Neutron Spectroscopy

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Ken Herwig lamented: Spectroscopists produce 1 good neutron out of 1,000,000,000,000,000 source neutrons, or equivalently for SNS

~1000 good neutrons per spectrometer per second

How many good neutrons are needed to produce a scientific paper?
~1,000,000

For SNS in one year,

1000n/s/instr x 18 instr x 4000h x 3600s/h = 2.6 x 10^{10} good neutrons

==> **260,000 papers**

If 2% are high-impact papers, SNS would produce

>5,000 *PRL*, *Nature*, & *Science* publications per year

What is the problem?

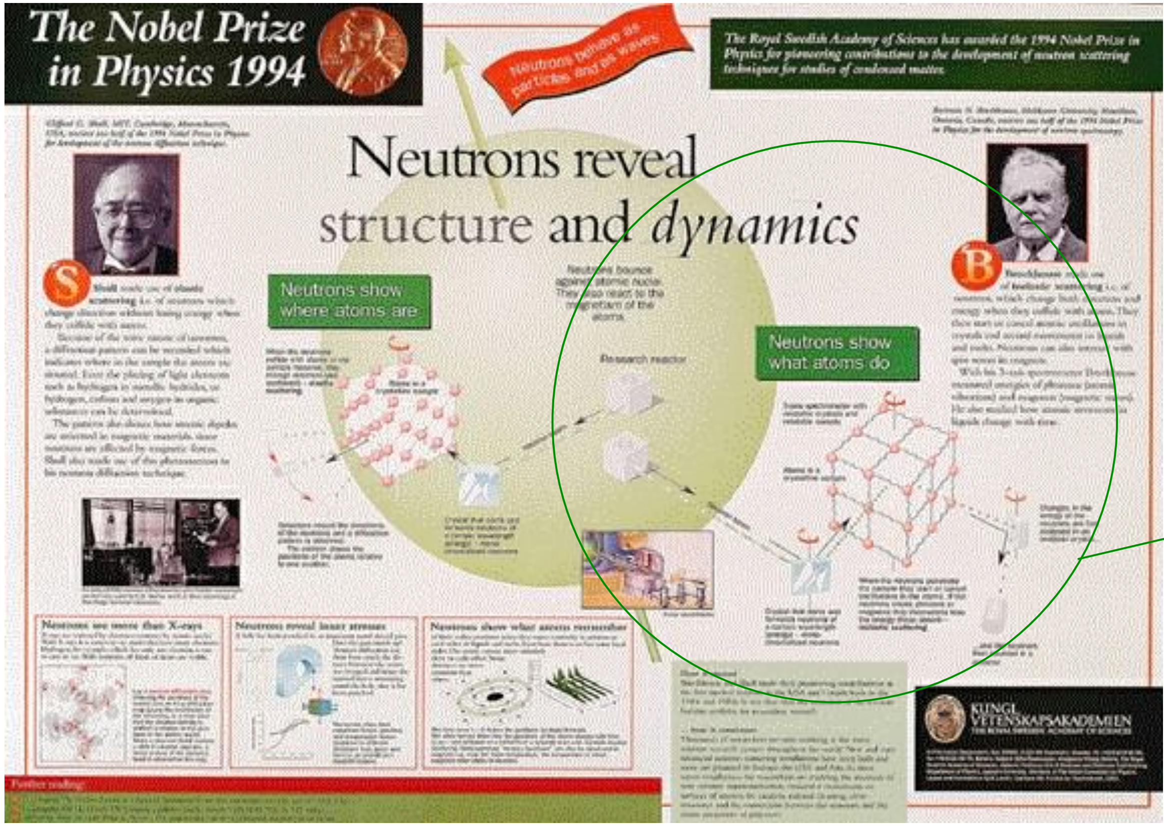
DESIGNING AND BUILDING A NEUTRON INSTRUMENT, The 2nd Erice School

Spectroscopy: A Philosophy

Engineer: 'Why can't the scientist be less crazy so to make engineering more reasonable?'

Scientist: 'Why can't the engineer be more straightforward to accommodate my simple scientific problem?'

