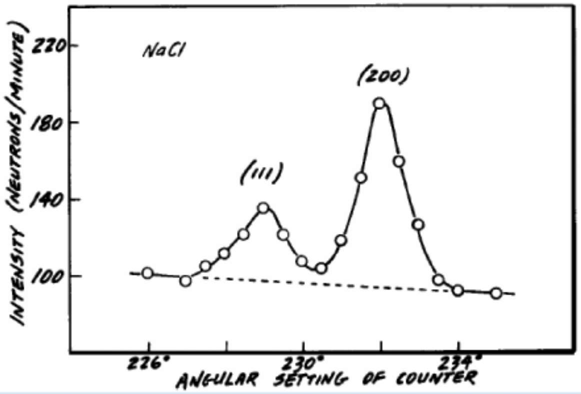
Applications of Neutron Scattering

Roger Pynn

Indiana University
and
Spallation Neutron Source

Some History



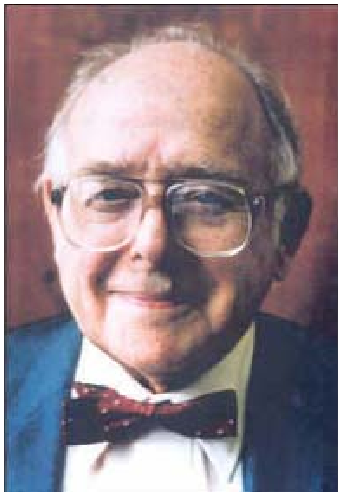
- 1932 – Chadwick discovers the neutron
- 1934 – thermalisation (Fermi)
- 1936 – scattering theory (Breit, Wigner)
- 1936 – wave interference (Mitchell, Powers)
- 1939 – fission

- 1945 – diffraction (Shull, Wollan), reflection, refraction
- 1948 – coherent & incoherent scattering (Shull, Wollan)
- 1948 – spallation
- 1949 – structure of AFM (Shull)

- 1951 – polarized neutrons (Shull & Wollan)
- 1955 – three axis spectrometer (Brockhouse)
- 1958 – rotons in helium (Palevsky, Otnes, Larsson)

- 1962 – Kohn anomalies
- 1960 – 79 – soft phonons & structural phase transitions
- 1969 – 79 – scaling and universality

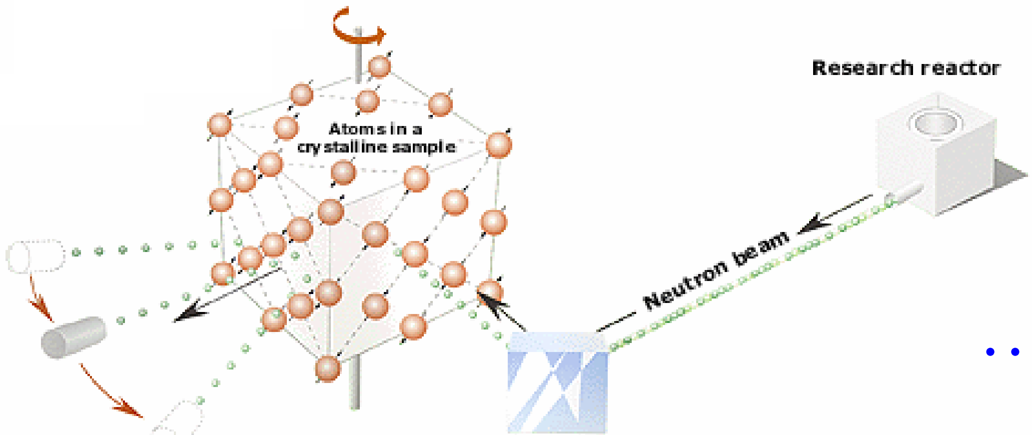
- 1972 – conformation of polymers
-
- 1994 – Nobel Prize for Shull and Brockhouse



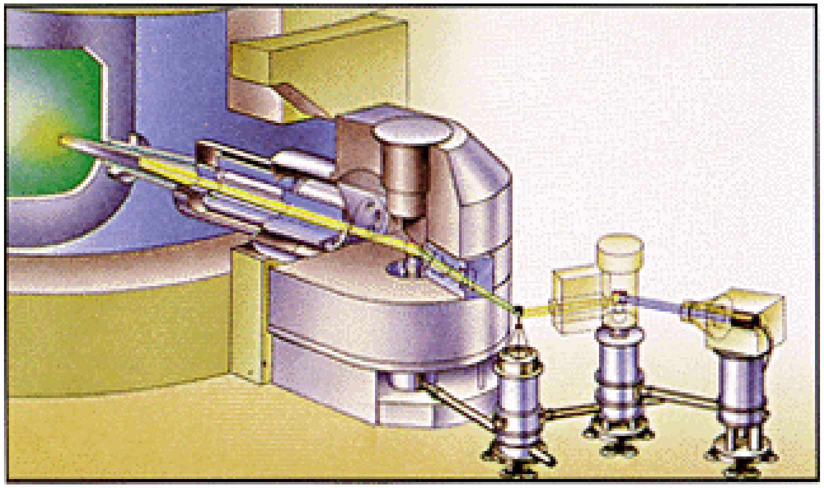
Cliff Shull (1915 – 2001)

The 1994 Nobel Prize in Physics – Shull & Brockhouse

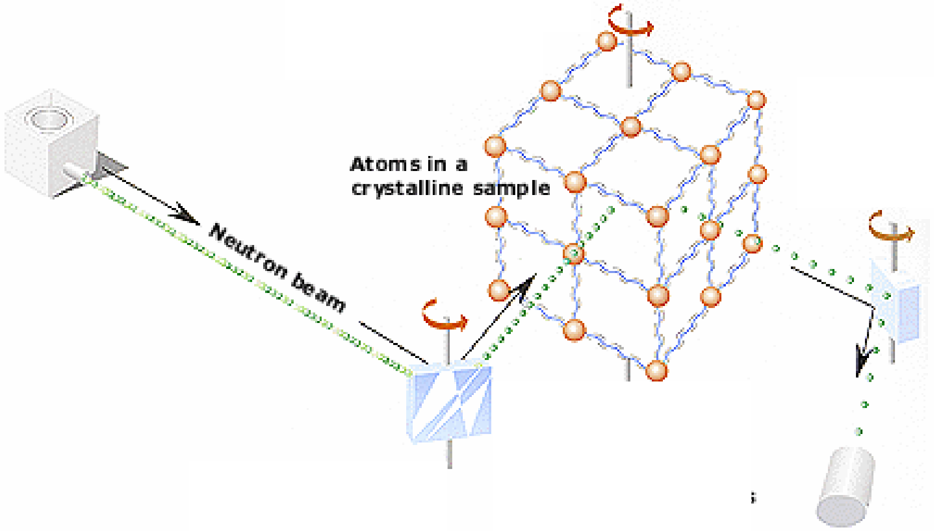
Neutrons show where the atoms are….



…and what the atoms do.

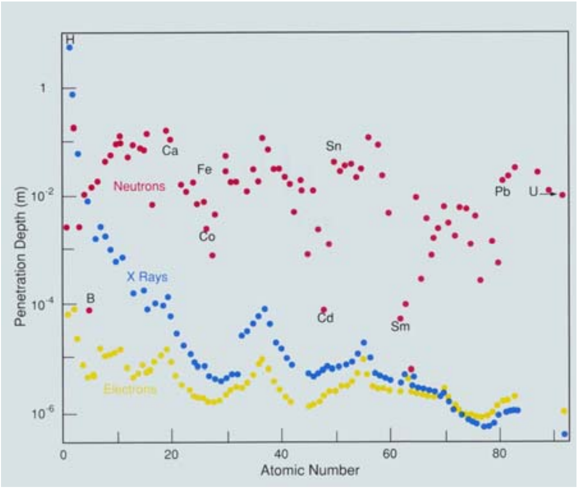


3-axis spectrometer



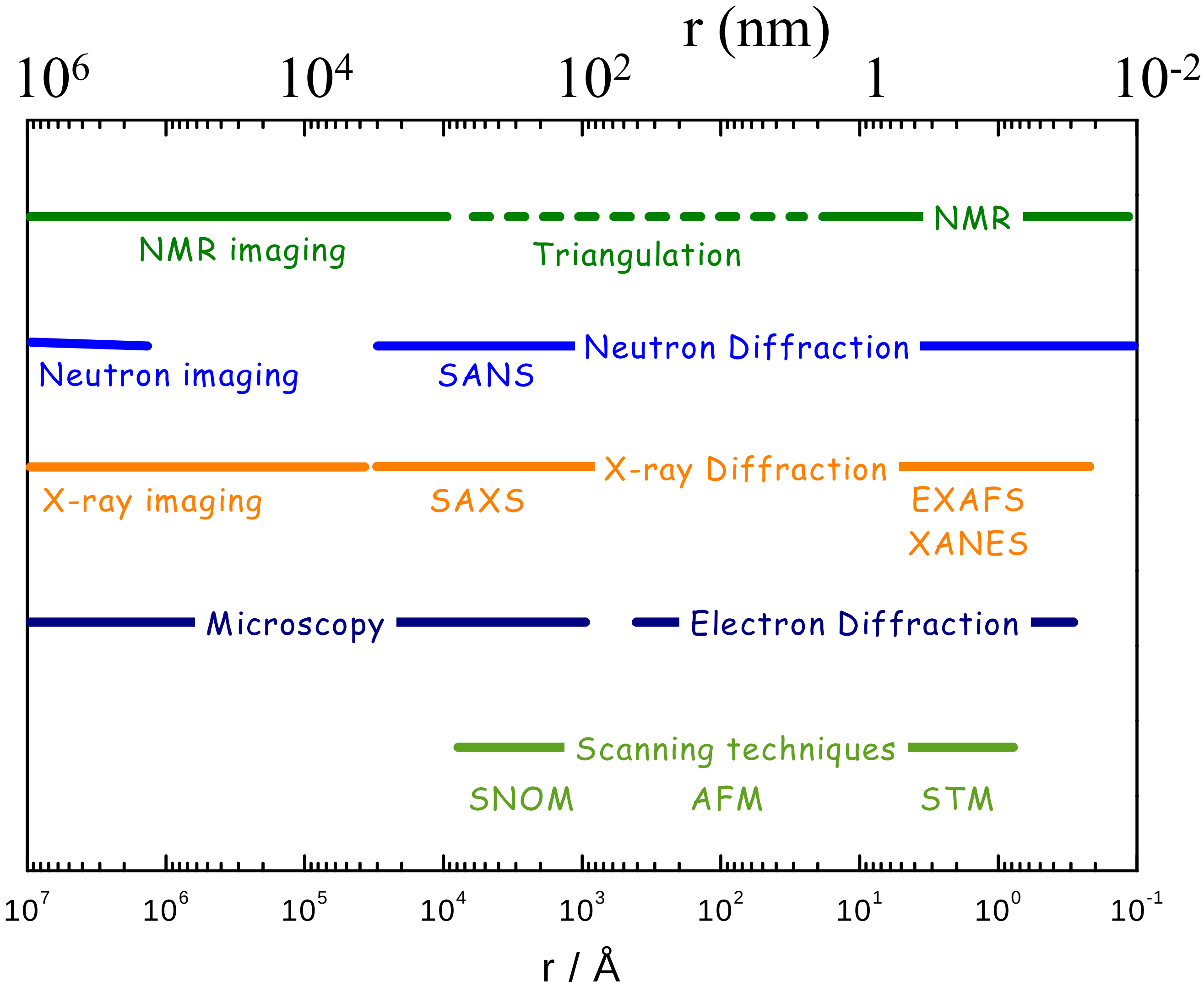
The Success of Neutron Scattering is Rooted in the Neutron's Interactions with Matter

- Nuclear and magnetic interactions of similar strength

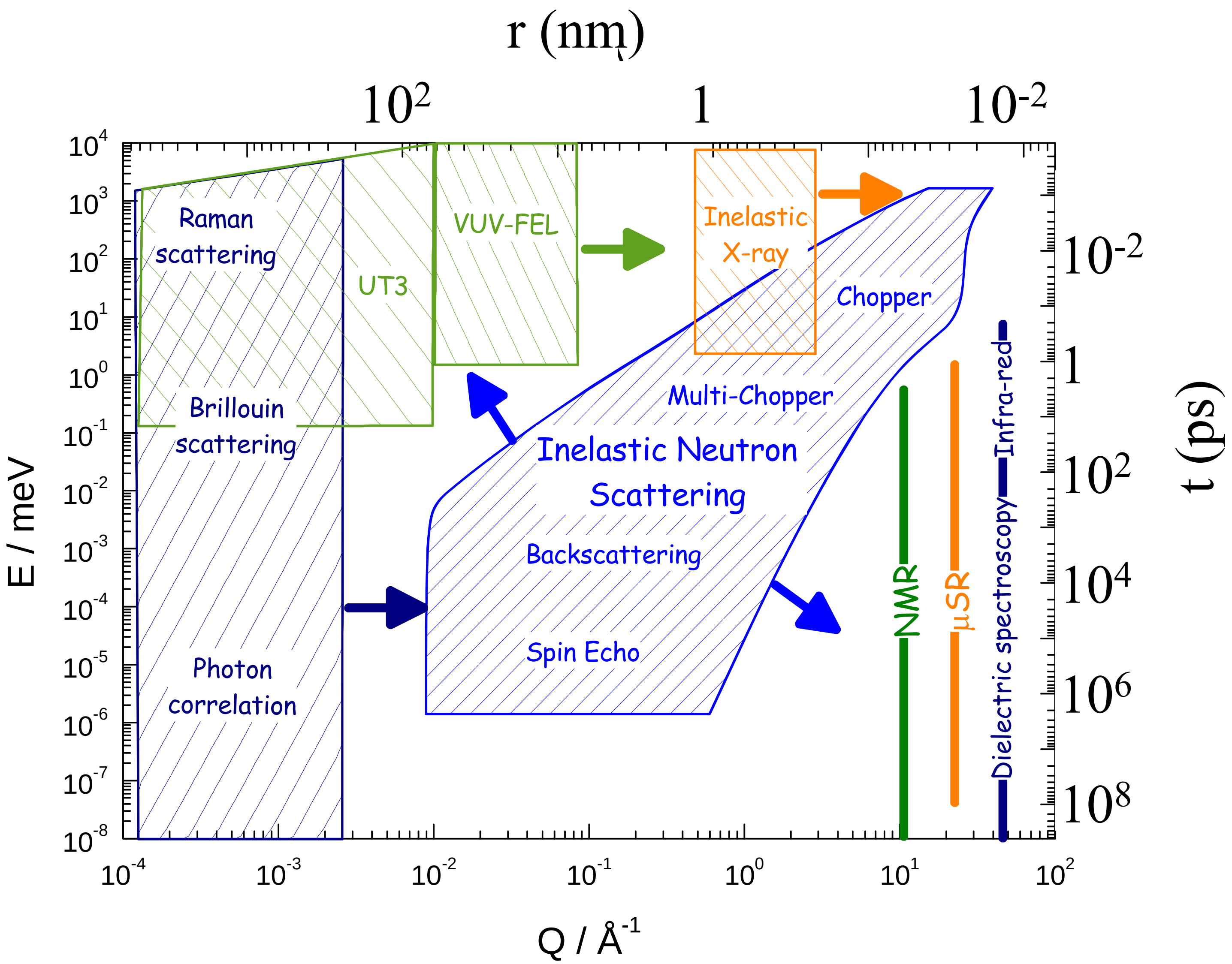


- Isotopic sensitivity (especially D and H)
- Penetrates sample containment
- Sensitive to bulk and buried structure
- Simple interpretation – provides statistical averages, not single instances
- Wavelength similar to inter-atomic spacings
- Energy similar to thermal energies in matter

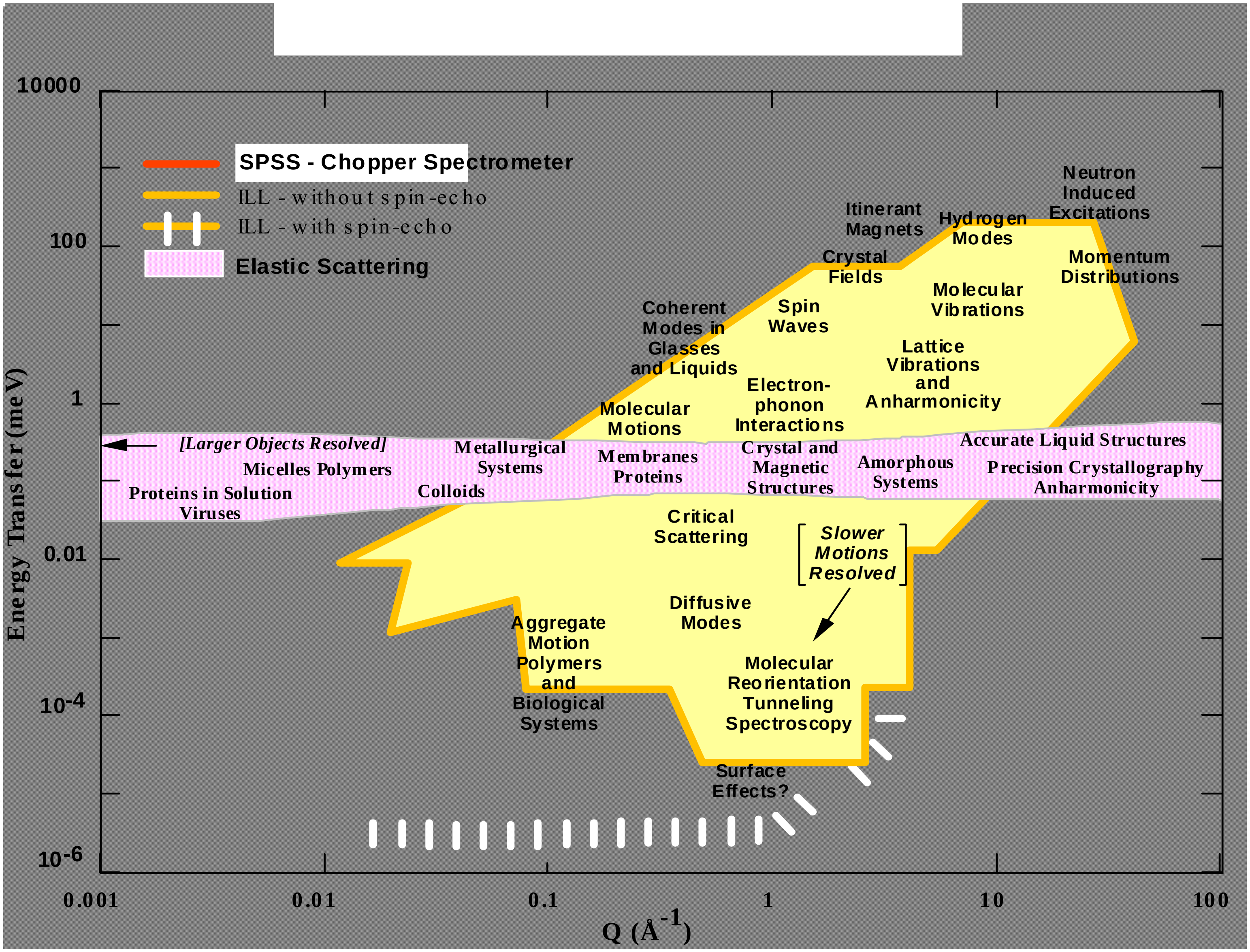
Neutron Scattering Complements Other Techniques in Length Scale….



