INTERPLAY BETWEEN QUANTUM MECHANICS AND SOFT MATTER

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CMMRC
WASHINGTON, DC
SEPTEMBER, 2013

OUTLINE & SCOPE

Soft condensed matter physics is generally regarded as mainly classical ($\hbar=0$) because it is typically concerned with objects at the nanoscale or larger.

Some categories where QM plays a role include:

(1)direct interplay between electrons and soft matter properties;

(2) quantum models for classical behavior;

(3) experimental tools to probe soft matter that rely in an essential way upon QM.

ELECTRONS AND SOFT MATTER

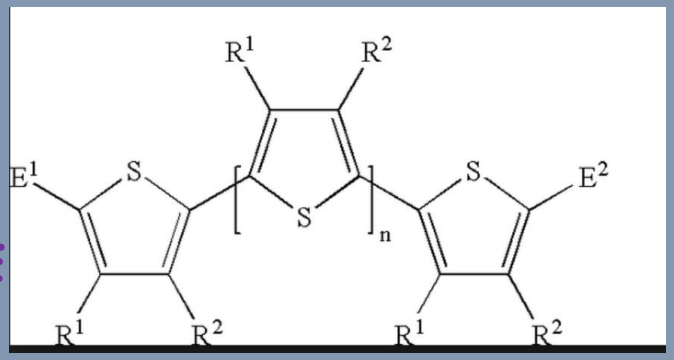
- BATTERIES, PHOTOVOLTAICS, FLEXIBLE ELECTRONICS where polymers are essential elements
- COORDINATION CHEMISTRY EFFECTS WITH TRANSITION METAL IONS AND SOFT MATERIALS….flexible lighting
- COMPENSATION OF ELECTRONIC CHARGES BY IONIC CHARGES IN AQUEOUS MEDIA…..screening of Schottky barrier by dissolved salts in doping of conjugated polymers
- CONDUCTIVITY OF CONJUGATED POLYMERS…hopping
- ELECTRON COUPLING TO BENDING MODES IN d=2..grapheme,
- ELECTRON DELOCALIZATION AND POLYMER RIGIDITY

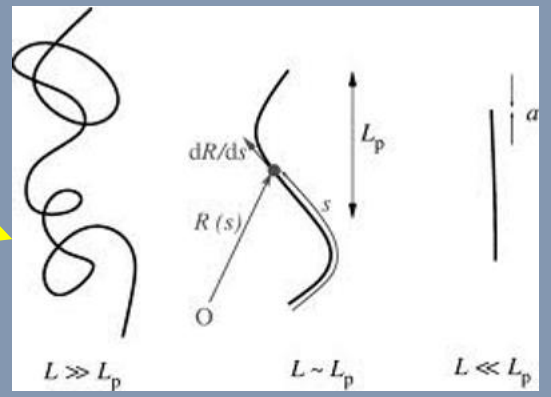
CONFORMONS-ELECTRON DELOCALIZATION AND POLYMER RIGIDITY

ELECTRON DOPED CONJUGATED POLYMER CHAIN

Π ELECTRON DELOCALIZATION STIFFENS GAUSSIAN POLYMER INTO A SEMI-FLEXIBLE CHAIN

POLYTHIOPHENE





TOY MODEL

- TIGHT BINDING Π ELECTRON HOPPING MATRIX ELEMENT t……all or nothing

$$\varepsilon(k) = 4t\sin^2(k/2),$$
$$k = \frac{p\pi}{\ell + 1}, p = 1, 2, 3 \ldots . \ell$$

- Loss of configurational entropy αT/rigid bond

ℓ is number of monomers per rigid segment

Rigid segment--- conformon….. analogous to polaron

CONFORMONS AT LOW DOPING-RESULTS

For r electrons (spinless for simplicity) in a conformon:

- Optimal conformon length ,

$$\ell \approx \ell_c (r + 1/2) \qquad \ell_c \approx \left(\frac{t}{\alpha T}\right)^{1/3} \approx 10$$

- Using transfer matrix method to do stat mech for concentration c of electrons:
  - For $c \le \sigma \equiv e^{-\frac{3\alpha\ell_c}{4}}$ Isolated one electron conformons
  - For $c \ge \sigma$ There are $p \approx N(c\sigma)^{1/2}$ conformons each containing $r \approx (c/\sigma)^{1/2}$ electrons. The chain stiffens and swells considerably.