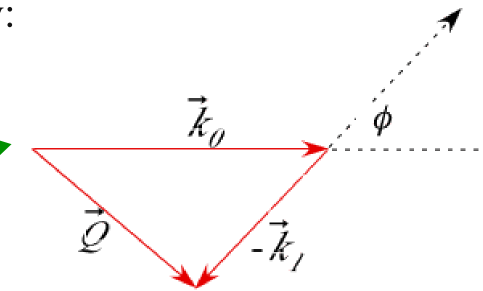
Spectroscopy: Dynamics & Excitations



To show what atoms do

Scattering wavevector

Scattering triangle defined by: $\vec{Q} = \vec{k}_0 - \vec{k}_1$



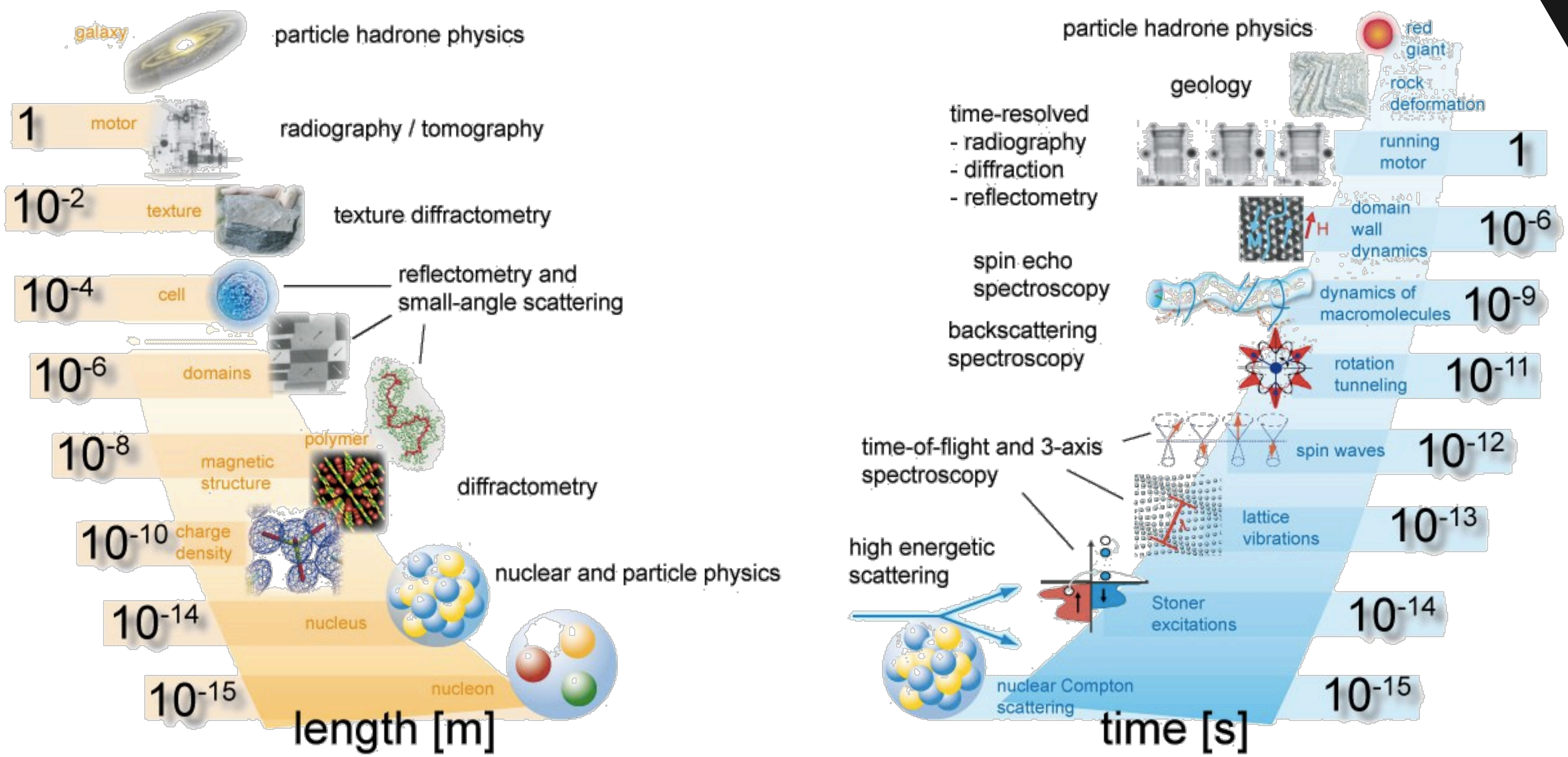
Neutron energy transfer $E = E_0 - E_1$

$E > 0$ *Neutron energy loss*

$E < 0$ *Neutron energy gain*

Spectroscopy has much to do with correlations of atoms' degrees of freedom over a range of characteristic time and length scales, to be revealed experimentally in the $(\vec{Q}, E)$ space.