……and Time Scale



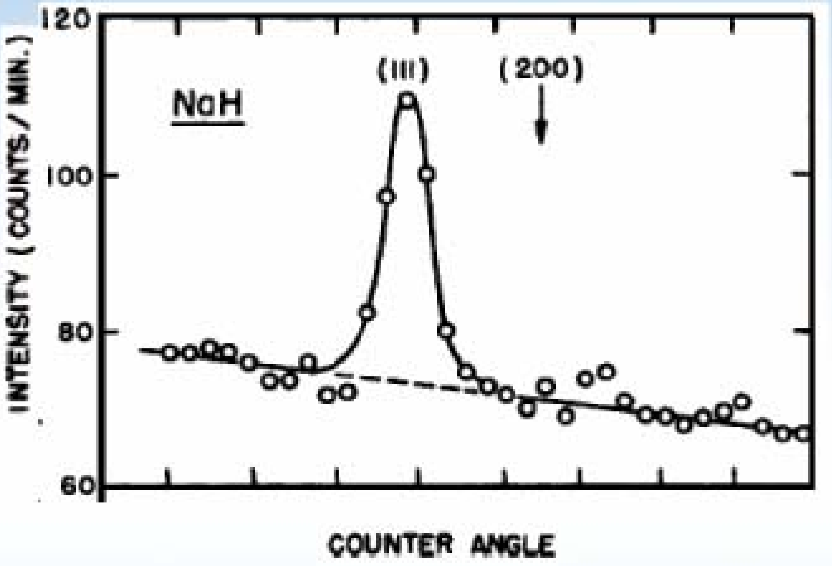
Many Condensed Matter Phenomena lie within the Ranges of Length & Time Seen by Neutron Scattering

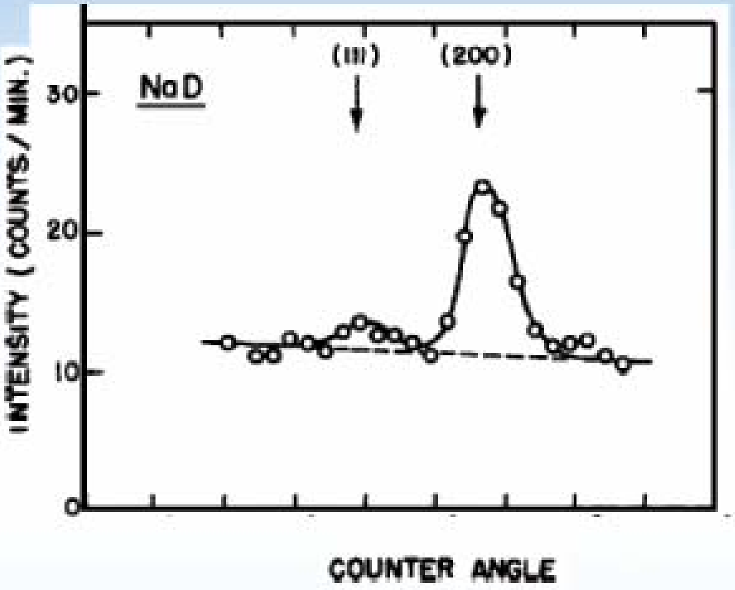


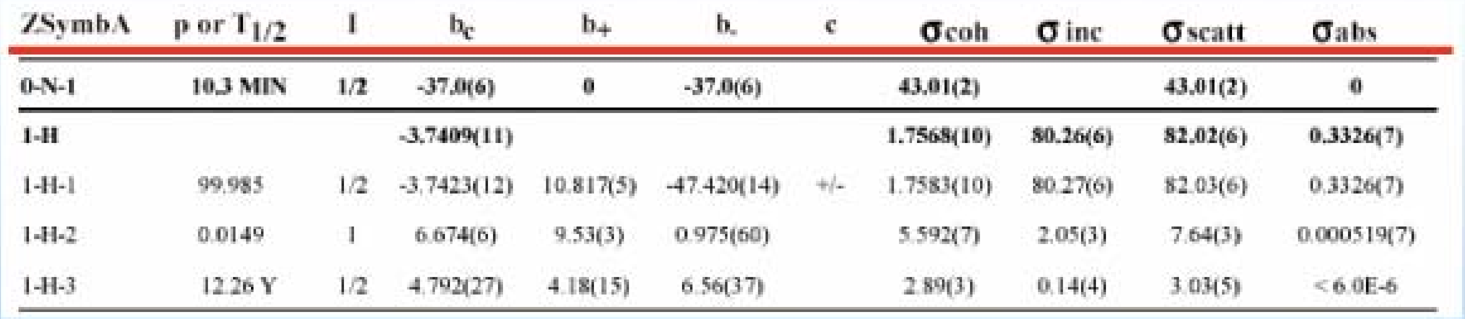
Early (pre 1970) Neutron Scattering Experiments Provided Underpinnings of Modern Understanding

- Localization of hydrogen in crystal structures
- Neel state of antiferromagnets & ferrimagnets
- Electronic distributions around atoms (form factors)
- Interatomic potentials in metals, semiconductors, rare gases, ionic crystals etc deduced from phonon dispersion curves
- Roton excitations in liquid ^{4}He
- Structural phase transitions (soft modes, central peaks)

Localization of Hydrogen and Deuterium

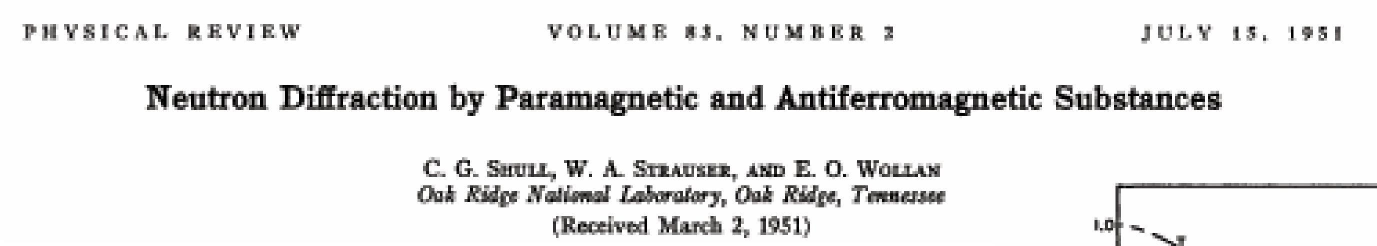






ZSymbA	p or $T_{1/2}$	I	b_c	b_+	b_-	c	σ_{coh}	σ_{inc}	σ_{scatt}	σ_{abs}
0-N-1	**10.3 MIN**	**1/2**	**-37.0(6)**	**0**	**-37.0(6)**		**43.01(2)**		**43.01(2)**	**0**
1-H			**-3.7409(11)**				**1.7568(10)**	**80.26(6)**	**82.02(6)**	**0.3326(7)**
1-H-1	99.985	1/2	-3.7423(12)	10.817(5)	-47.420(14)	+/-	1.7583(10)	80.27(6)	82.03(6)	0.3326(7)
1-H-2	0.0149	1	6.674(6)	9.53(3)	0.975(60)		5.592(7)	2.05(3)	7.64(3)	0.000519(7)
1-H-3	12.26 Y	1/2	4.792(27)	4.18(15)	6.56(37)		2.89(3)	0.14(4)	3.03(5)	< 6.0E-6

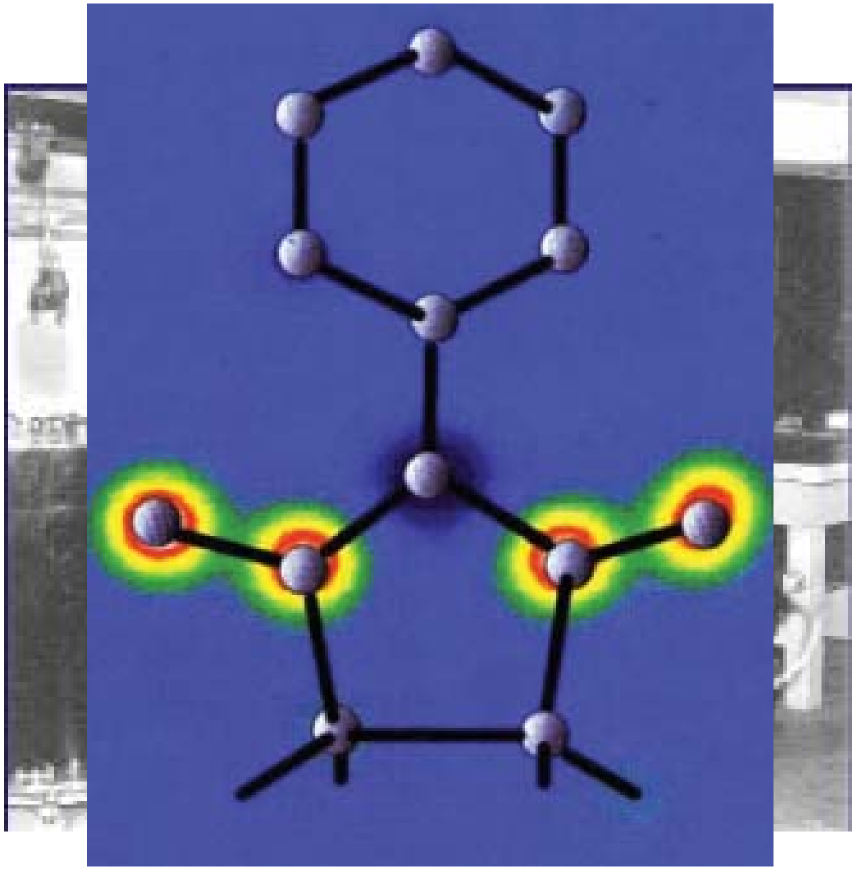
after C.G. Shull, E.O. Wollan, G.A. Morton, and W.L. Davidson, *Phys. Rev.* **73**, 482 – 487 (1948)



PHYSICAL REVIEW VOLUME 83, NUMBER 2 JULY 15, 1951

Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. SHULL, W. A. STRAUSER, AND E. O. WOLLAN
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received March 2, 1951)



Magnetic form factors

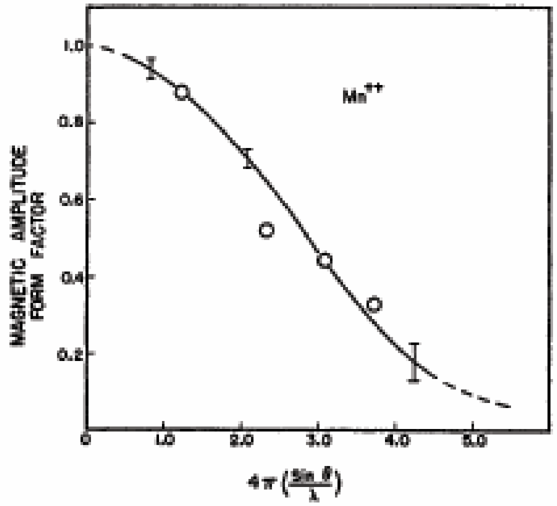


FIG. 2. Magnetic amplitude form factor for Mn++ ions. The curve is that obtained from paramagnetic diffuse scattering with estimated error as shown. The points represent values of the form factor obtained from the low temperature antiferromagnetic reflections of MnO.

Magnetic phase transitions

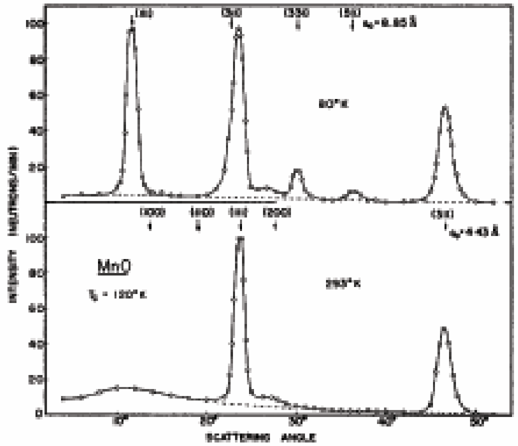


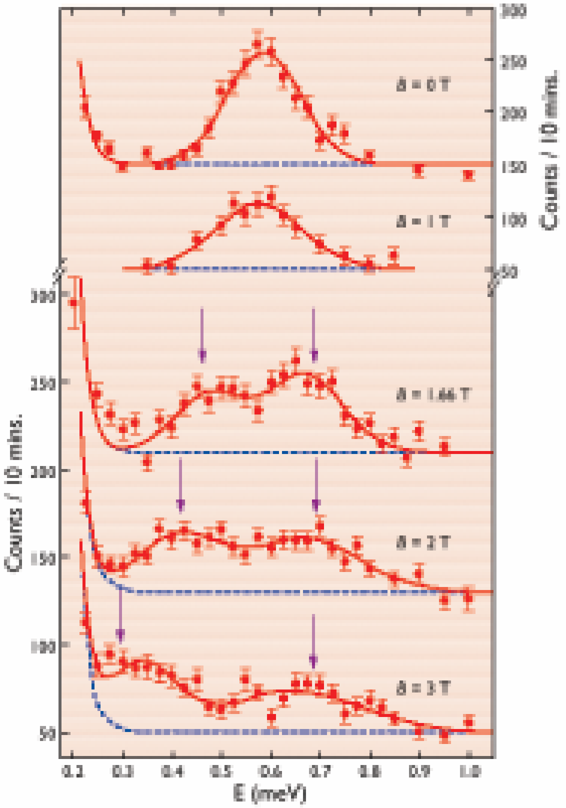
FIG. 4. Neutron diffraction patterns for MnO taken at liquid nitrogen and room temperatures. The patterns have been corrected for the various forms of extraneous, diffuse scattering mentioned in the text. Four extra antiferromagnetic reflections are to be noticed in the low temperature pattern.

A modern version –
spin density in a free radical

Traditional Magnetic Scattering Experiments

- Magnetic structures
- Magnetic phase diagrams
- Magnetic excitations

Quantum fluctuations in quasi-1D Heisenberg AFM



Mn-perovskites

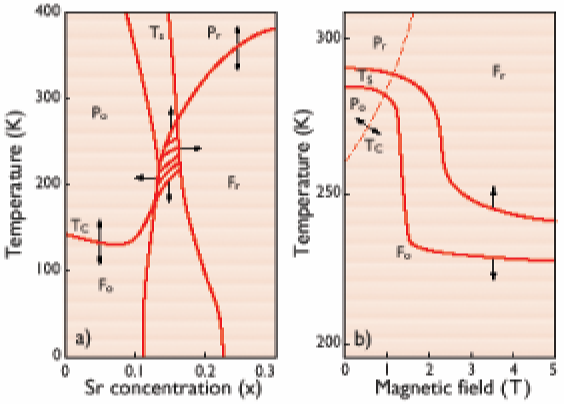
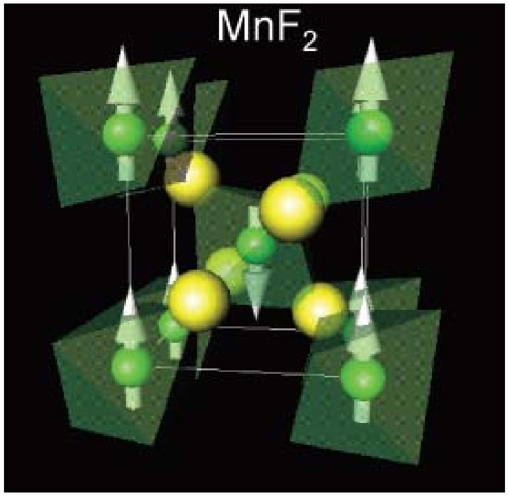
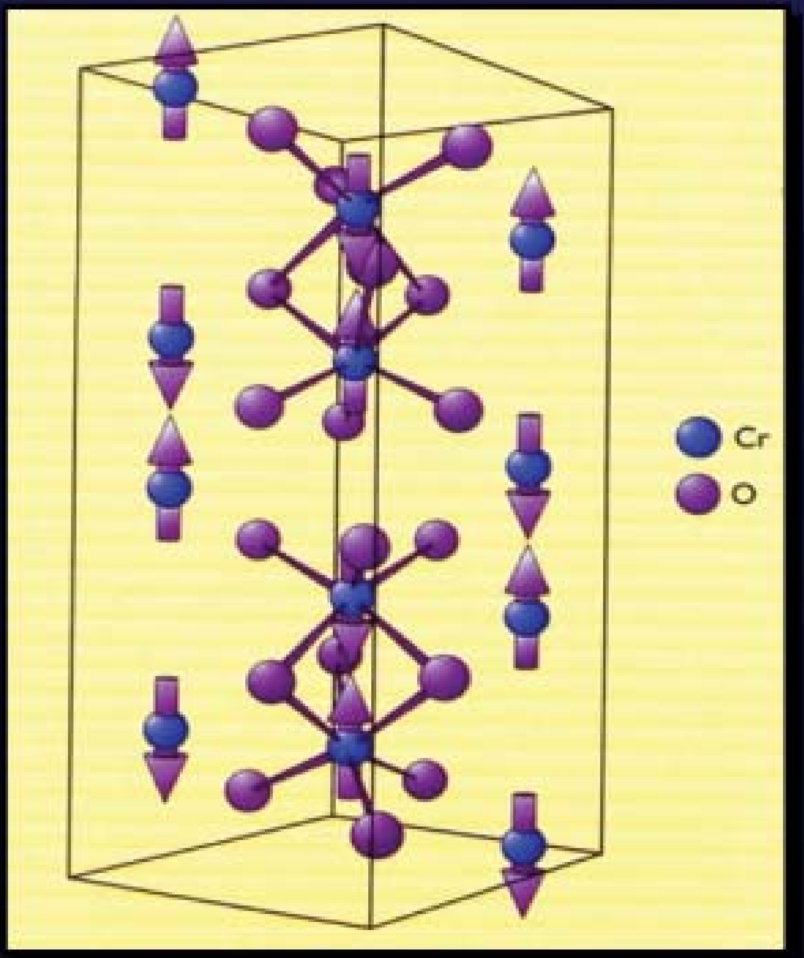


Figure 3: a) The x-T phase diagram of $La_{1-x}Sr_xMnO_3$ (based on [1]), and **b)** the H-T phase diagram of $La_{0.835}Sr_{0.165}MnO_3$ (based on [2], and experiments on D3 [3]).