……..

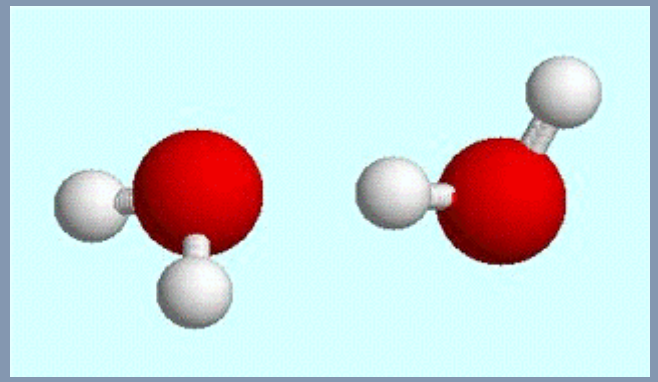
QUANTUM MODELS

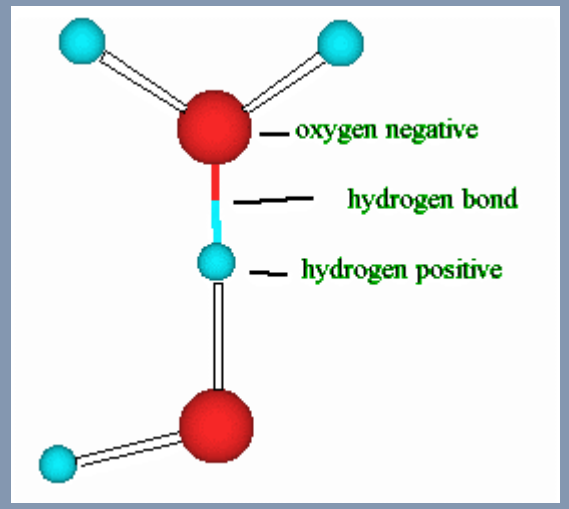
Analog calculations using quantum models may be easier because of the finite state counting