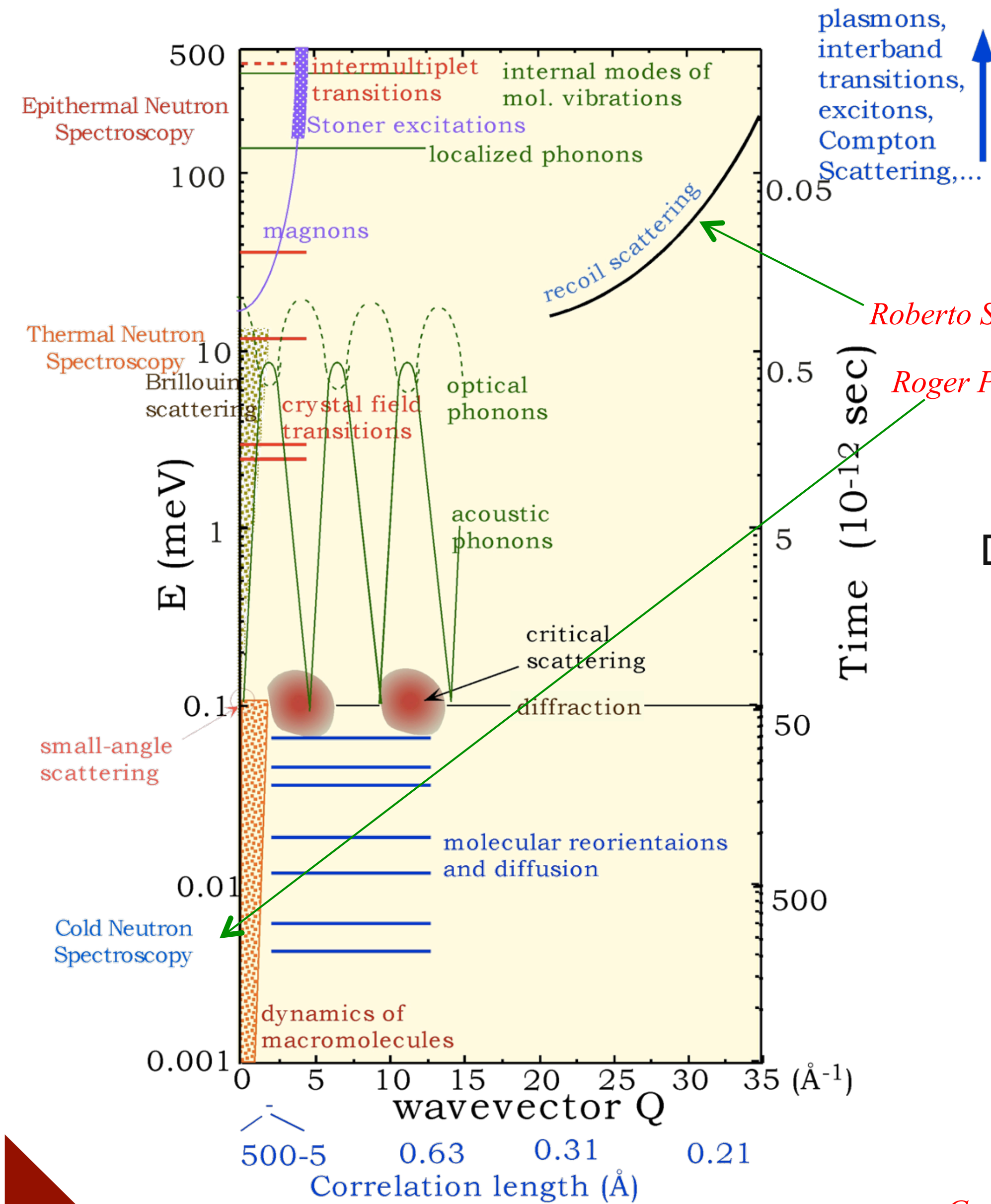
The Time and Length Scales



Thomas Hansen: Overview of a Neutron Scattering Instrument

We need a suite of spectrometers to cover the $(\vec{\mathrm{x}},t)$ scales, as wide in range and as precise in resolution as possible.