Polarised Neutrons - magnetic structures



Magnetic structure within magneto-electric domains in anti-centrosymmetric Cr_20_3

Brown et al, J Phys: Condensed Matter 10, 663 (1998)

Viewgraph courtesy of Bob Cywinski

PHYSICAL REVIEW VOLUME 128, NUMBER 3 NOVEMBER 1, 1962

Crystal Dynamics of Lead. I. Dispersion Curves at 100°K

B. N. Brockhouse,* T. Arase,† G. Caglioti,‡ K. R. Rao,§ and A. D. B. Woods
Neutron Physics Branch, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada

(Received June 4, 1962)

Brockhouse's first 3 axis spectrometer at NRU reactor in 1959

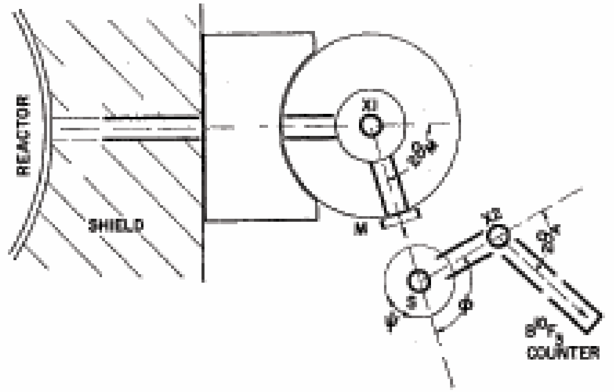
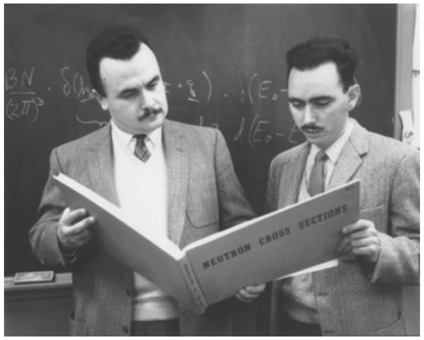
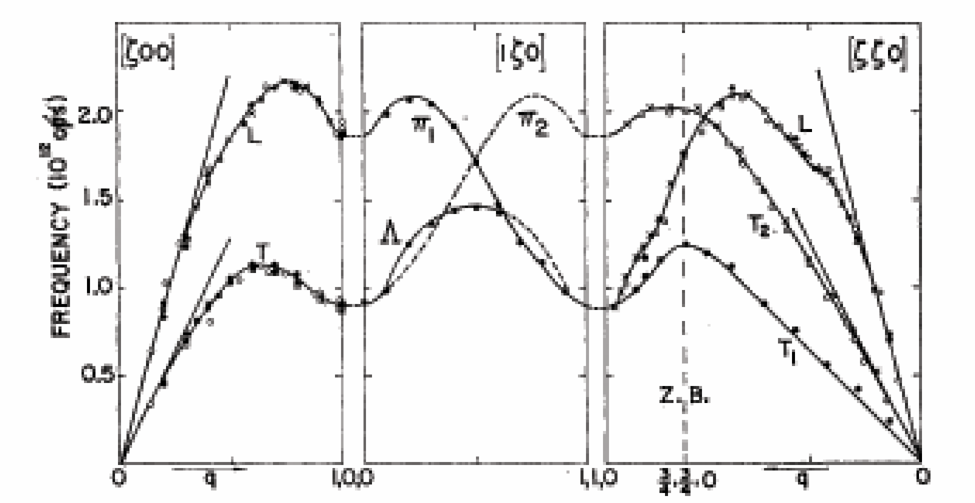
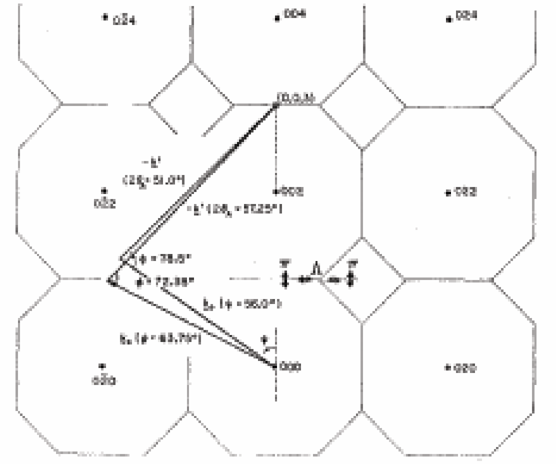


FIG. 1. Schematic drawing of the apparatus.



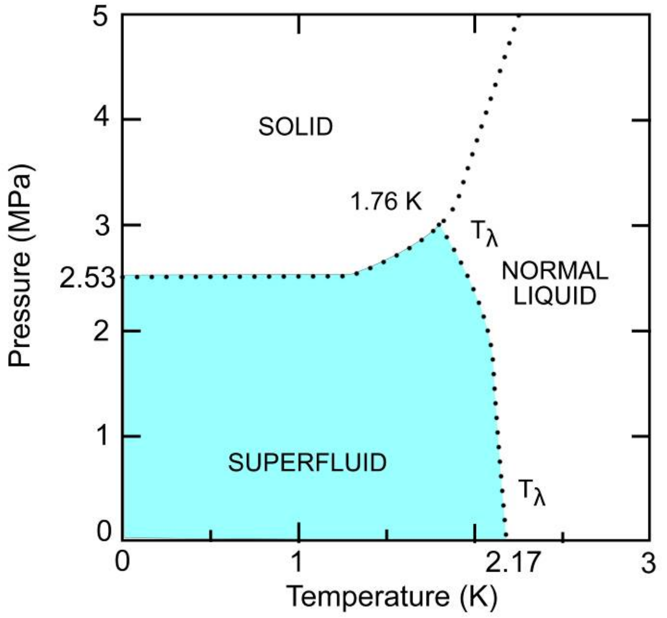
Brockhouse and Woods

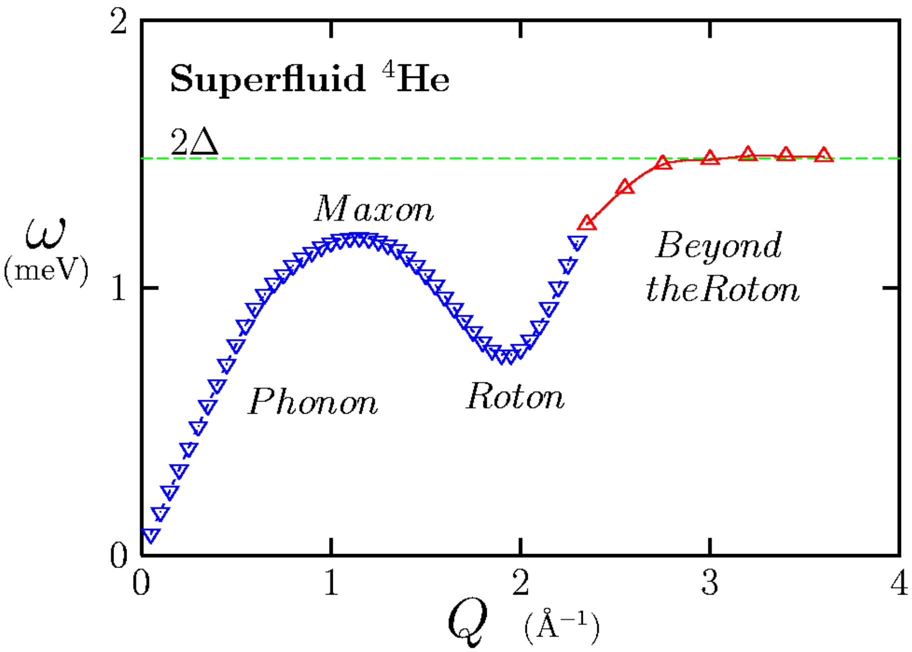


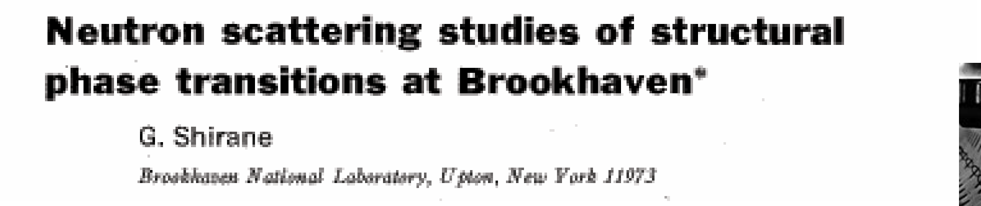


The constant-Q method

Roton Minimum in Superfluid ^{4}He was Predicted by Landau







Neutron scattering studies of structural phase transitions at Brookhaven*

G. Shirane

Brookhaven National Laboratory, Upton, New York 11973

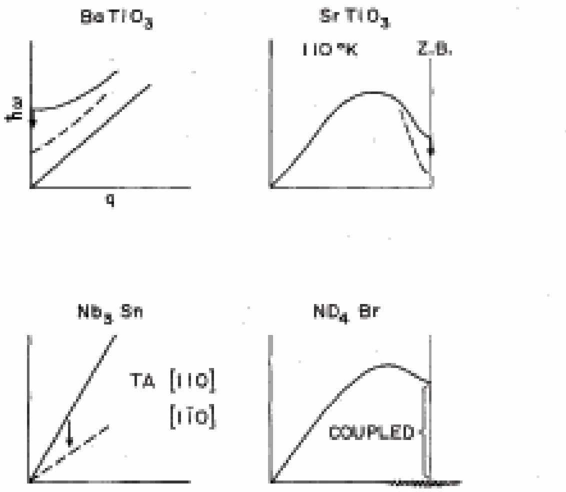


FIG. 3. Typical soft mode (arrows) phase transitions studied at Brookhaven. These represent temperature-dependent phonon dispersion relations ħω vs q.

Gen Shirane

Tormod Riste

SrTiO$_3$ looked like a simple mean-field displacive phase transition described by a soft-mode theory until Riste discovered the Central Peak

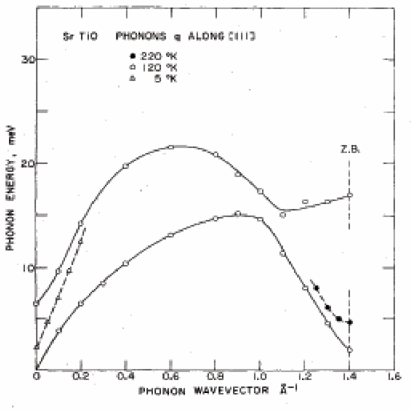
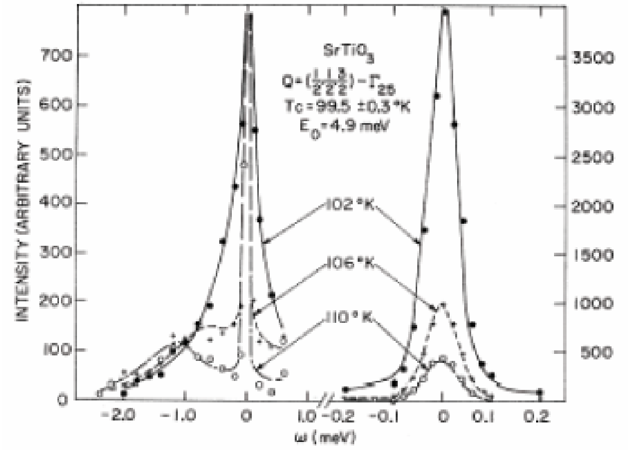
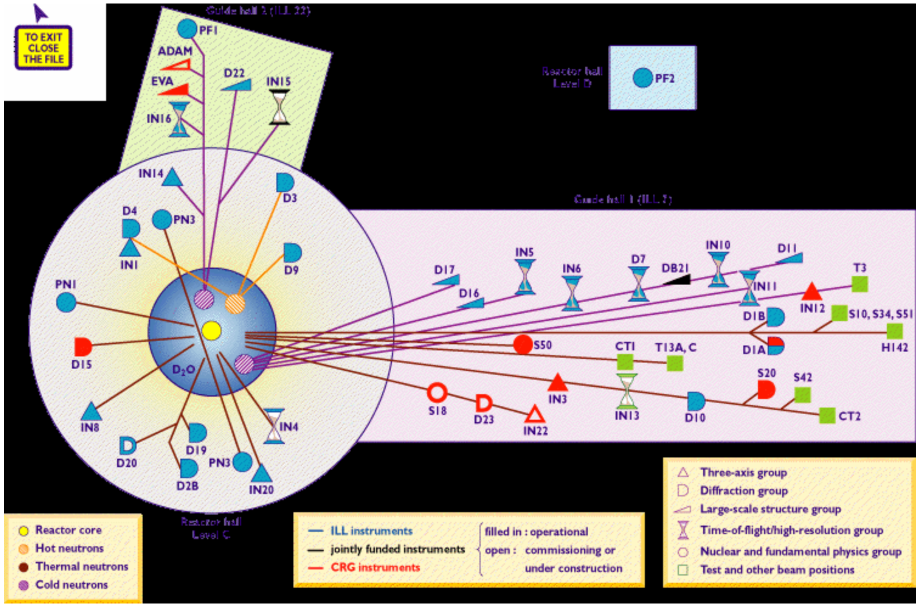


FIG. 6. Temperature-dependent phonon modes in SrTiO$_3$ measured by Shirane and Yamada (1969). The 110°K transition is caused by the soft mode at the zone boundary. Soft mode near the origin is due to incipient ferroelectricity.



With the Construction of the ILL, Neutron Scattering Instrumentation became More Specialized

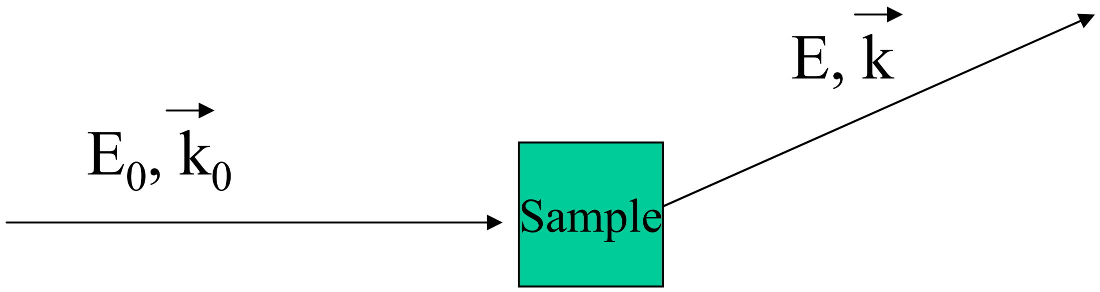


The issue is that neutron scattering is a signal-limited technique.

Even the ILL doesn't produce many neutrons!!

	Brightness *(s^{-1} m^{-2} $ster^{-1}$)*	*dE/E* *(%)*	*Divergence* *($mrad^2$)*	*Flux* *(s^{-1} m^{-2})*
Neutrons	10^{15}	2	10 x 10	10^{11}
Rotating Anode	10^{16}	3	0.5 x 10	5×10^{10}
Bending Magnet	10^{24}	0.01	0.1 x 5	5×10^{17}
Wiggler	10^{26}	0.01	0.1 x 1	10^{19}
Undulator (APS)	10^{33}	0.01	0.01 x 0.1	10^{24}

Neutron Scattering is Really Quite Simple…..
…..at least, in Principle



$$\hbar\vec{Q} = \hbar(\vec{k} - \vec{k}_0)$$
$$\hbar\omega = E - E_0$$

$$\text{Momentum} = \hbar k; \quad \text{Energy} = \hbar^2 k^2/2m_n$$

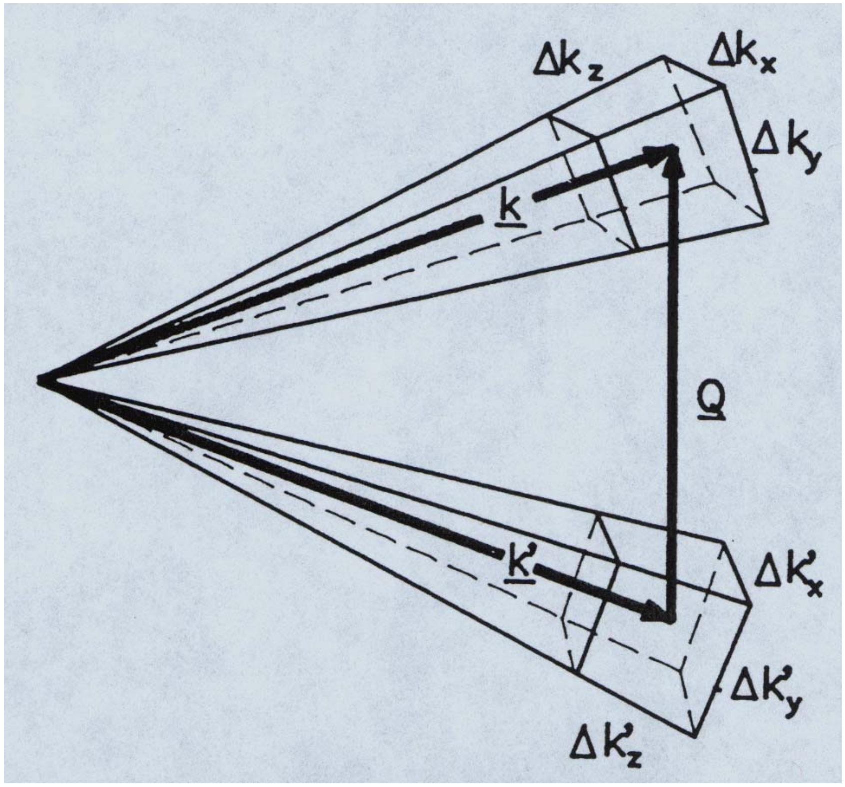
- Measure the number of scattered neutrons as a function of $\vec{Q}$ and ω
- The result is the scattering function $S(\vec{Q},\omega)$ that depends only on the properties of the sample

- All we need to do is to prepare a neutron beam with wavevector $\vec{k}_0$ and measure the intensity of neutrons scattered with wavevector $\vec{k}$

Instrumental Resolution

- Uncertainties in the neutron wavelength & direction of travel imply that Q and E can only be defined with a certain precision

- When the box-like resolution volumes in the figure are convolved, the overall resolution width is the quadrature sum of the box sizes. Small “boxes” give good resolution.