- HUBBARD MODEL FOR HYDROGEN BOND NETWORKS

HUBBARD MODEL FOR HYDROGEN BOND NETWORKS

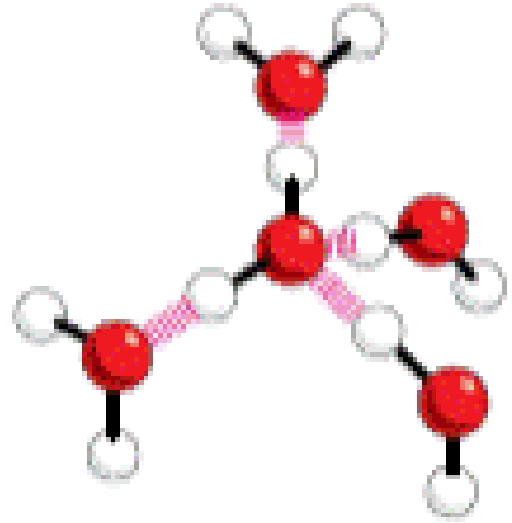
Water Structure





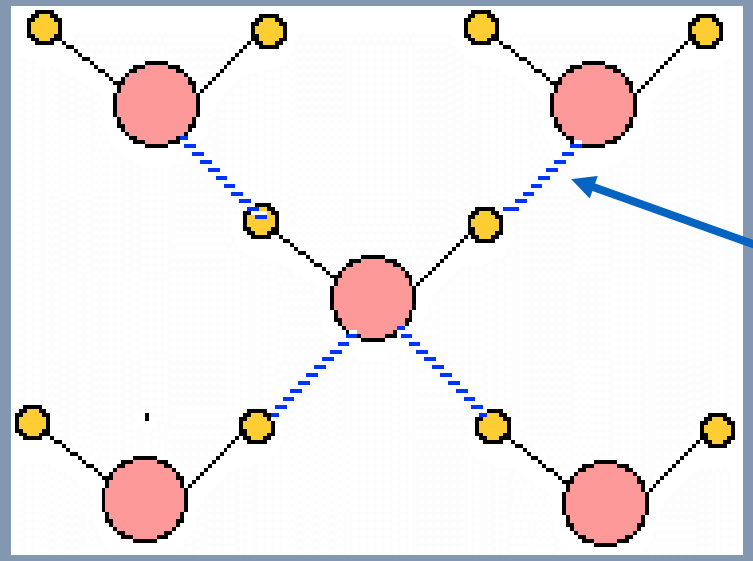
WATER STRUCTURE

Molecules of water join together transiently in a hydrogen-bonded lattice. Even at 37°C, 15% of the water molecules are joined to four others in a short-lived assembly known as a "flickering cluster."



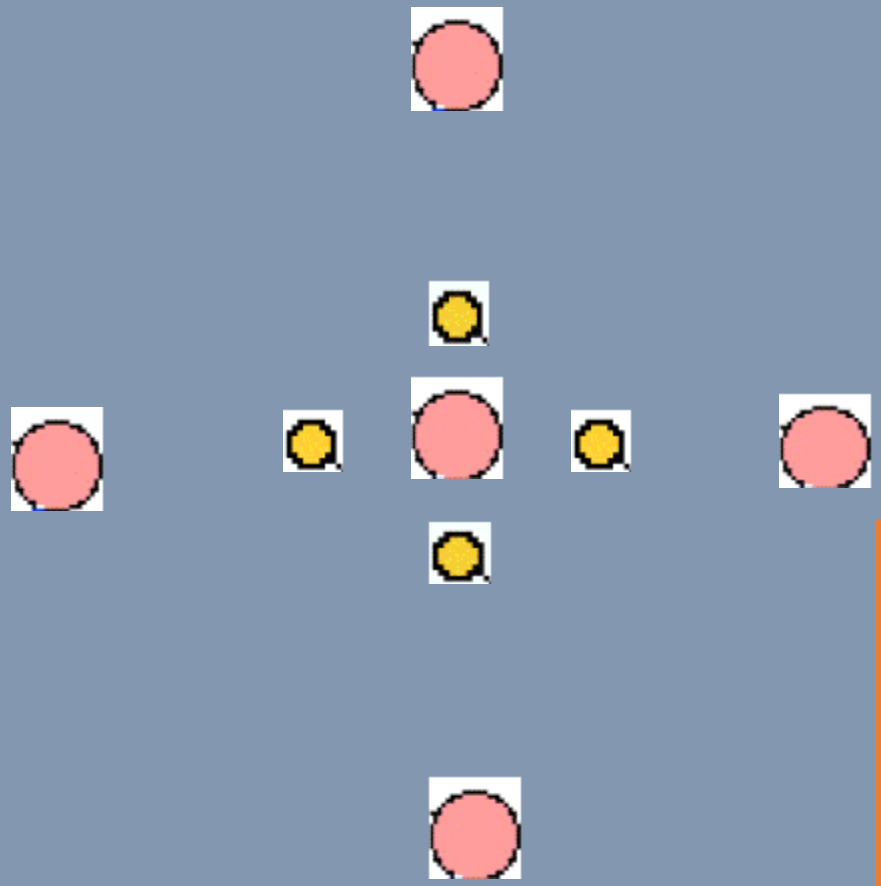
The cohesive nature of water is responsible for many of its unusual properties, such as high surface tension, specific heat, and heat of vaporization.