Inelastic Scattering: Matching the (Q,E) Window

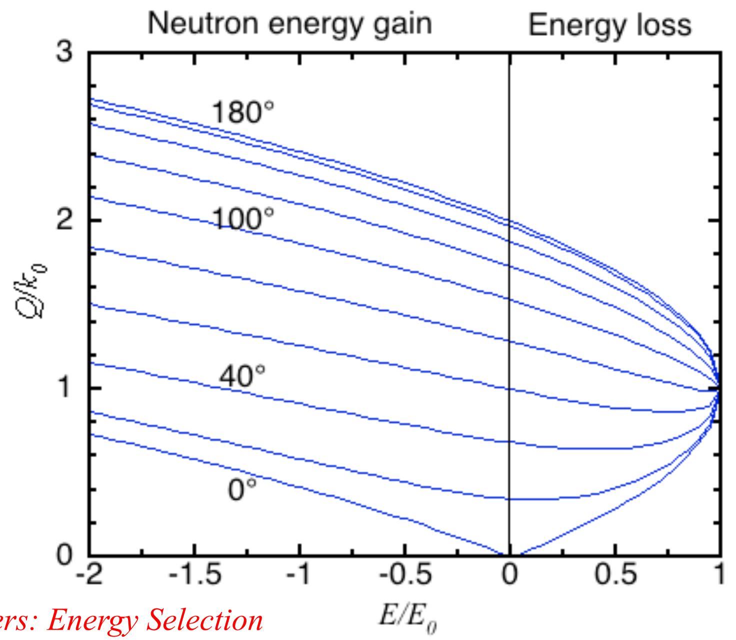


Identify the length & time scales of your problem, choose the appropriate spectrometer(s) to achieve the measurements.

Roberto Senesi: Deep Inelastic Neutron Scattering

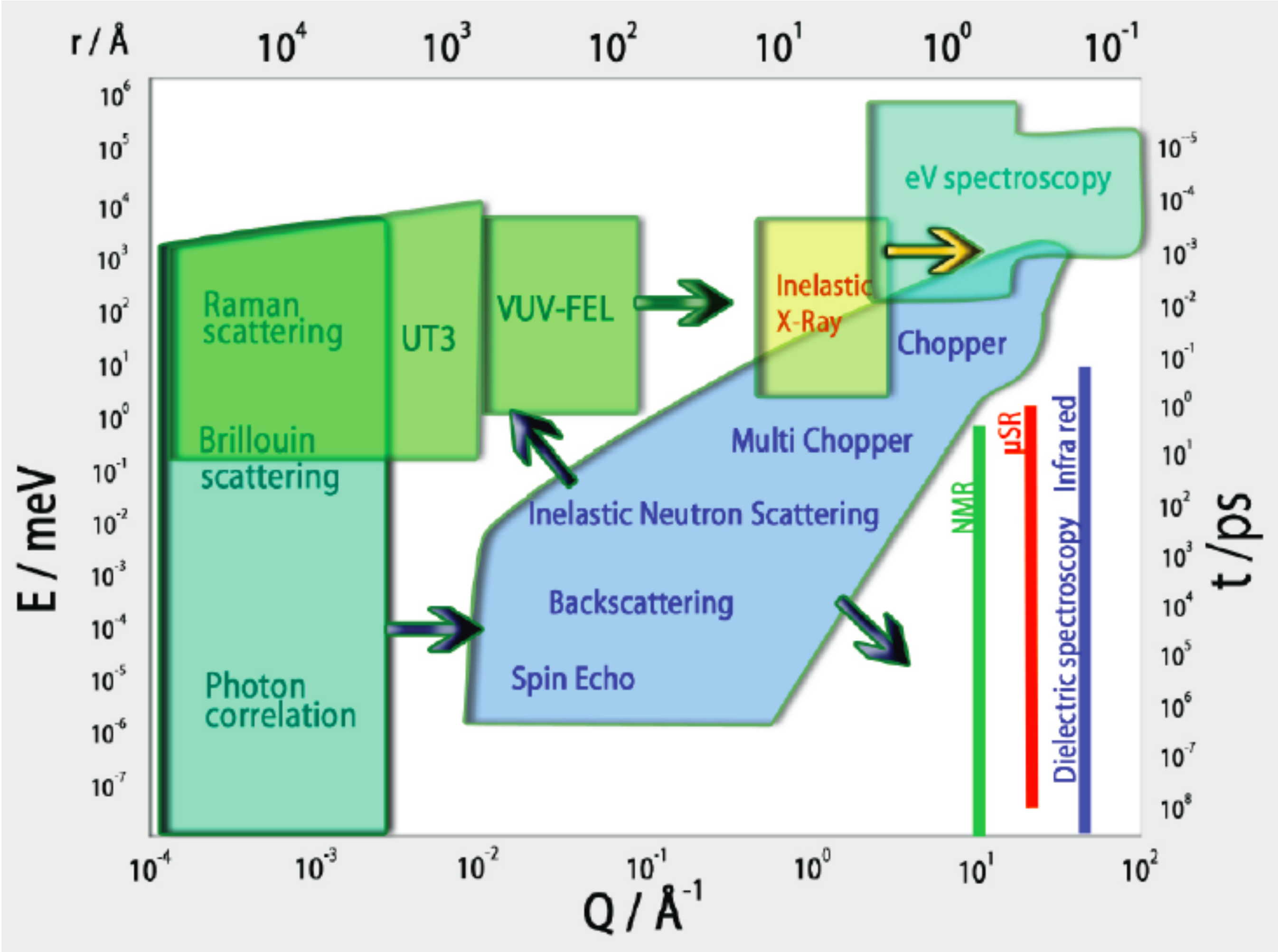
Roger Pynn: Spin-Echo Spectroscopy

Direct Geometry: $\left(\frac{Q}{k_0}\right)^2 = 2 - \frac{E}{E_0} - 2\cos\phi\sqrt{1-\frac{E}{E_0}}$