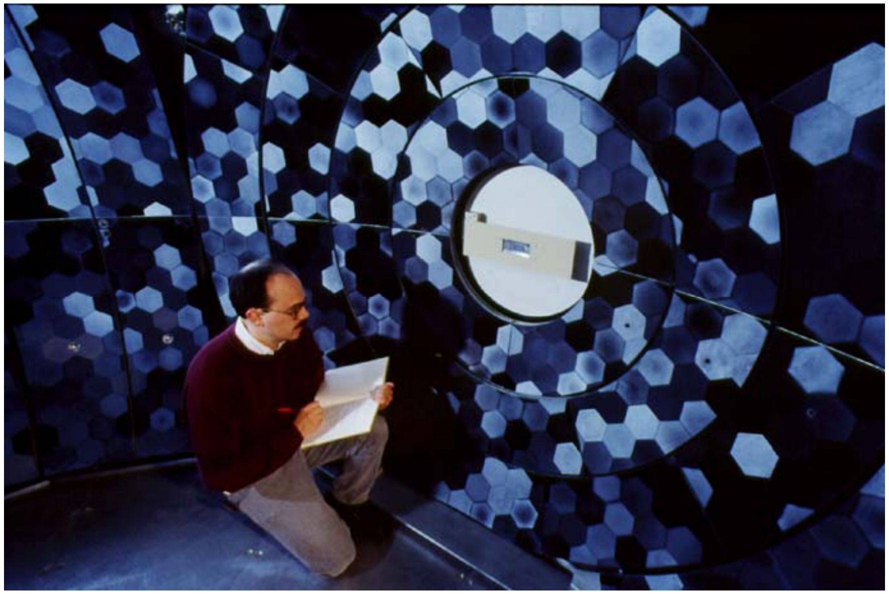


- The total signal in a scattering experiment is proportional to the product of the “box” sizes

The better the resolution, the lower the count rate

Examples of Specialization of Spectrometers: Optimizing the Signal for the Science

- Small angle scattering [$Q = 4\pi \sin\theta/\lambda$; $(\delta Q/Q)^2 = (\delta\lambda/\lambda)^2 + (\cot\theta\ \delta\theta)^2$]
  - Small diffraction angles to observe large objects => long (20 m) instrument
  - poor monochromatization ($\delta\lambda/\lambda \sim 10\%$) sufficient to match obtainable angular resolution (1 cm^2 pixels on 1 m^2 detector at 10 m => $\delta\theta \sim 10^{-3}$ at $\theta \sim 10^{-2}$))
- Back scattering [$\theta = \pi/2$; $\lambda = 2\,d \sin\theta$; $\delta\lambda/\lambda = \cot\theta + \ldots$]
  - very good energy resolution (~neV) => perfect crystal analyzer at $\theta \sim \pi/2$
  - poor Q resolution => analyzer crystal is very large (several m^2)



Neutron Scattering Instrumentation is Designed to Compromise between Intensity & Resolution

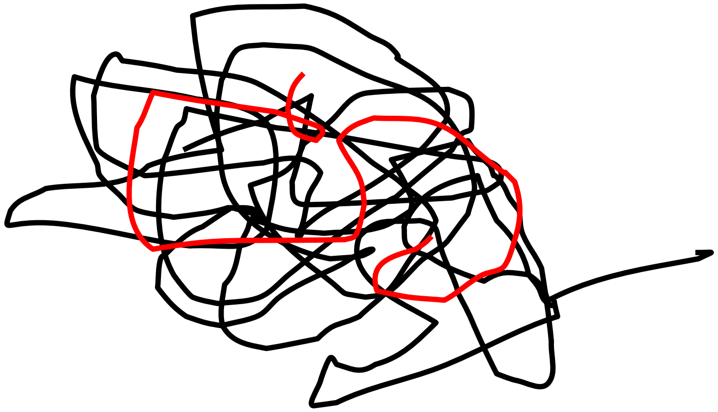
- Maxwellian distribution of neutron velocities $P(v) \sim \frac{1}{T^{3/2}} e^{-\frac{1}{2}mv^2/kT}$
- Liouville's theorem – the (6-dimensional) phase space density of non-interacting particles cannot be increased by conservative forces
  - Brighter sources => colder moderators or non-equilibrium neutron production
- We can only increase scattered intensity at a given ($\vec{Q}$,E) by increasing the phase space volume
- Design instruments to have good resolution in the direction of ($\vec{Q}$,E) space that is important for the science
- Neutron optics & instrumentation is designed to:
  - Maintain neutron brightness
  - Provide good resolution in a chosen direction in ($\vec{Q}$,E) space
  - Simultaneously measure as many resolution elements [i.e. ($\vec{Q}$,E) points] as is useful

Neutron Scattering often Provides Definitive Answers Condensed-Matter Questions

- Microstructure in complex (i.e. macromolecular) fluids
- Structures of thin film systems
- Atomic arrangements in nano-particles
- Superconductivity in MgB_2
- The location of protons in biomolecular crystals

Microstructure of Macromolecular Fluids

- In ‘72 SANS was used to probe the statistics of polymer chains
  - $R_g \sim N^{1/2}$
  - Contrast variation method was used



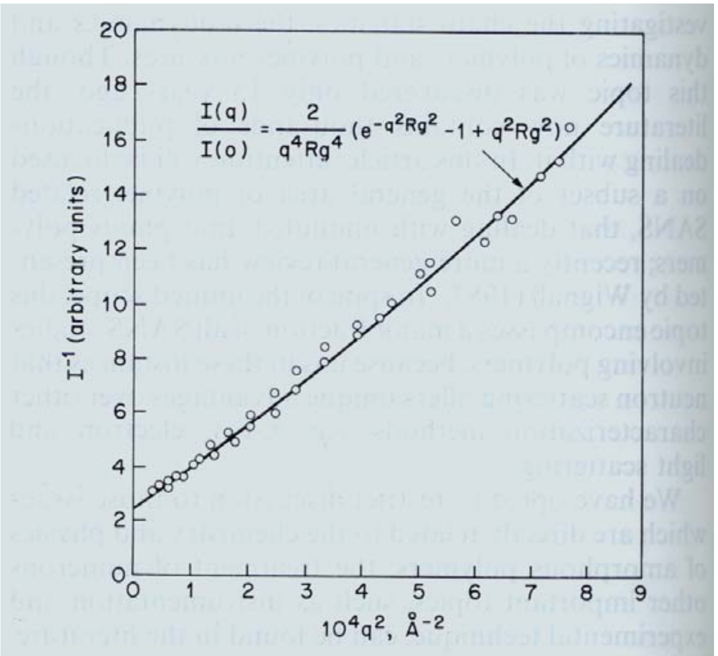
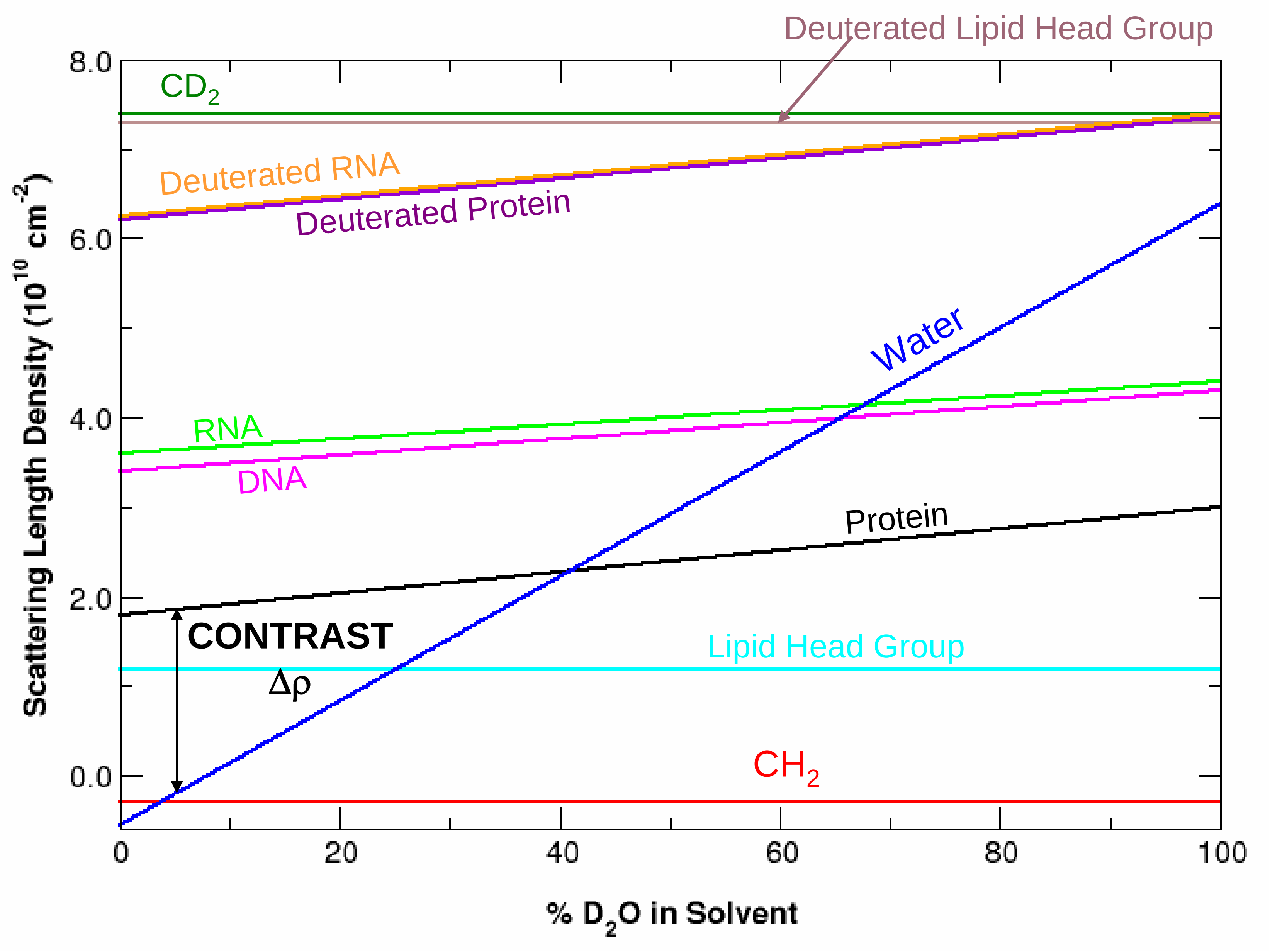
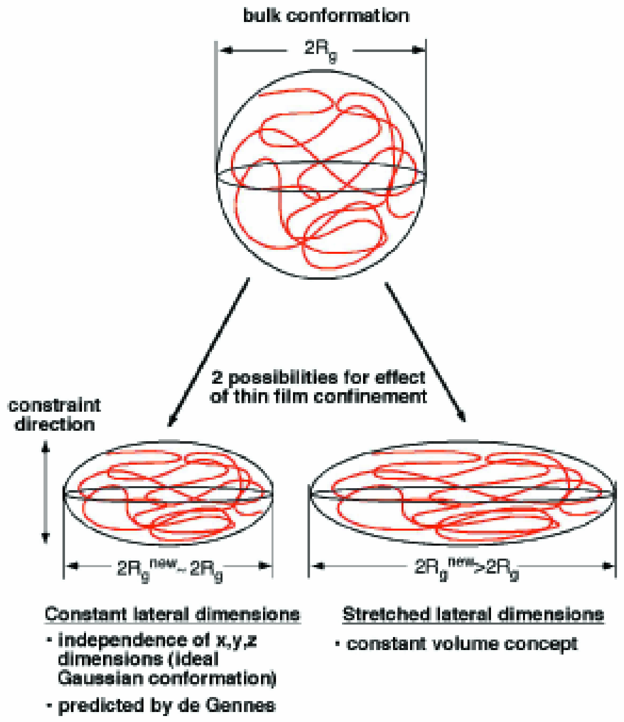


Fig. 1. SANS results obtained by Kirste, Kruse & Schelten (1972) for 1·2% deuterated poly(methyl methacrylate) (PMMA) in normal PMMA (mol. wt of 250 000) plotted in Ornstein–Zernike form. The solid curve represents a Debye function [equation (1)]. This was one of the first quantitative demonstrations of Gaussian coil behavior for bulk polymers.

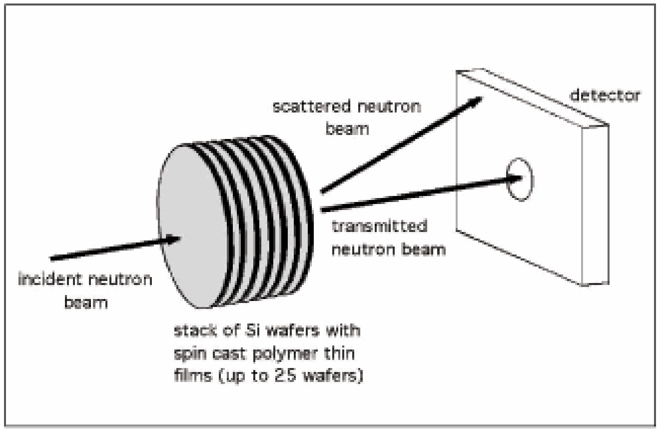
Contrast Variation is an Important Technique



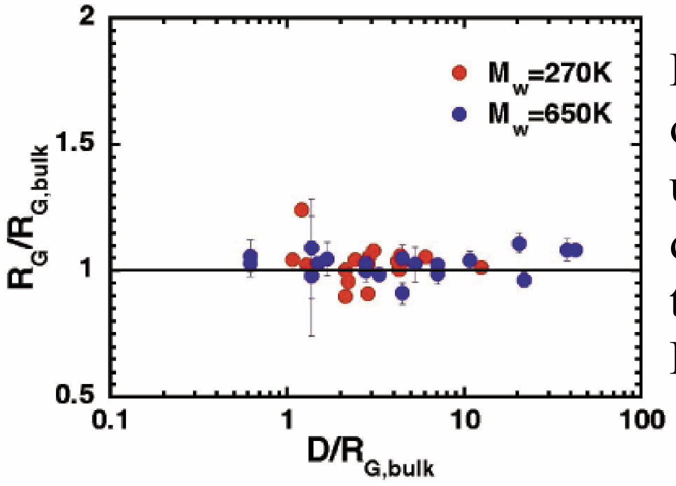
A More Difficult Experiment is to Probe Chain Conformation in Thin Films



R.L. Jones, S.K. Kumar, D.L. Ho, R.M. Briber, T.P. Russell, *Nature*, 1999, 400, 146



Thin films of 25% d-PS & 75% PS spun on to Si wafers. 25 wafers => 250 nm or larger total polymer thickness



R_g in the plane of the film is unchanged down to film thickness of $R_g/2$

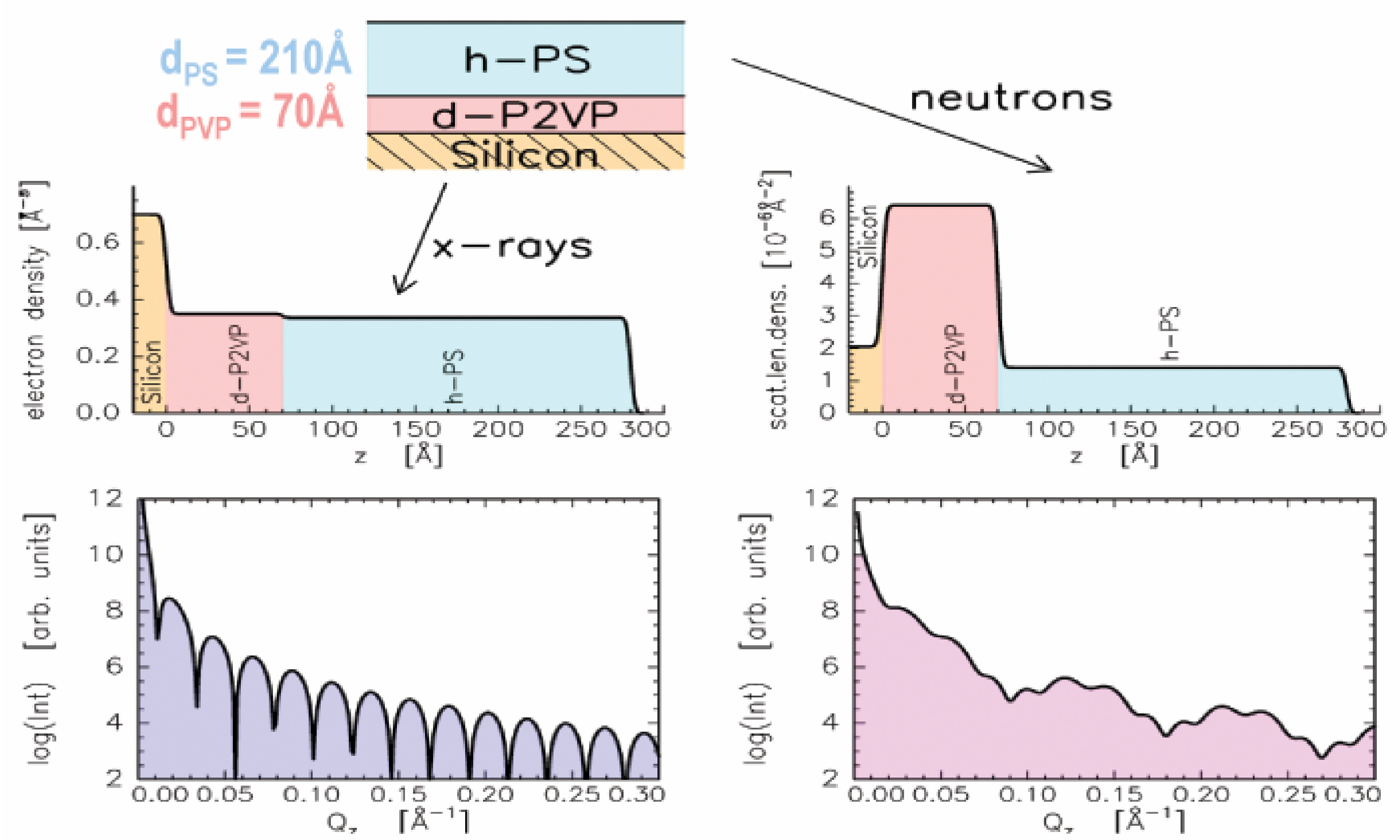
Shows a limitation of neutron scattering for nano-science: normally need large samples