Ice



Crystalline Fields Break Rotational Symmetry

Model- Basins

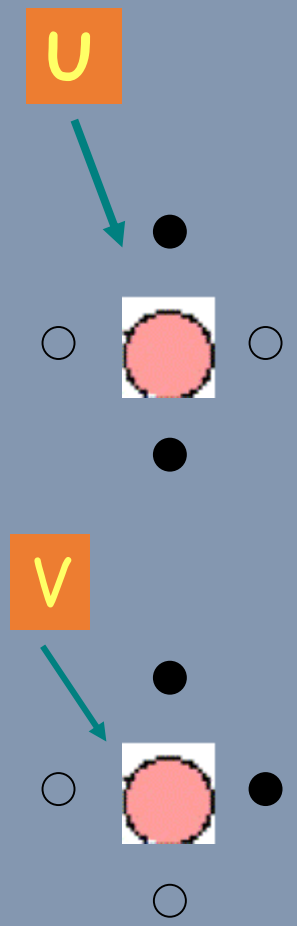


Crystal field basins ◯ may be occupied by (0,1) protons.

Strong Coulomb Repulsion

Spinless Fermions

Single Molecule Energies



s-p hybridiztion → U>V

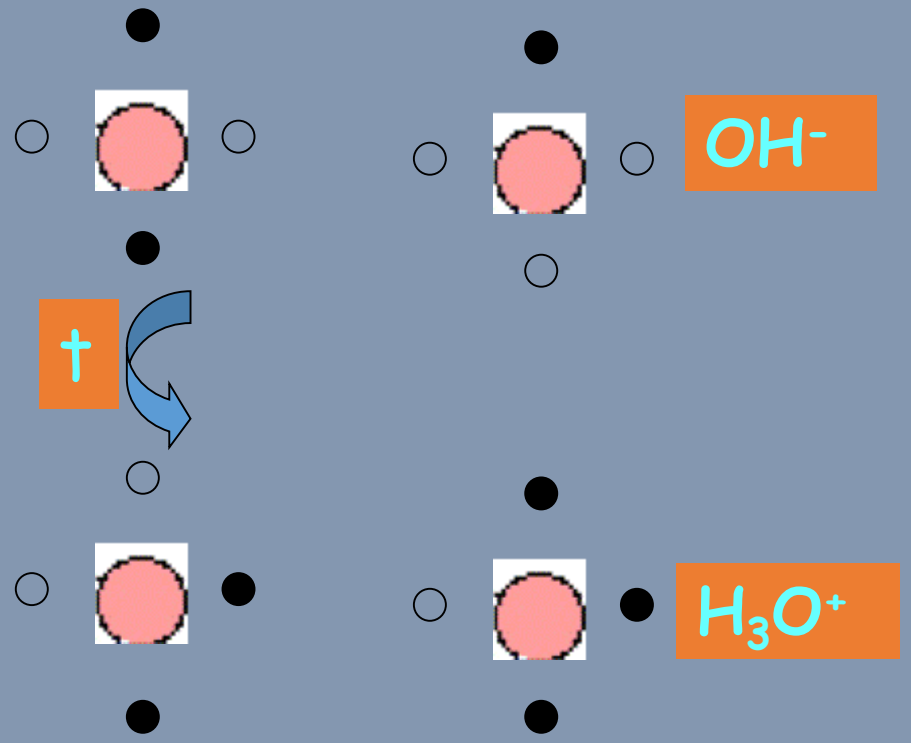
$2H_2O \rightleftharpoons OH^- + H_3O^+$

hydroxyl

hydronium

10^{14} ions/cm^3 => U~20 k_BT

Hydrogen Bonds and the Hubbard Model



➲ Treat basins as Fermion states

➲ t is matrix element to transfer a proton from one basin to another associated with a nearest neighbor O- -

