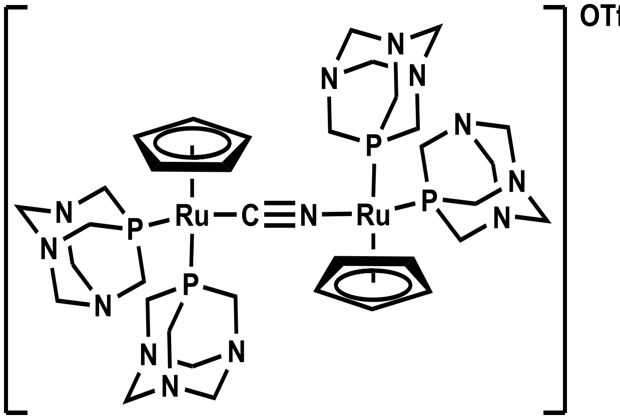
The Importance of Scientific Computing

- Few soft matter studies are from simple compounds
- Consider organo-metallic materials (Romerosa Nievas et al, HiFi)
  - used as green solvents
  - Polymer species with magnetic, and non magnetic, ion inclusions
  - In this study: La, Cd or Ru
- Team wanted to investigate not only the influence of the linkage on molecular dynamics and reaction rates but also the ion!
- Technique chosen: Level Crossing Resonance

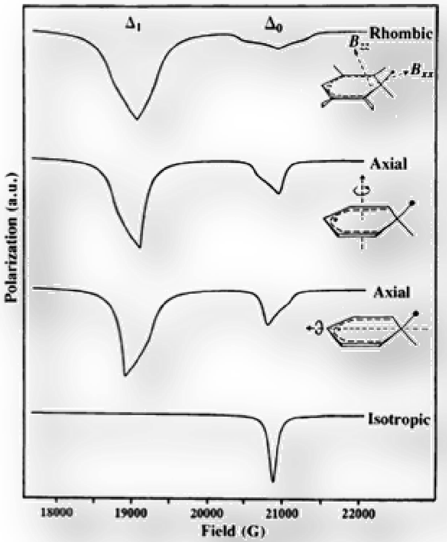


organo-metallic compounds for use as green solvents

$\{[\{(PTA)_2CpRu\text{-}\mu\text{-}CN\text{-}RuCp(PTA)_2\}\text{-}\mu\text{-}CoCl_3\text{-}]\}_n$

The Importance of Scientific Computing

- For systems, such as simple molecules, with well defined muon addition sites
  - Resonances are sharp and well separated
  - Molecular Dynamics: resonance line shape provides information about molecular dynamics in the solid state
  - Radical reaction rates can be measured from the broadening of resonances, which are a function of reactant concentration.

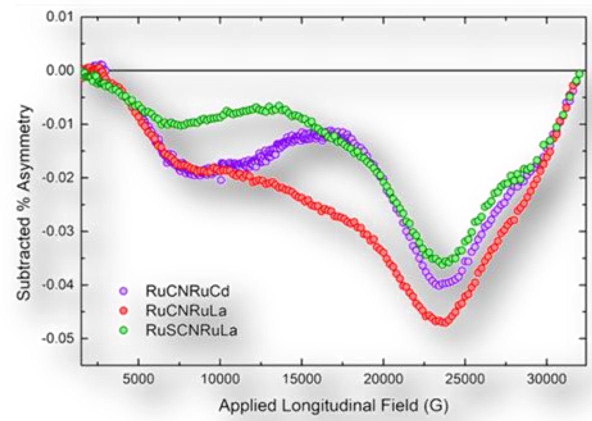


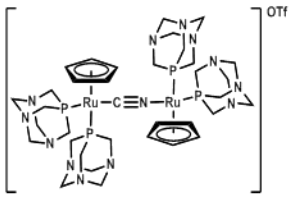
Simulated powder pattern for the Δ_1 resonance of the cyclohexadienyl type radical in the static case (top), for fast rotation about two different axes (middle two entries), and for fast isotropic motion

McKenzie, Annu Rep Prog Chem., 2013, 109, 65-112

The Importance of Scientific Computing

- For systems, such as simple molecules, with well defined muon addition sites
  - Resonances are sharp and well separated
  - Molecular Dynamics: resonance line shape provides information about molecular dynamics in the solid state
  - Radical reaction rates can be measured from the broadening of resonances, which are a function of reactant concentration.
- But for more complex systems …
  - While the influence of ion type and linkage is clear …
  - … collaboration with Scientific Computing is of paramount importance if multiple spectral contributions are to unravelled





organo-metallic compounds for use as green solvents

{[{$(PTA)_2$CpRu-μ-CN-RuCp$(PTA)_2$}-μ-$CoCl_3$-]}$_n$

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Considerations

- Due to the possible number of muon addition sites in soft matter systems, studies benefit greatly from supporting DFT predictions and site calculation methods

- However, predictive modelling to support a beam time applications and guide an experimental plan will facilitate success

- Sufficient measurement time to complete a study is paramount

    - Don't be afraid to ask for month of beam time if you can justify it!

- On the plus side, for solution work only a few *mg's* of material is needed

Have an idea for a 'soft matter' experiment ?

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