Neutron Scattering often Provides Definitive Answers Condensed-Matter Questions

- Microstructure in complex (i.e. macromolecular) fluids
- Structures of thin film systems
- Atomic arrangements in nano-particles
- Superconductivity in MgB_2
- The location of protons in biomolecular crystals

Structures of Thin Films using Reflectometry

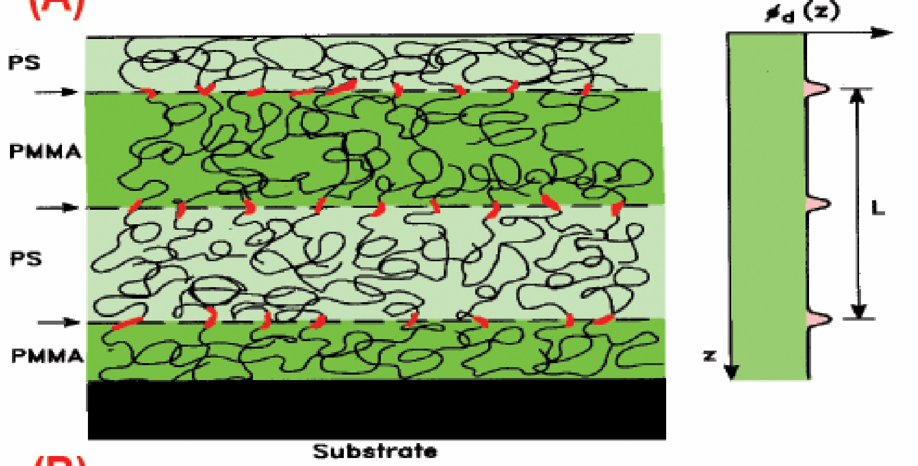
- Neutron reflectometry was invented in the 1980's to probe interfaces & layered structures such as polymer films or magnetic layers



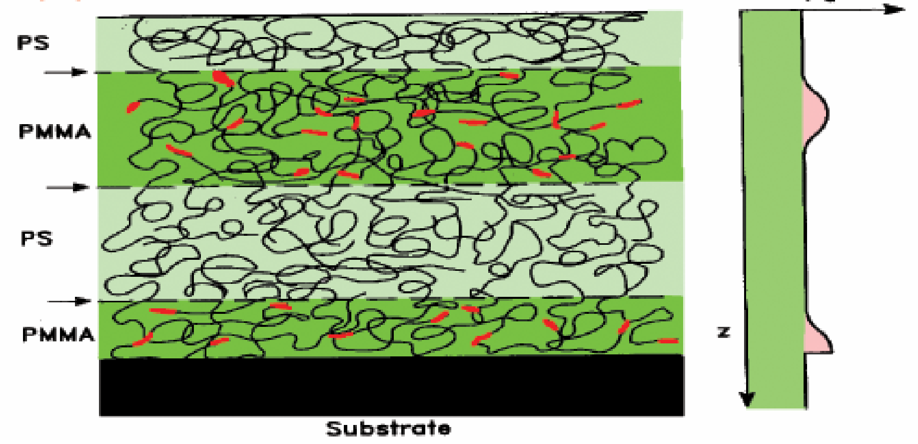
Graphic from Metin Tolan

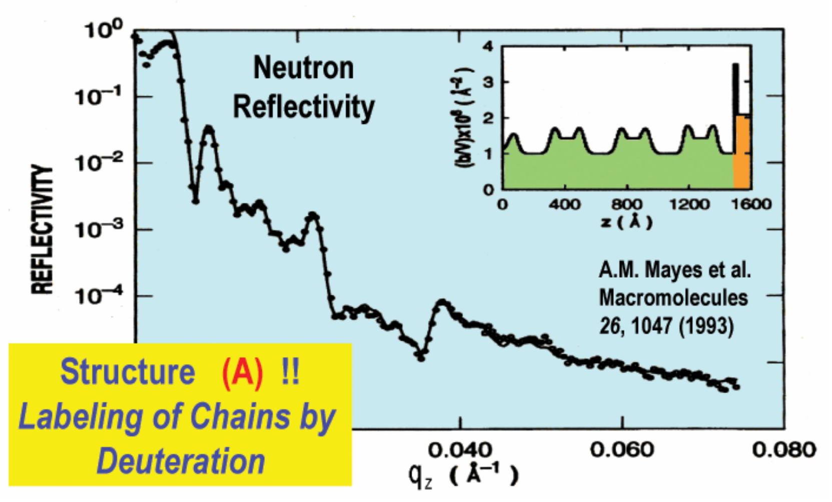
Where are the Chain Ends in an Annealed Diblock Copolymer Film – A or B?

(A)



(B)

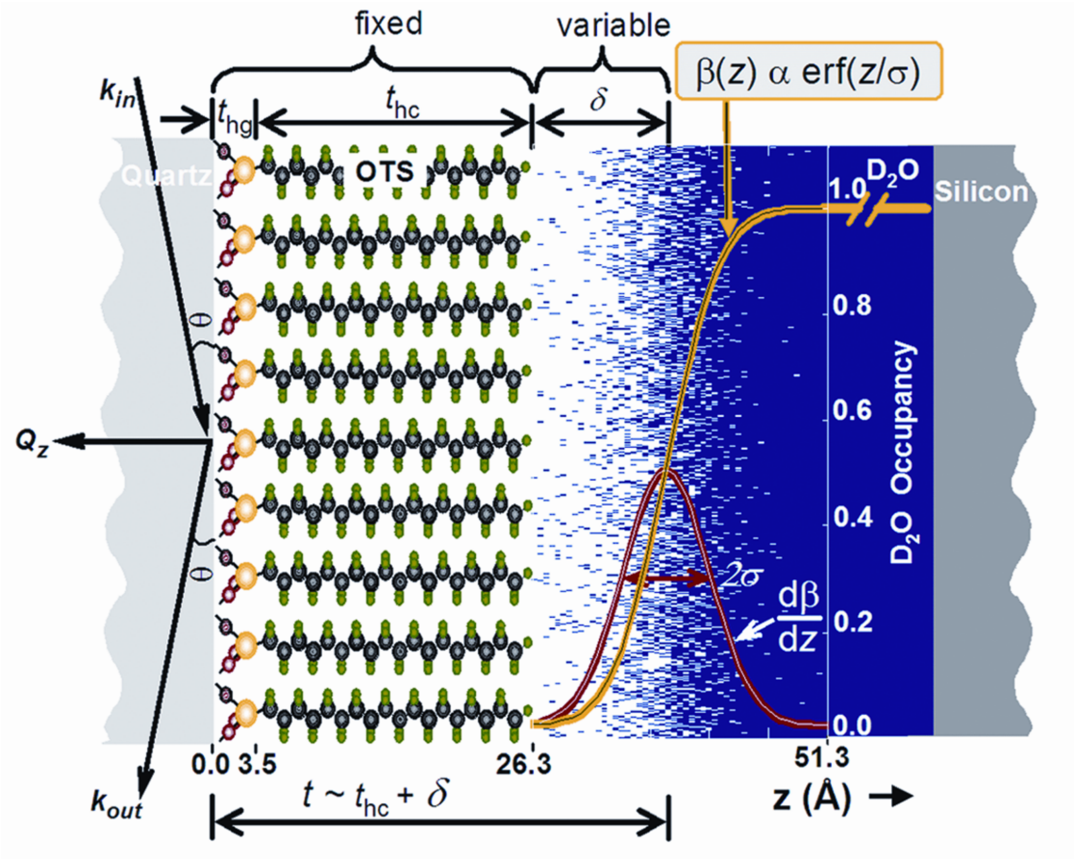




A.M. Mayes et al.
Macromolecules
26, 1047 (1993)

Structure (A) !!
Labeling of Chains by Deuteration

Neutron Reflectometry has Revealed Reduced Water Density at a Hydrophobic Surface



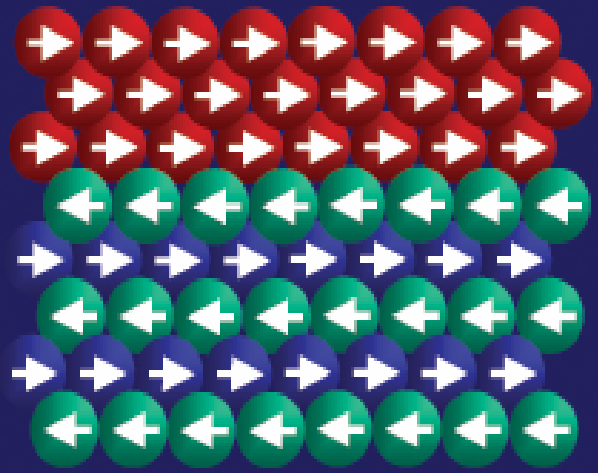
Interface width, δ, depends on the amount of dissolved gases

Dhaval A. Doshi, Erik B. Watkins, Jacob N. Israelachvili, Jaroslaw Majewski, PNAS (2005)

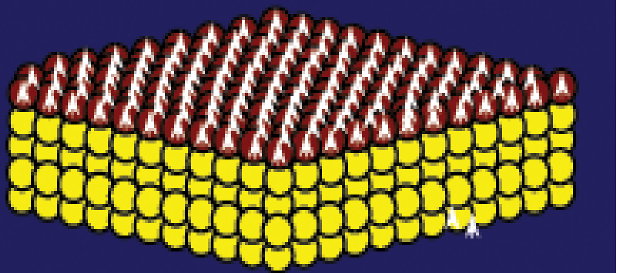
New challenges for magnetic neutron scattering

Spin valves

Exchange bias

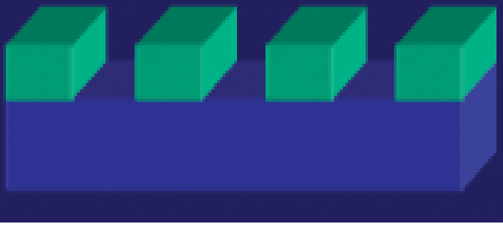


Magnetic films,
dimensionality effects

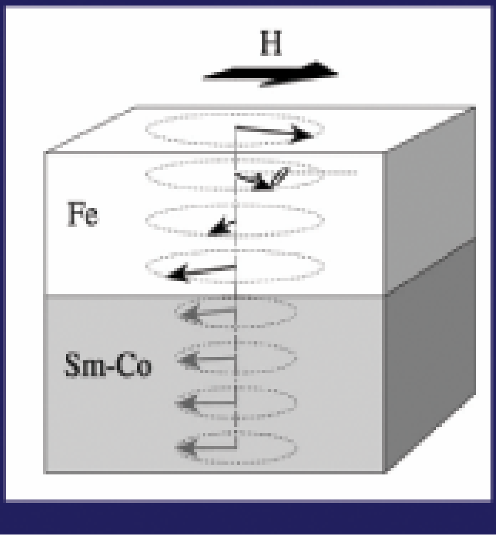


FM – Semiconductor

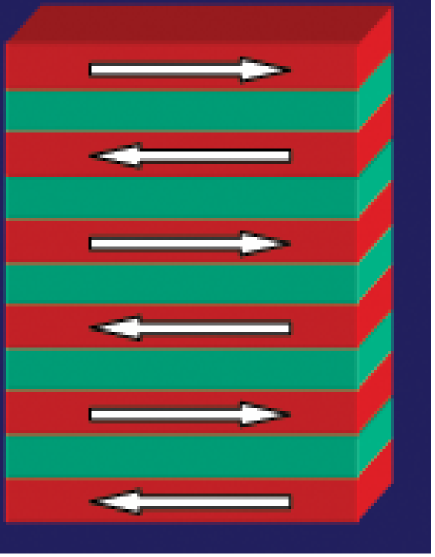
Lateral structures



Exchange springs

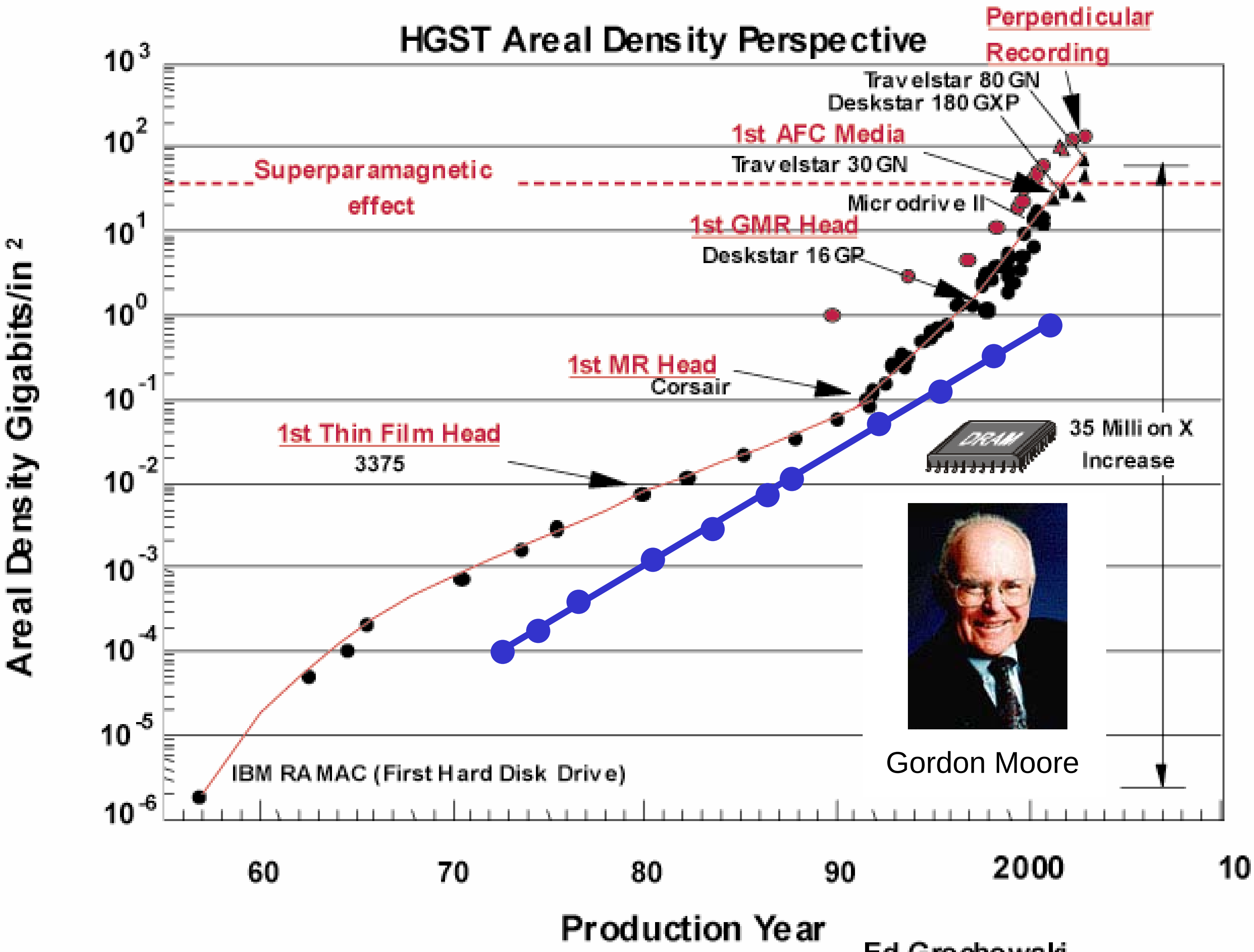


Exchange
coupling



VG from
Hartmut Zabel

HGST Areal Density Perspective

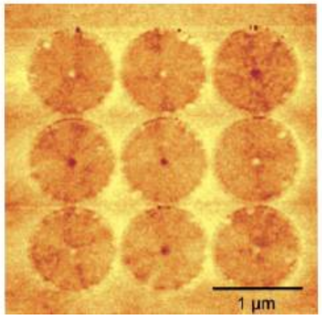


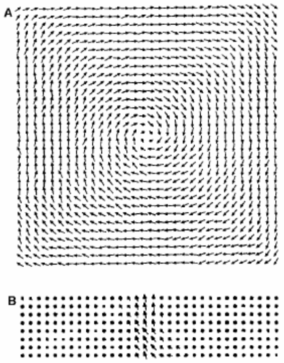
Ed Grochowski

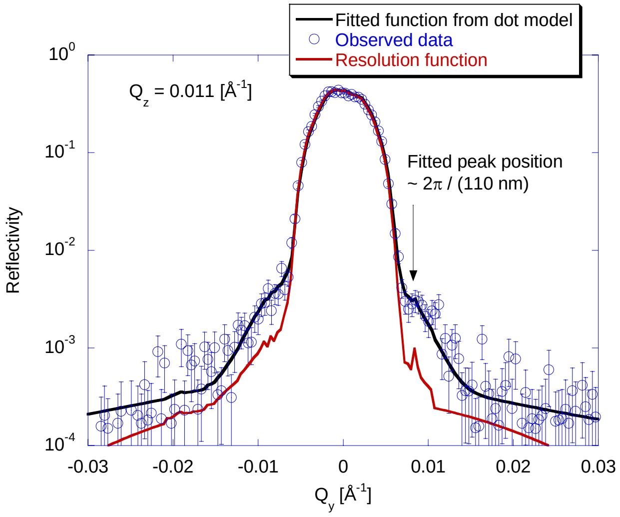
arpers2003a.prz

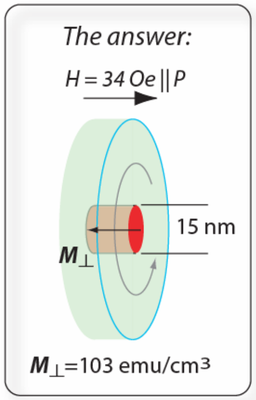
Vortex State in Thin Films of Magnetic Dots