H-bond energy ~ $-t^2/V$ ~ $5k_BT$

$t \sim 10k_BT$ Intermediate Coupling

H Bond is proton resonating between two waters

Hydrophobic Interaction

Quantum Soft Matter Probes

- Magnetic resonance techniques
  - Dynamic Overhauser effect to study motions
- Neutron scattering techniques

  Spin Echo Small Angle Neutron Scattering
  - SESANS

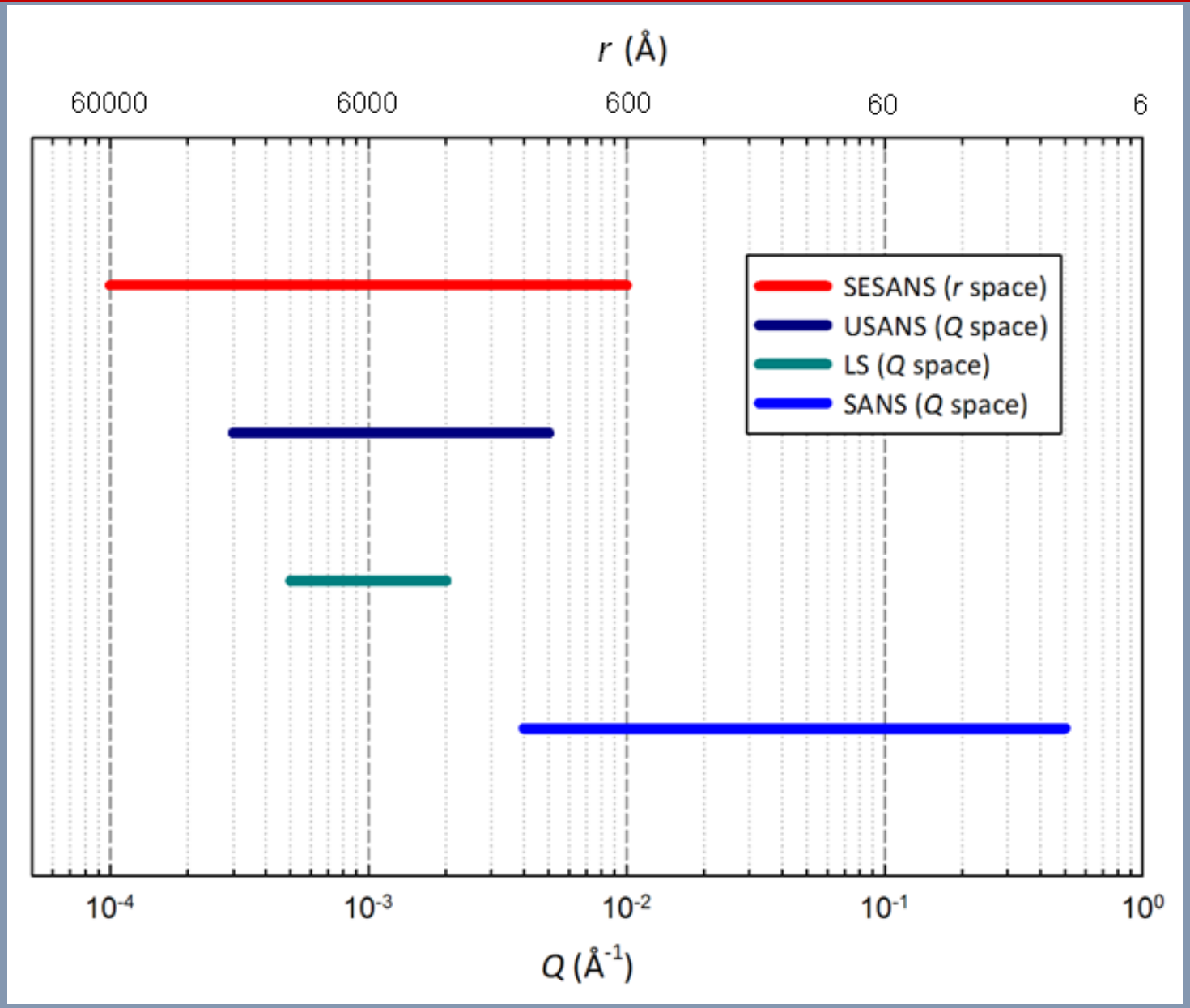
Spin-Echo Small-Angle Neutron Scattering (SESANS)