Shinjo *et al.*,
Science **289**, 930 (2000)



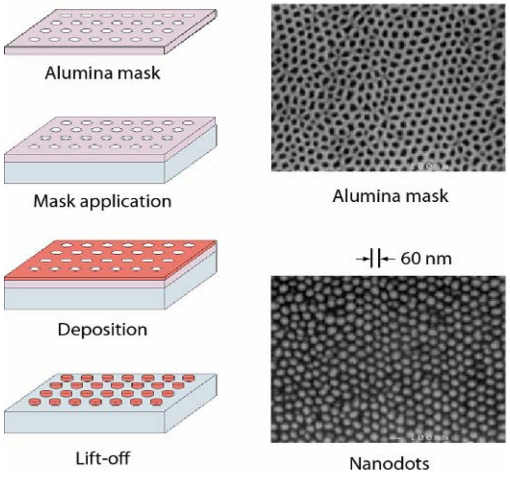






Large (~1 µm) magnetic dots (above) are visible with MFM or neutron reflection. Small (~ 65 nm) dots are harder to see

65 nm diameter dots spaced ~110 nm apart



- GINS experiment with polarized neutrons
- Determined total moment in vortex state in each dot
- At the limit of today’s neutron technology

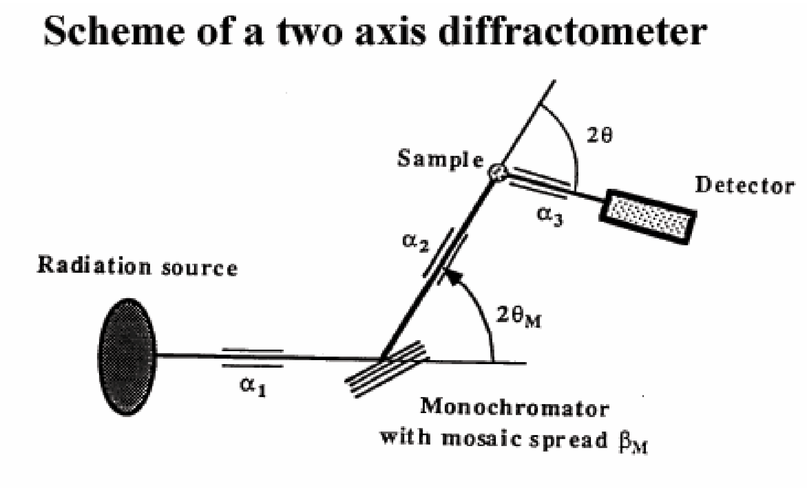
I.K. Schuller, S.K. Sinha, M. R. Fitzsimmons et al.

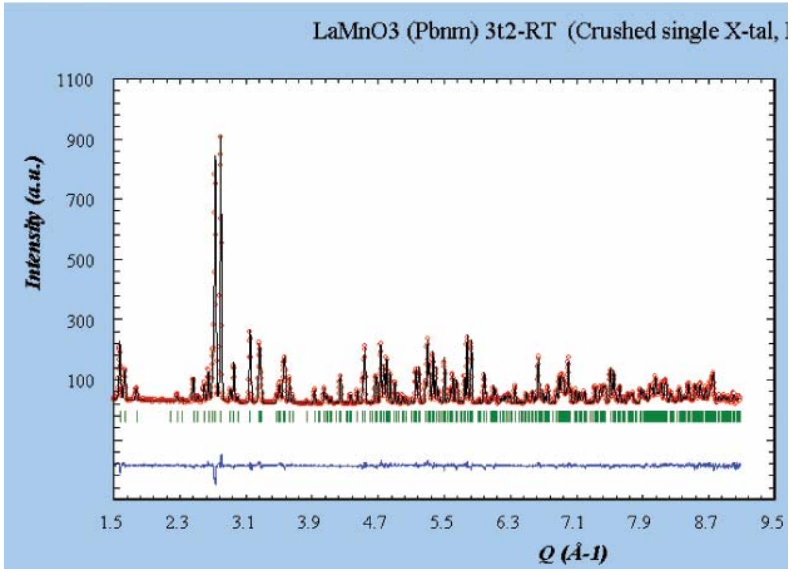
Neutron Scattering often Provides Definitive Answers Condensed-Matter Questions

- Microstructure in complex (i.e. macromolecular) fluids
- Structures of thin film systems
- Atomic arrangements in nano-particles
- Superconductivity in MgB_2
- The location of protons in biomolecular crystals

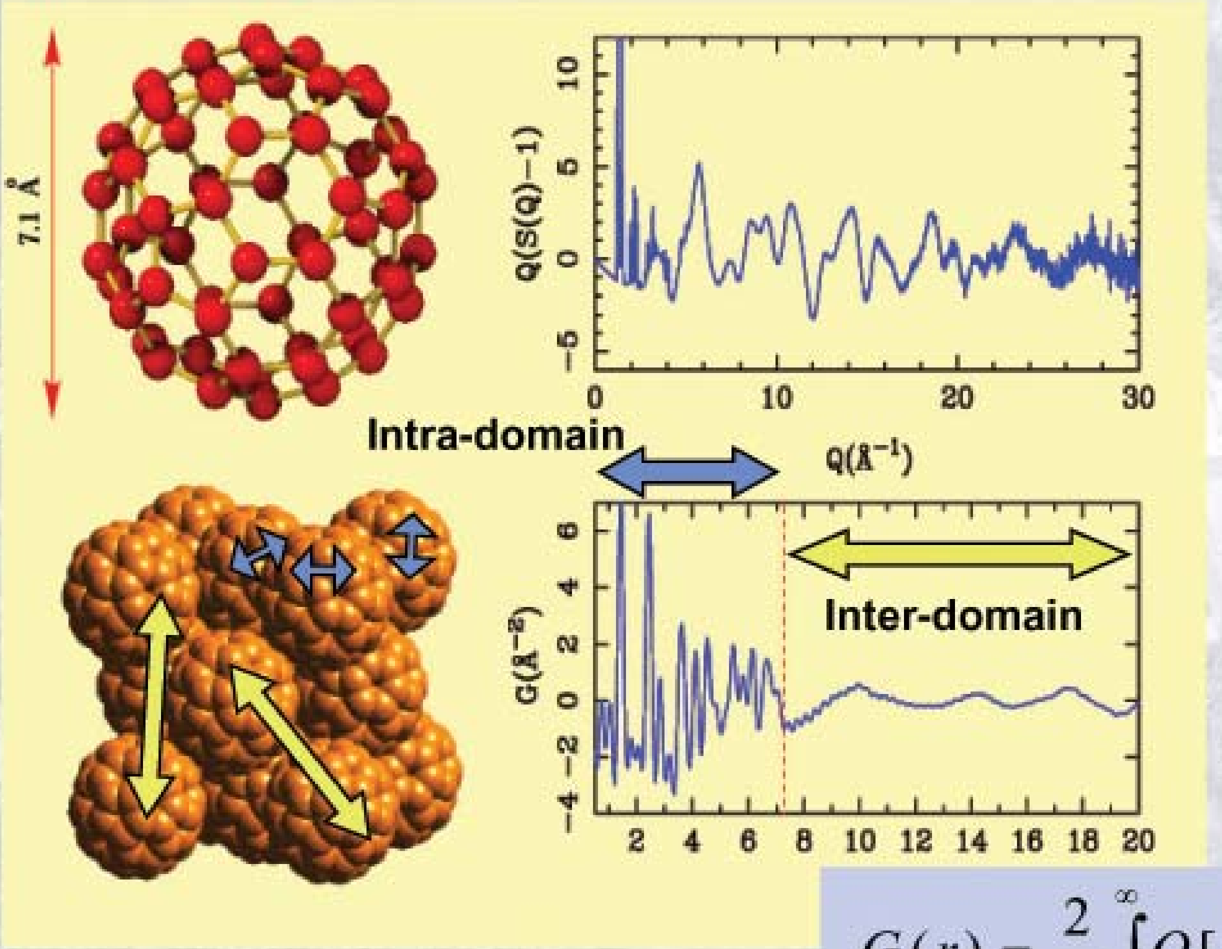
Is Short-Range Atomic Order the Same in Bulk and in Nano-Particles of Gold?

- Traditionally, we measure diffraction patterns and analyze the Bragg peaks to determine the structure assuming long-range periodic structure
  - Structure in the diffuse scattering between peaks is “background”





What is a PDF? Look at pair correlations as a function of separation



Example:
C_{60} - 'Bucky balls'

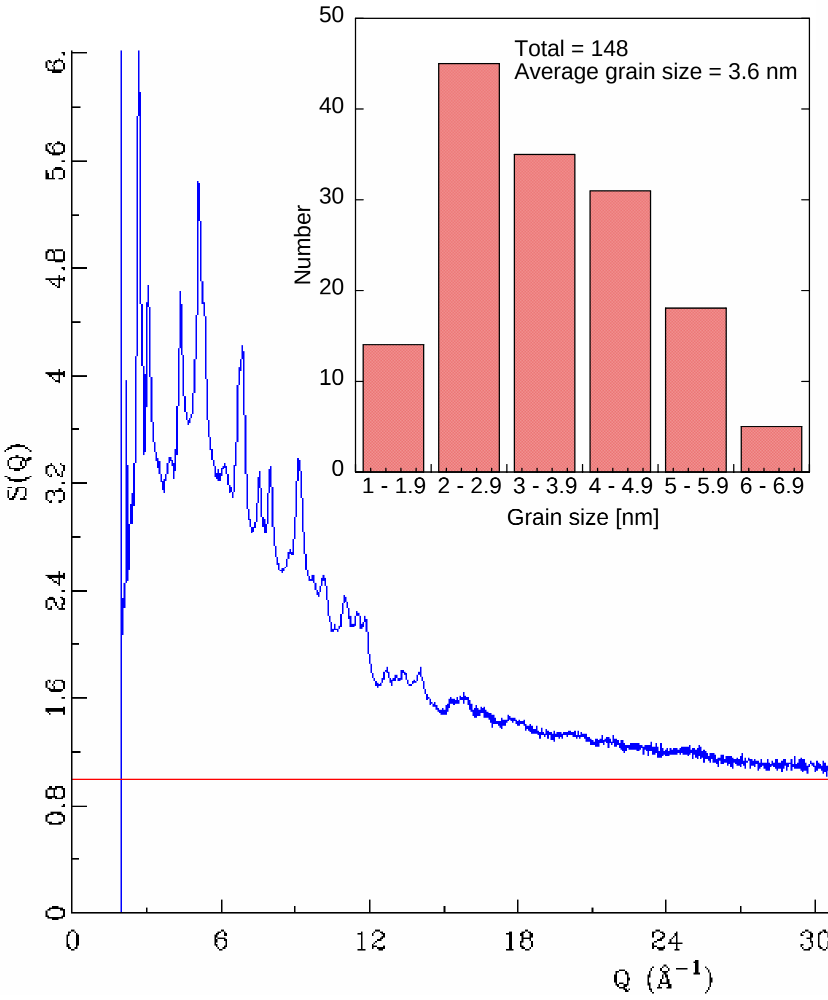
The PDF (similar to the Patterson) is obtained via Fourier transform of the normalized total scattering S(Q):

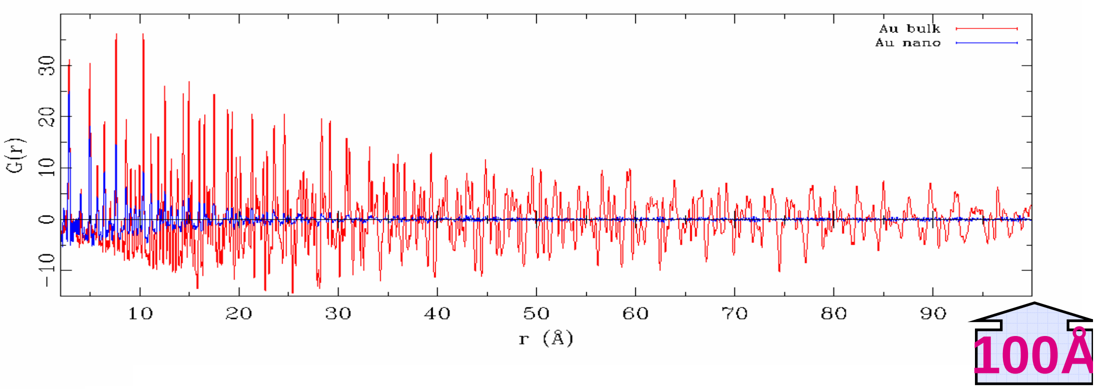
$$G(r) = \frac{2}{\pi}\int_0^{\infty} Q[S(Q)-1]\sin(Qr)\,dQ$$

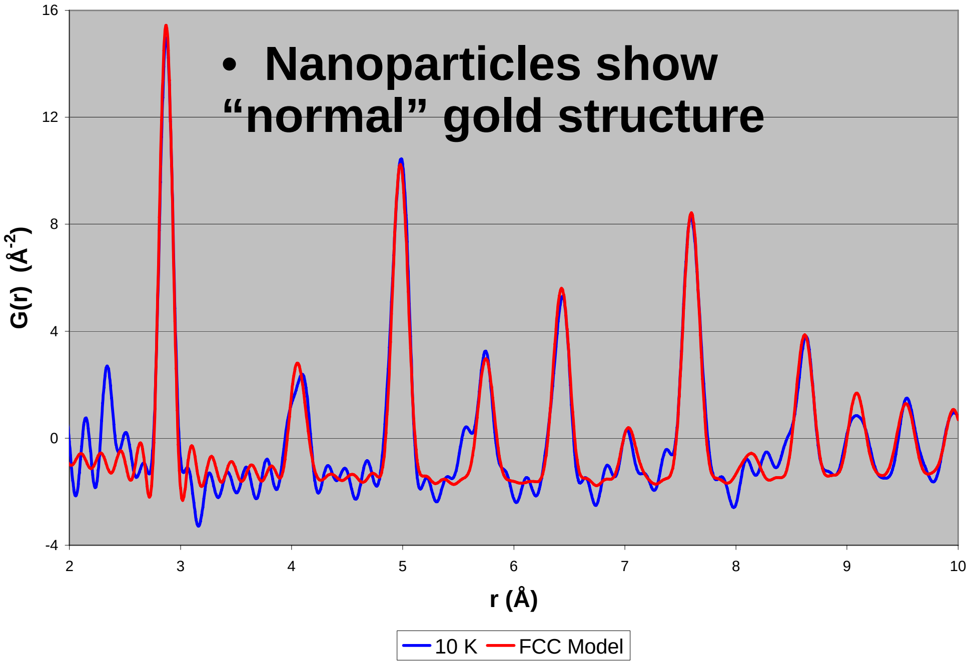
$$Q = 4\pi\sin\theta/\lambda$$

Viewgraph courtesy of Thomas Proffen

Neutron PDF Shows that Gold Nano-Particles Appear to have the Bulk Structure







- **Nanoparticles show “normal” gold structure**

K. Page, T. Proffen (LANL), R. Seshadri and A. Cheetham (UCSB)

Neutron Scattering often Provides Definitive Answers Condensed-Matter Questions

- Microstructure in complex (i.e. macromolecular) fluids
- Structures of thin film systems
- Atomic arrangements in nano-particles
- Superconductivity in MgB_2
- The location of protons in biomolecular crystals

The Neutron Scattering Society of America

www.neutronscattering.org

Press Release May 1, 2006

Dr. Taner Yildirim

is the recipient of the

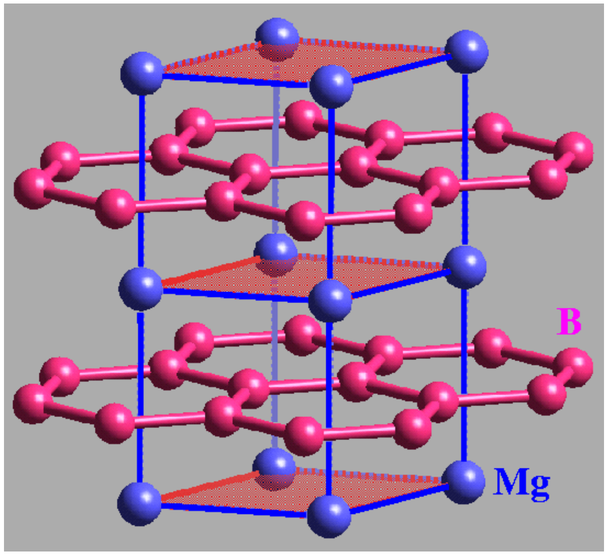
2006 Science Prize

of the Neutron Scattering Society of America with the citation:

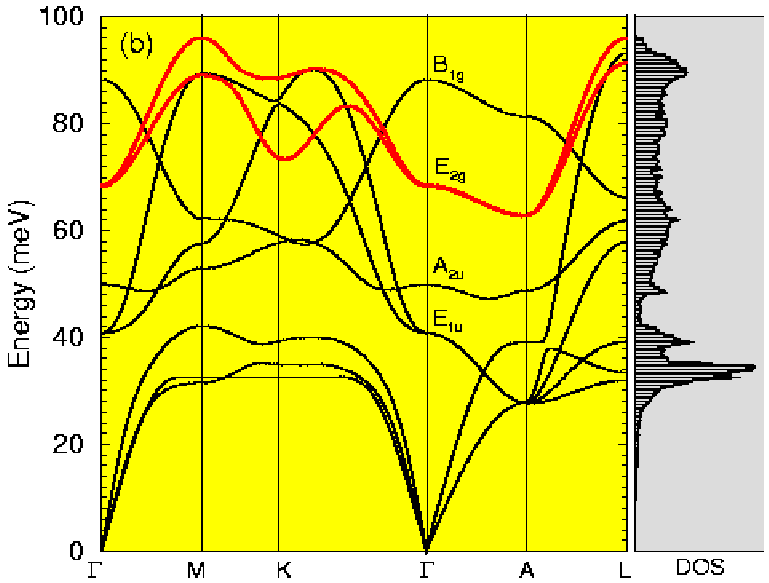
"For his innovative coupling of first principles theory with neutron scattering to solve critical problems in materials sciences"

MgB_2 Superconducts at 40K. Why?

- Yildirim did first-principles calculation of phonons in MgB_2 (particulary anharmonicity & electron-phonon interaction) & compared with neutron scattering



Crystal structure is layered

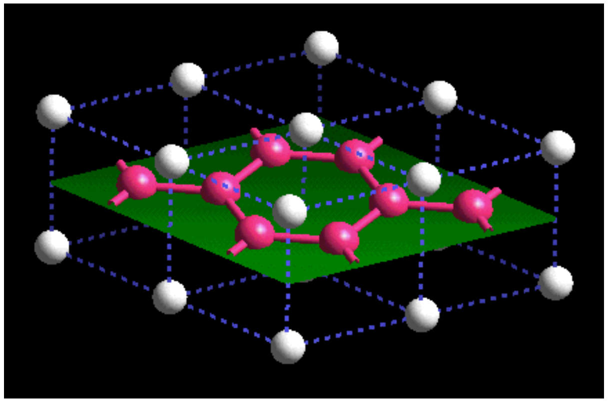


- Optic & acoustic modes separated
- Red modes frequencies dominated by e-p interaction

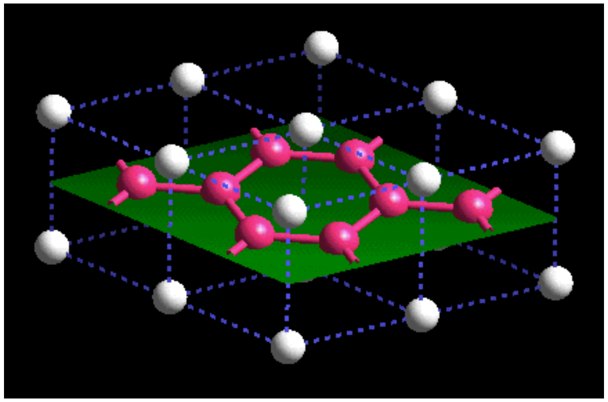
Graphics courtesy of Taner Yildirim

Motions Associated with Zone Center Modes

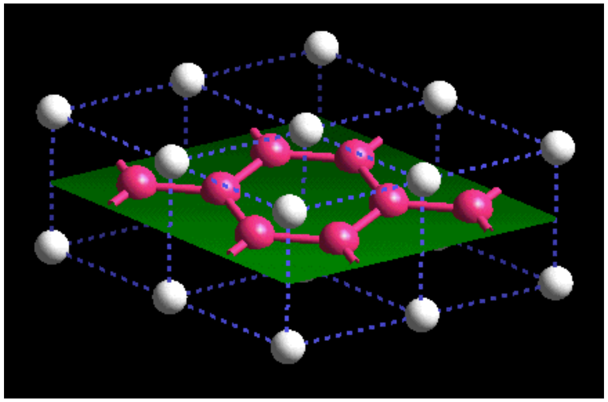
E_{1u}



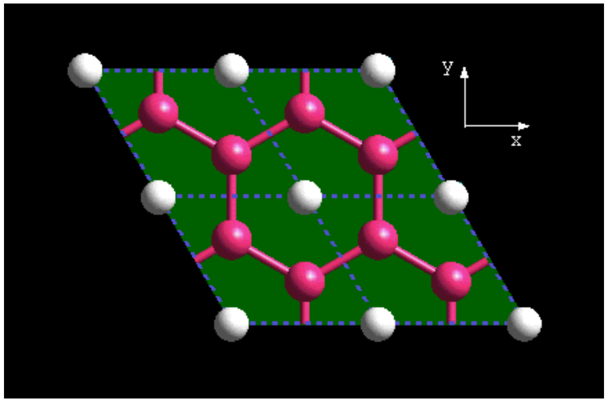
A_{2u}



B_{1g}



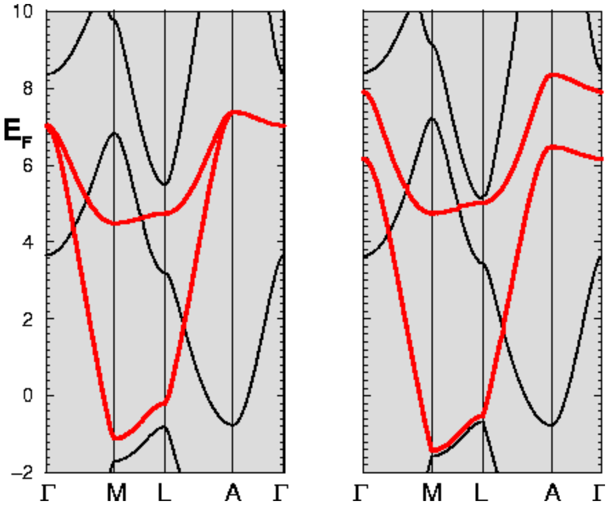
E_{2g}

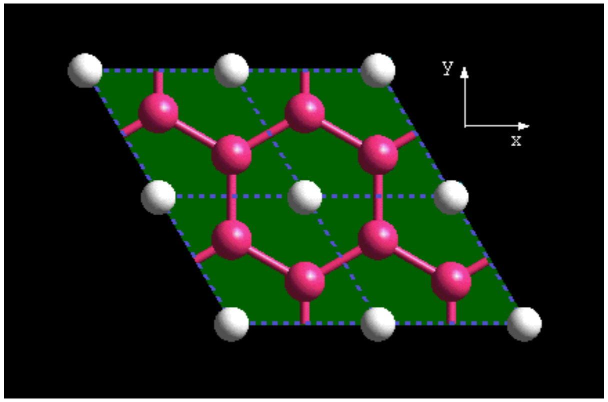


Very anharmonic

The Large Displacements Associated with E_{2g} Cause Large Electron-Phonon Coupling

- Because the effective potential for the E_{2g} mode is shallow and wide, the B atom-motions are large amplitude
- This causes significant overlap of electron shells and significant effects on the band structure close to E_F
- The strong e-p interaction causes the “high” T_c





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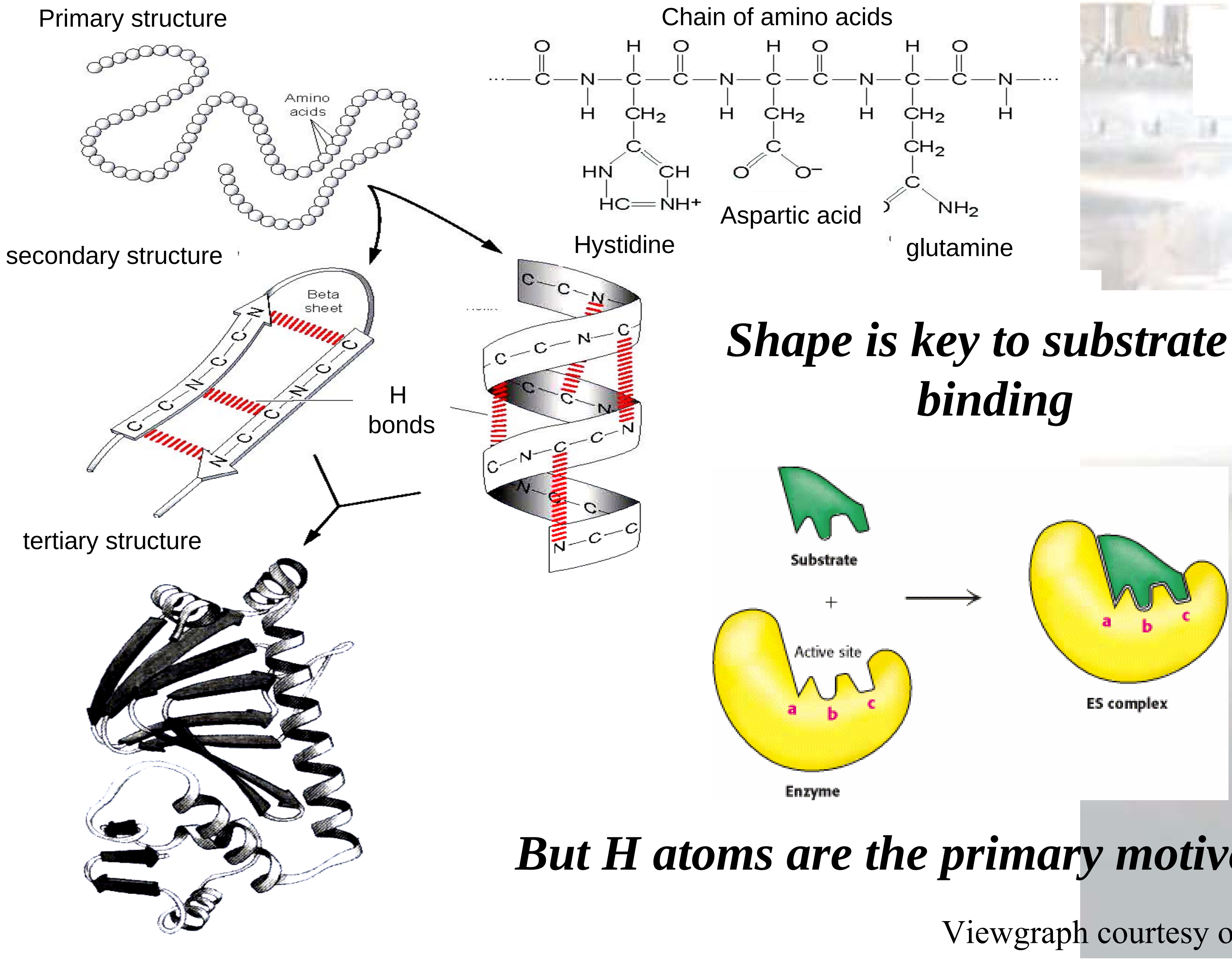
How Enzymes Work: *shuffling atoms about in chemical reactions that make cells come alive*



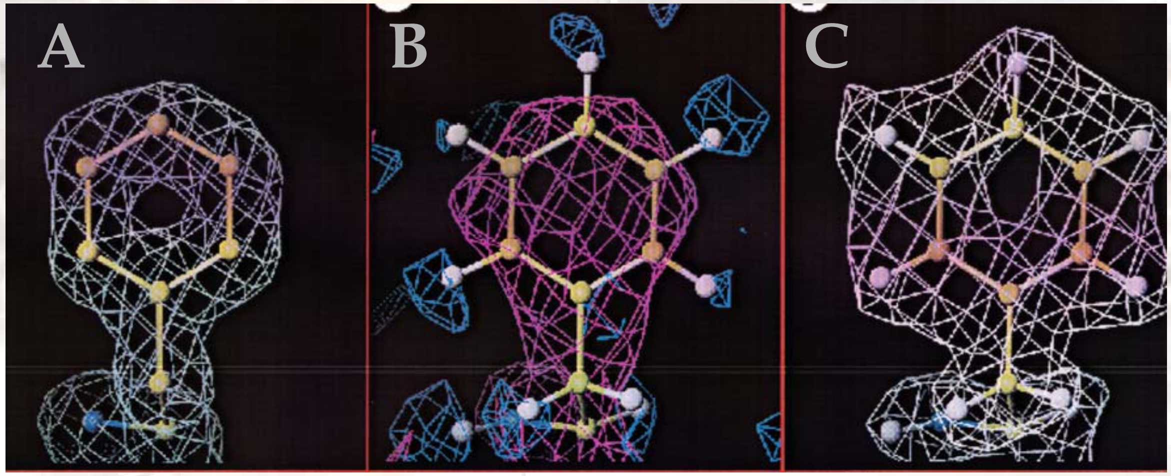
Shape is key to substrate binding

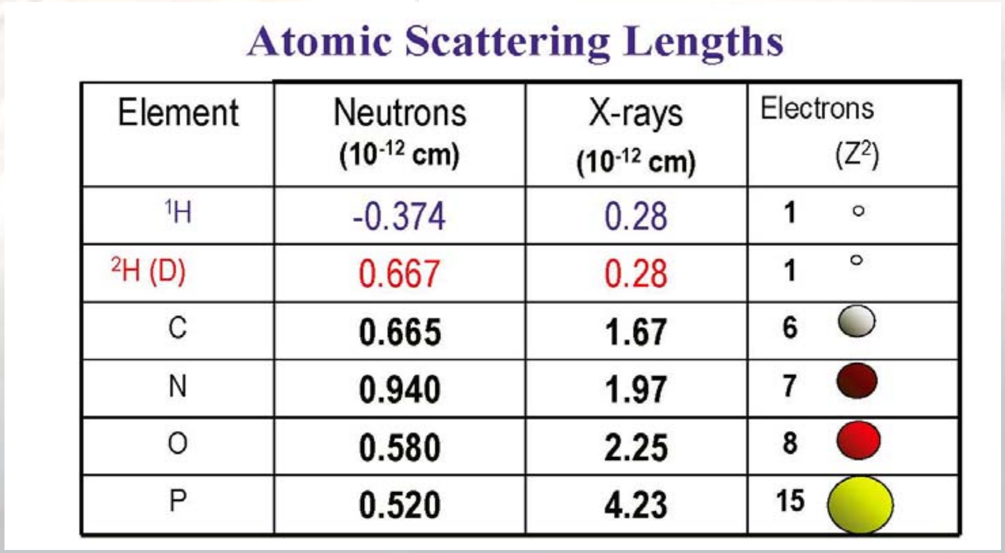
But H atoms are the primary motive force

Viewgraph courtesy of Paul Langan

Visualizing H atoms with neutrons

Scattering density of a phenylalanine residue of myoglobin from a) X-ray Data b) neutron data and c) neutron data from perdeuterated protein





Atomic Scattering Lengths

Element	Neutrons (10^{-12} cm)	X-rays (10^{-12} cm)	Electrons (Z^2)
^{1}H	-0.374	0.28	1 ∘
^{2}H (D)	0.667	0.28	1 ∘
C	**0.665**	**1.67**	**6** ●
N	**0.940**	**1.97**	**7** ●
O	**0.580**	**2.25**	**8** ●
P	**0.520**	**4.23**	**15** ●

Viewgraph courtesy of Paul Langan

What do we Need to do Better?

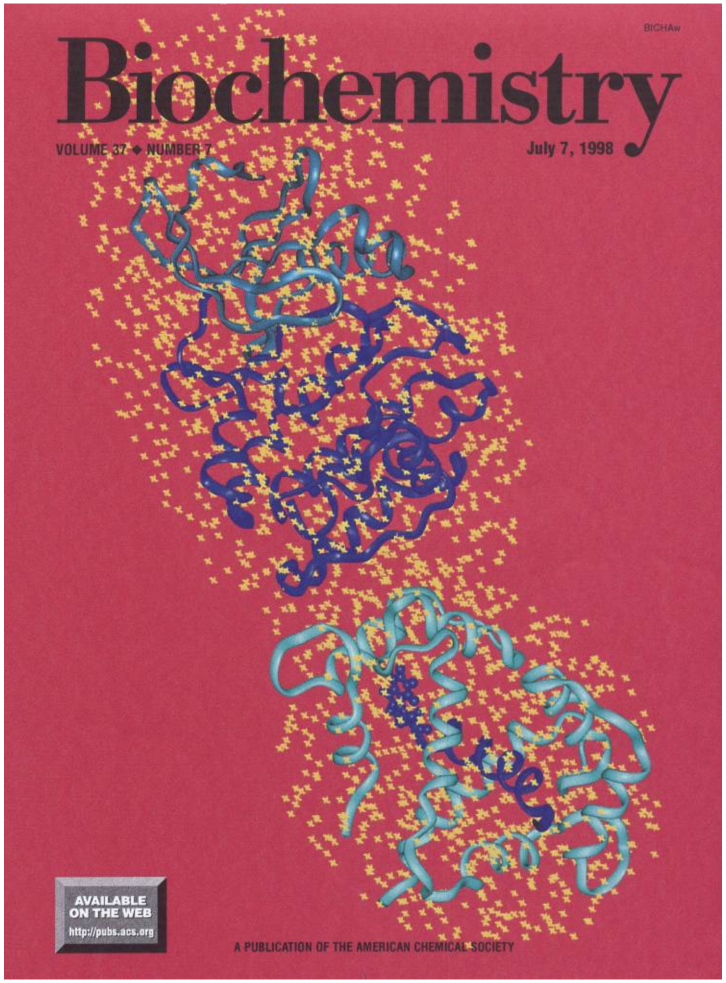
- Exploit complementarity of techniques

- Generate pictures not S(Q,E)
  - Couple neutron scattering and advanced computing
  - Prototypes exist for powder diffraction, SANS and quasielastic scattering

Integration of Structural Biology Tools Yields Insight into Enzyme Activation by Calmodulin

Crystallography – structure of the catalytic core of the enzyme and reveals the location of the catalytic cleft.

High field NMR with isotope labeling – high resolution solution structure of calmodulin complexed with its binding domain from the enzyme.

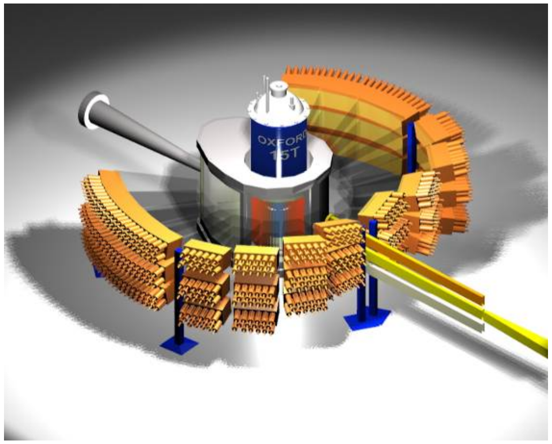


Neutron scattering with isotope labeling – shapes and positions of the Myosin Light Chain Kinase enzyme and calmodulin in the Ca^{2+}-calmodulin activated complex.