Slides courtesy of Xin Li and Roger Pynn (Indiana University)

- Elastic scattering technique to investigate structure

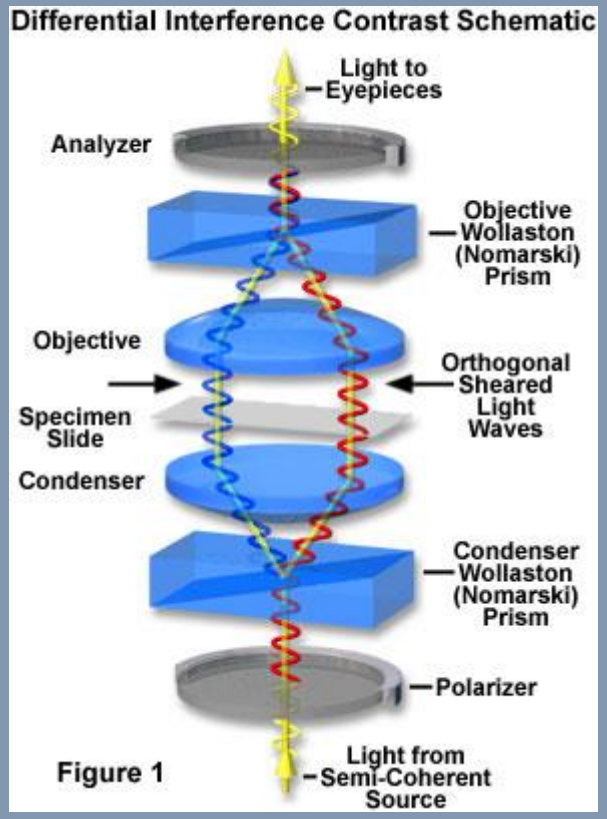
Real space correlation function

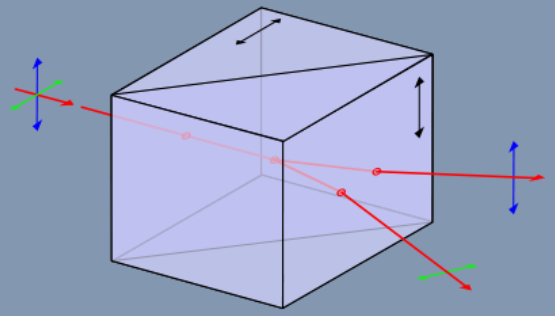
SESANS Length Scale



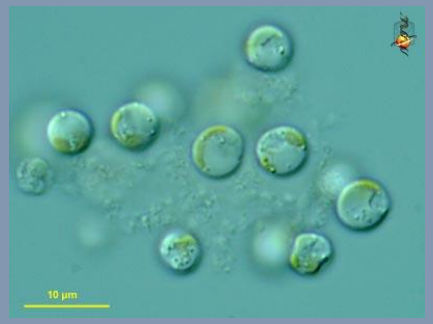
Neutron Alalogue of Differential Interference Contrast Microscopy

Beautiful real-space images at about 1 micron resolution





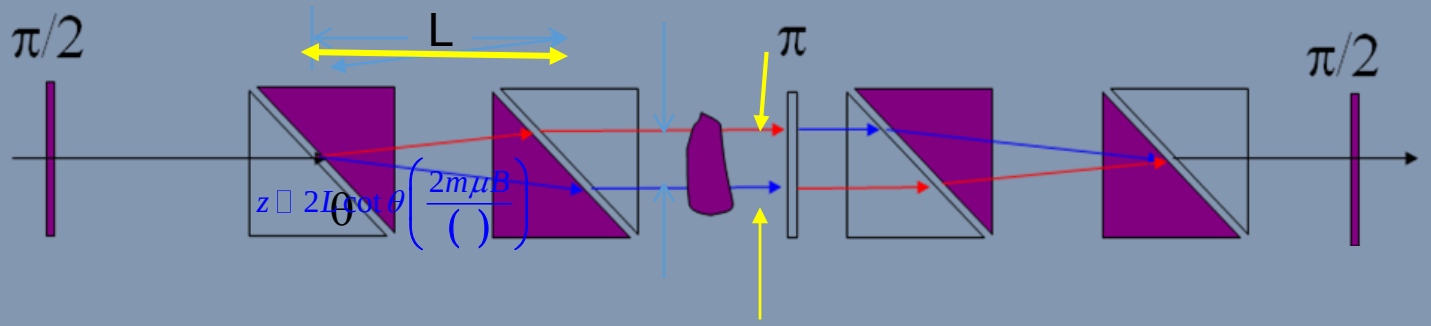
Wollaston Prism



Eukaryotic Algae

Two polarization states of light "visit" neighboring parts of a sample and interfere to produce contrast that depends on the phase difference between the paths.

SESANS

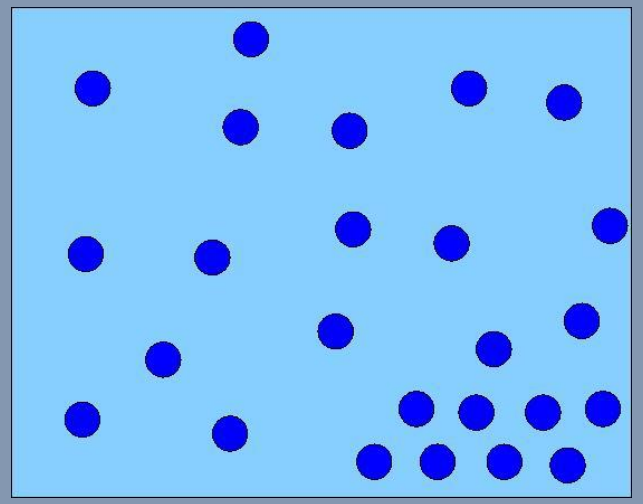


Triangular regions have oppositely directed magnetic fields to change neutron wavelength

Spin Echo length $z \approx 2L\cot\theta\left[\frac{2m\mu B}{(\hbar k_0)^2}\right]$

SESANS measures a real-space correlation function as a function of z

SESANS & SANS Measure Different Transforms of the Debye Correlation Function



Local Particle Density ρ(r)

Debye Correlation Function

$$\gamma(r) = \frac{1}{V}\left\langle \int_V \rho(\vec{r}')\rho(\vec{r}'+\vec{r})d^3\vec{r}' \right\rangle$$