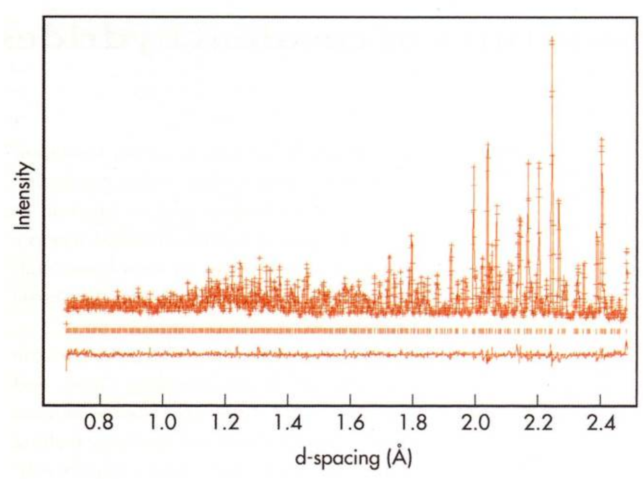
Use computational modeling based on crystallographic data to determine molecular shapes under various binding conditions

Krueger *et al.*, 1997 **Biochemistry** *36:* 6017.

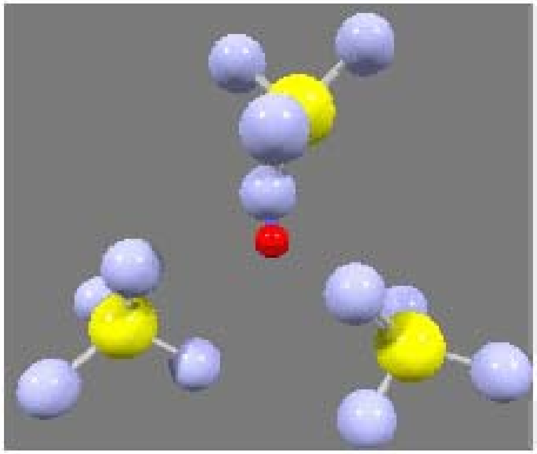
Pictures & Movies are Today's Standard for Nano-Science Research



Today's Route



We need to provide images or movies



Reverse Monte Carlo of $CsDSO_4$ fitted to diffraction data (McGreevy)

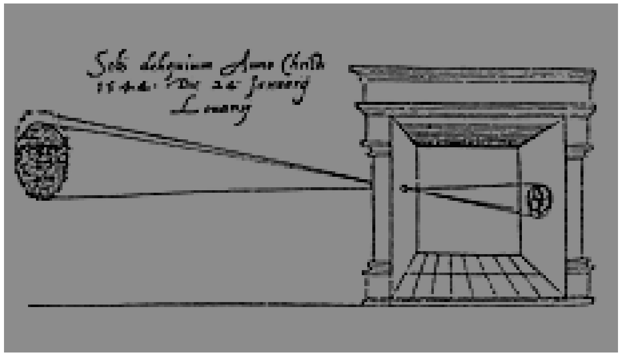
What do we Need to do Better?

- Exploit complementarity of techniques

- Generate pictures not S(Q,E)

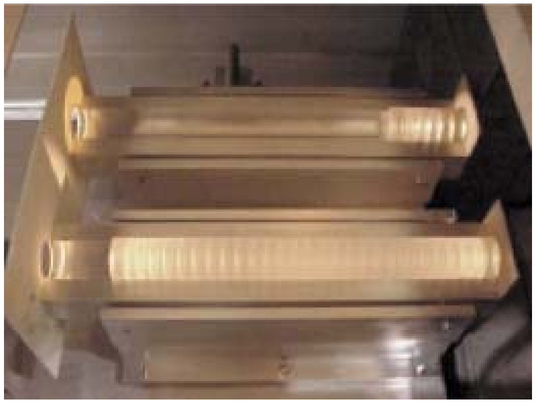
- Make better use of the neutrons we have
  - Use the best known technology to optimize instrumentation
  - Develop better neutron focusing devices

Improved Neutron Optics



Pin-hole → Lens

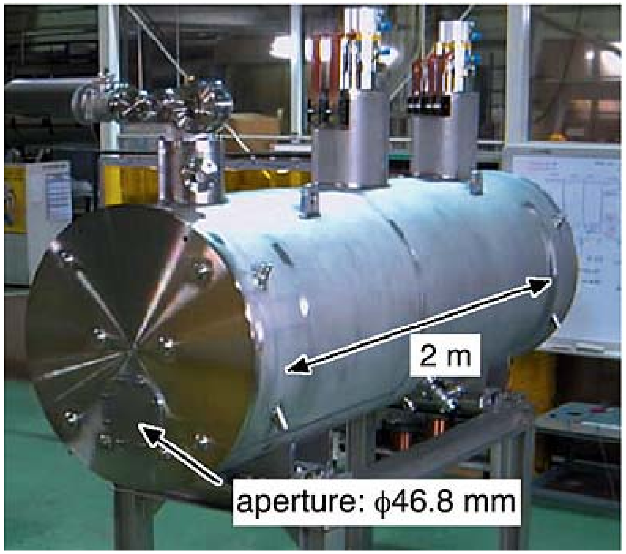
MgF_2
CRL
at NIST

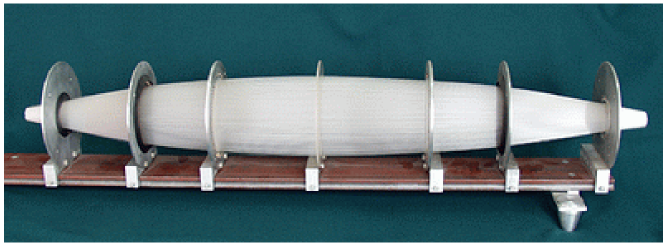


18 Å

8.4 Å

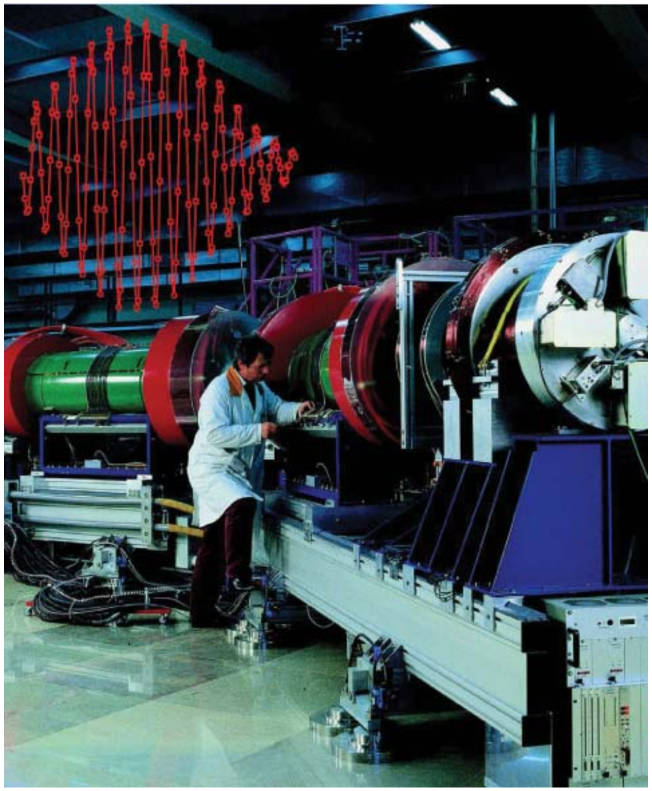
Superconducting hexapole
lens at RIKEN



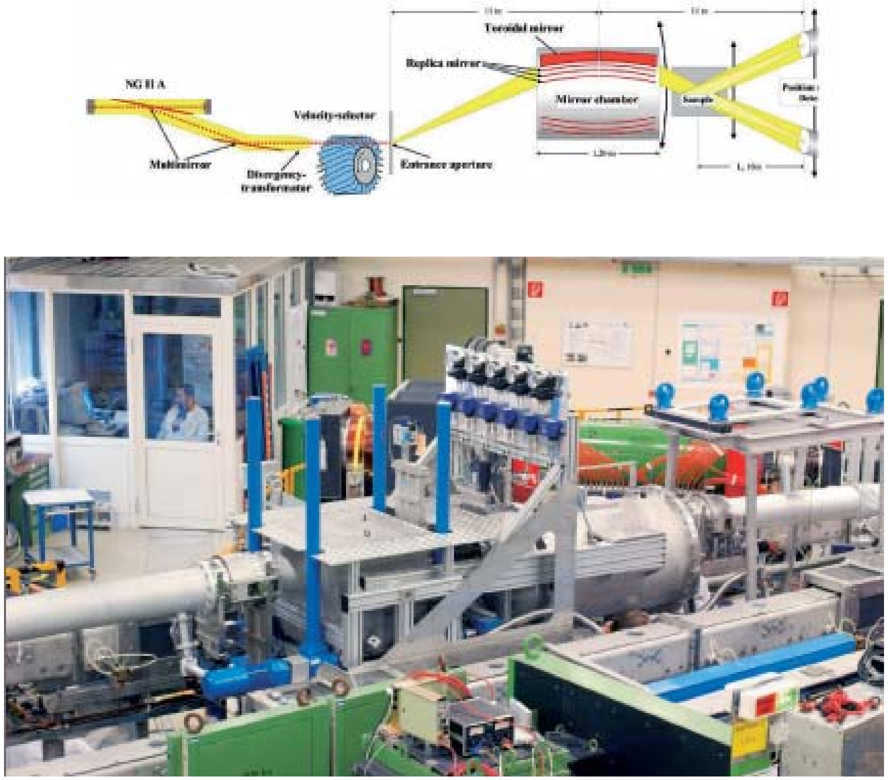


Kumakhov
lens

Optical Elements Extend the Reach of Neutron Nano-Imagers



IN15 – ILL



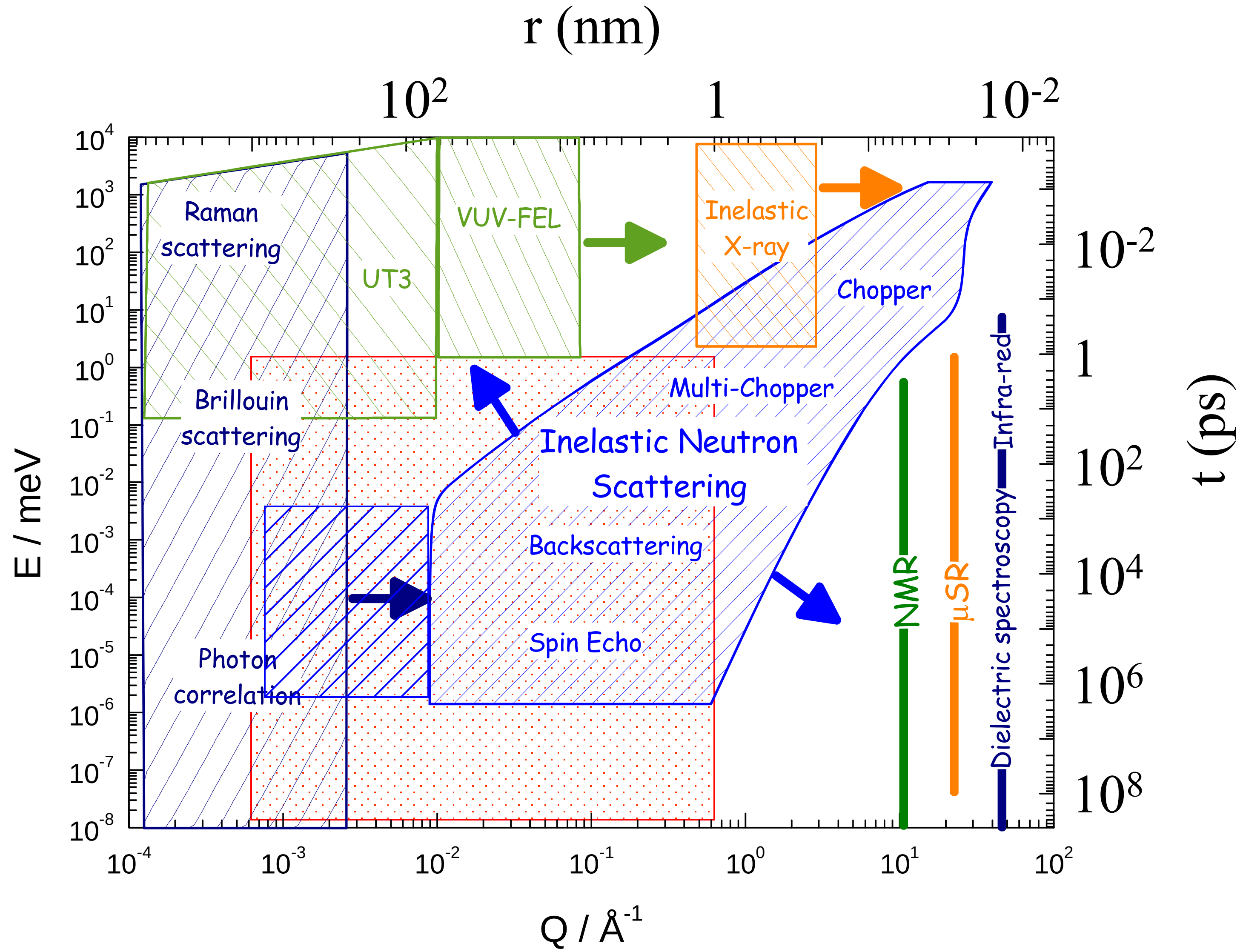
KWS-3 – Julich

Focusing torroidal mirrors provide higher intensity and allow smaller values of Q to be reached on SANS & neutron spin echo instruments

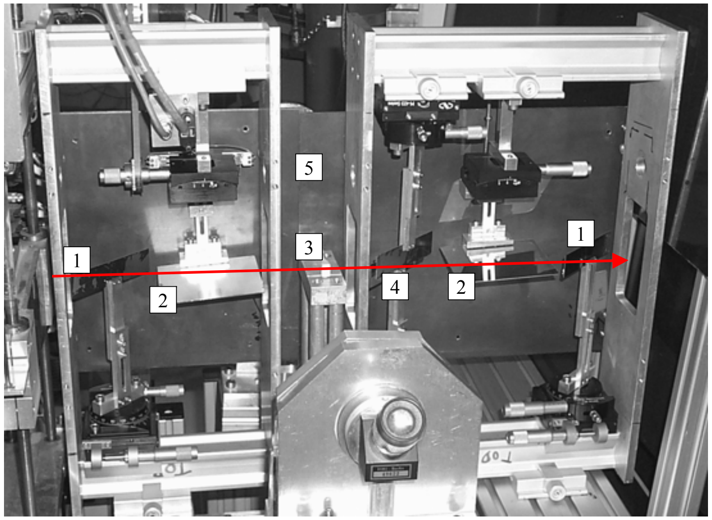
What do we Need to do Better?

- Exploit complementarity of techniques
- Generate pictures & movies not S(Q,E)
- Make better use of the neutrons we have
- Design and build better neutron nanoscopes
  - Extend accessible length and time scales
  - Allow nano-length-scales to be reached without loss of neutron intensity that arises from beam collimation, e.g by using the Neutron Spin Echo method
  - Make more use of pump-probe techniques

Extension of the NSE Length-Scale Domain

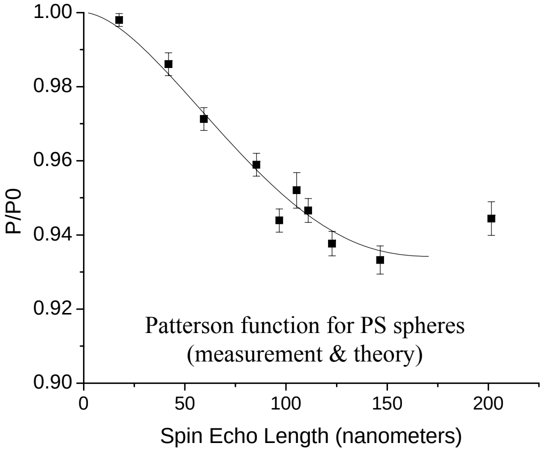


High Angular Resolution Neutron Scattering without Beam Collimation

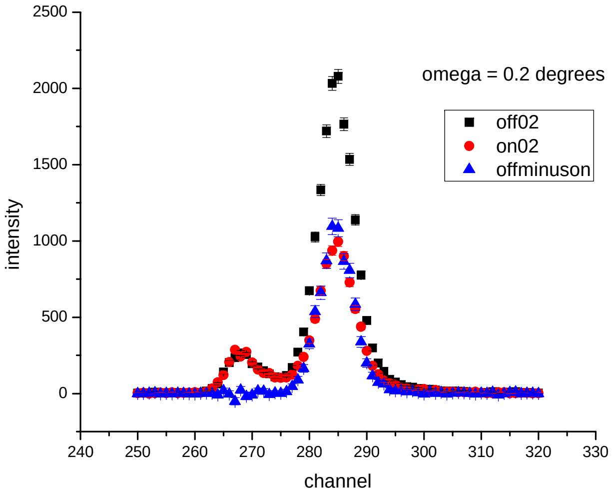


- Thin, magnetized $Ni_{0.8}Fe_{0.2}$ films on silicon wafers (labelled 1, 2 & 4) are the principal physical components used for this new method.

- High angular resolution is obtained using Neutron Spin Echo.



A 200 nm correlation distance was achieved for SANS



Specular neutron reflection (blue) was separated from diffuse reflection with high fidelity. Black and red data include diffuse scattering

What do we Need to do Better?

- Exploit complementarity of techniques
- Generate pictures & movies not S(Q,E)
- Make better use of the neutrons we have
- Design and build better neutron nanoscopes
- Coordinated research effort on neutron instrumentation
  - Vision – a suite of neutron nanoscopes that probe the right length and time scales in weakly scattering samples
  - Possibility exists to optimize the SNS second target station & its instruments for nanoscience and biology if we start soon

END