SANS

SESANS

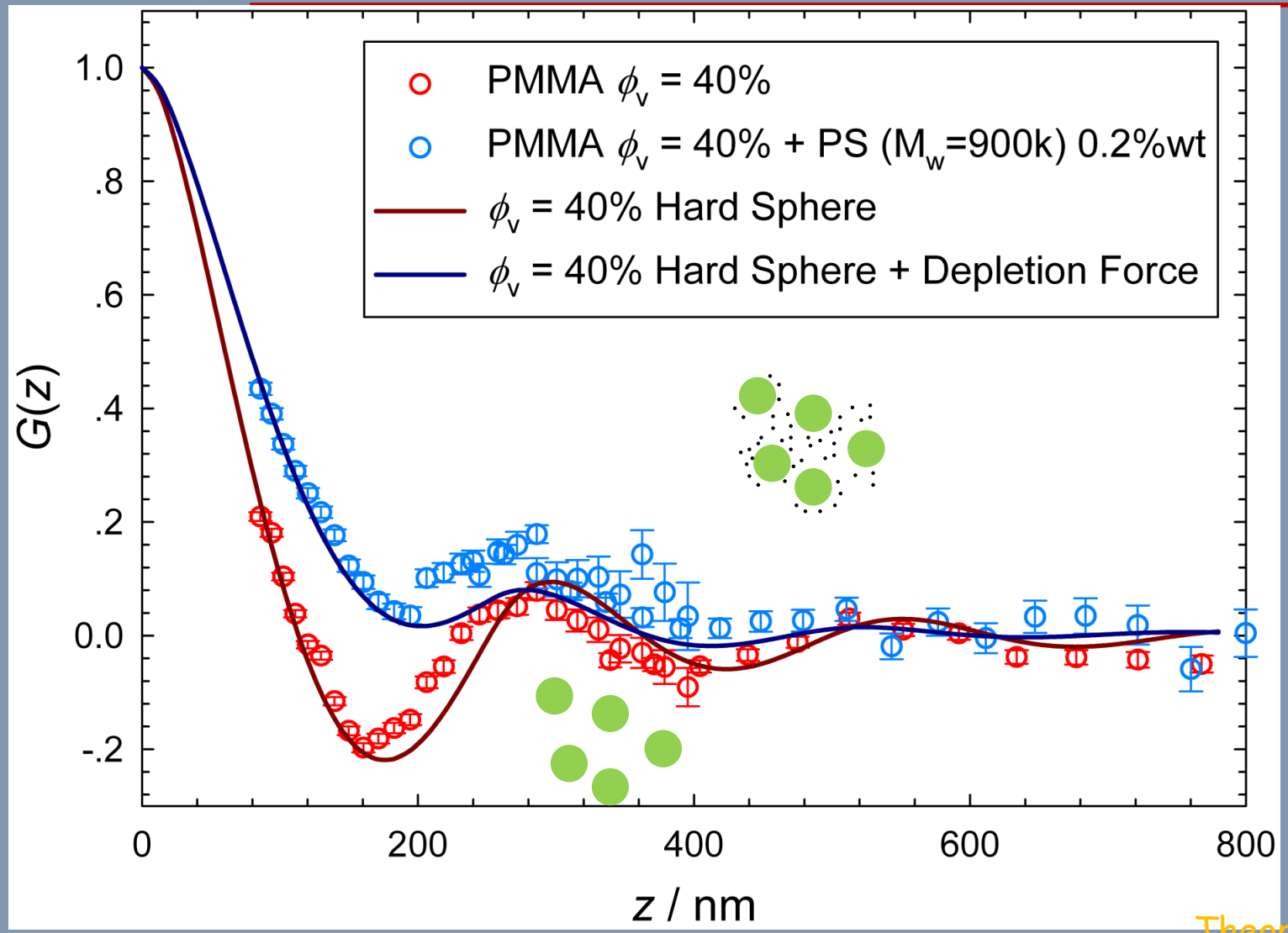
$$I(Q) = \frac{d\Sigma}{d\Omega}(Q) = 4\pi\int_0^\infty \gamma(r)J_0(Qr)r^2dr$$

Fourier

$$G(z) = 2\int_z^\infty \gamma(r)\frac{r}{\sqrt{r^2-z^2}}dr$$

Abel

Hard Sphere vs. Adhesive Hard Sphere



Unpublished experiments at LANSCE by Xin Li and Roger Pynn

Theoretical Predictions:
T. Kruglov *J. Appl. Cryst.* **38**, 721 2005
Li *et al. J. Chem. Phys.* **132** 174509 2010

We are usually completely wrong in predicting the future in science. However while waiting for unexpected discoveries, I believe that these categories merit some exploration.

Thanks for listening!