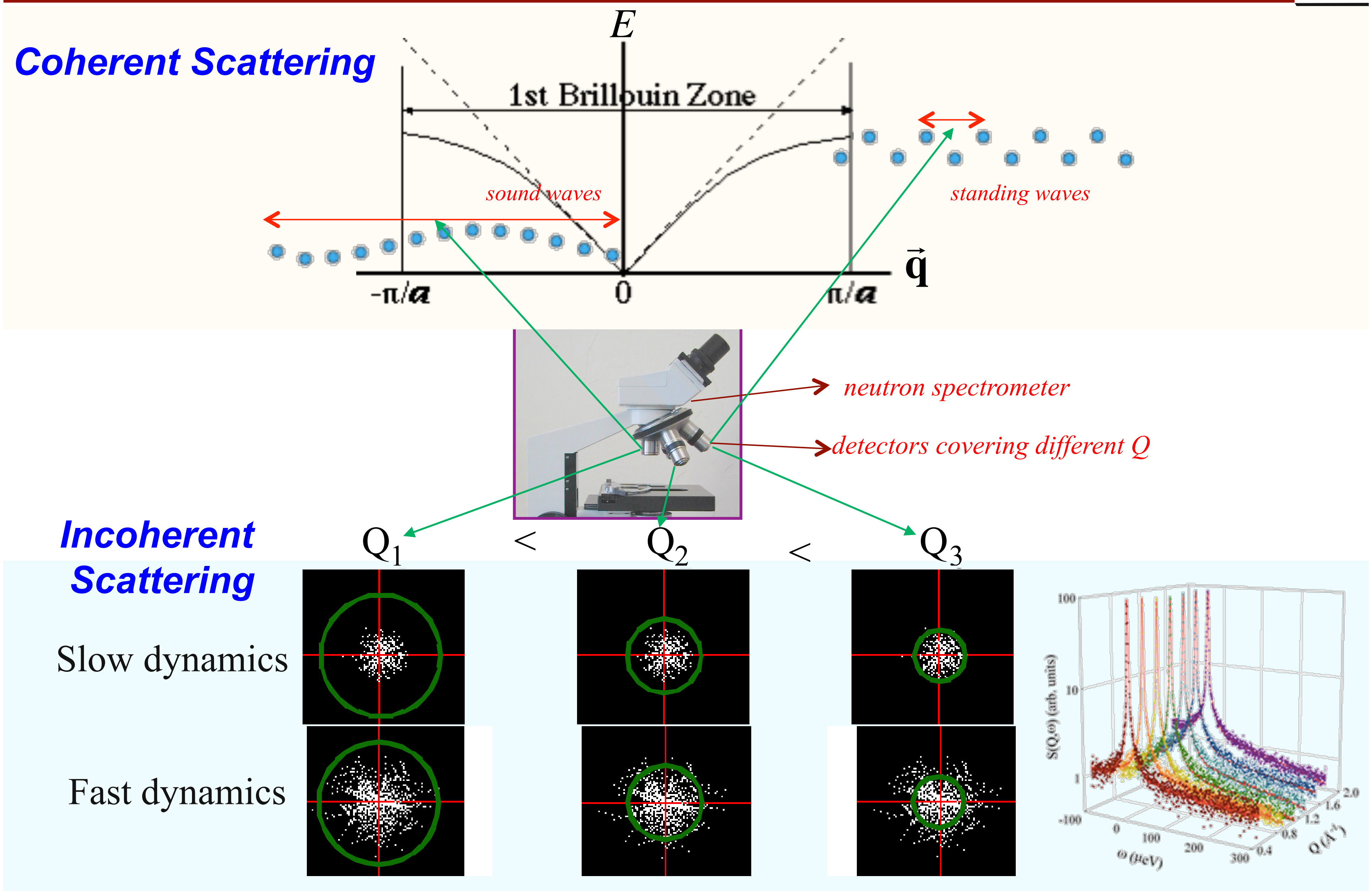


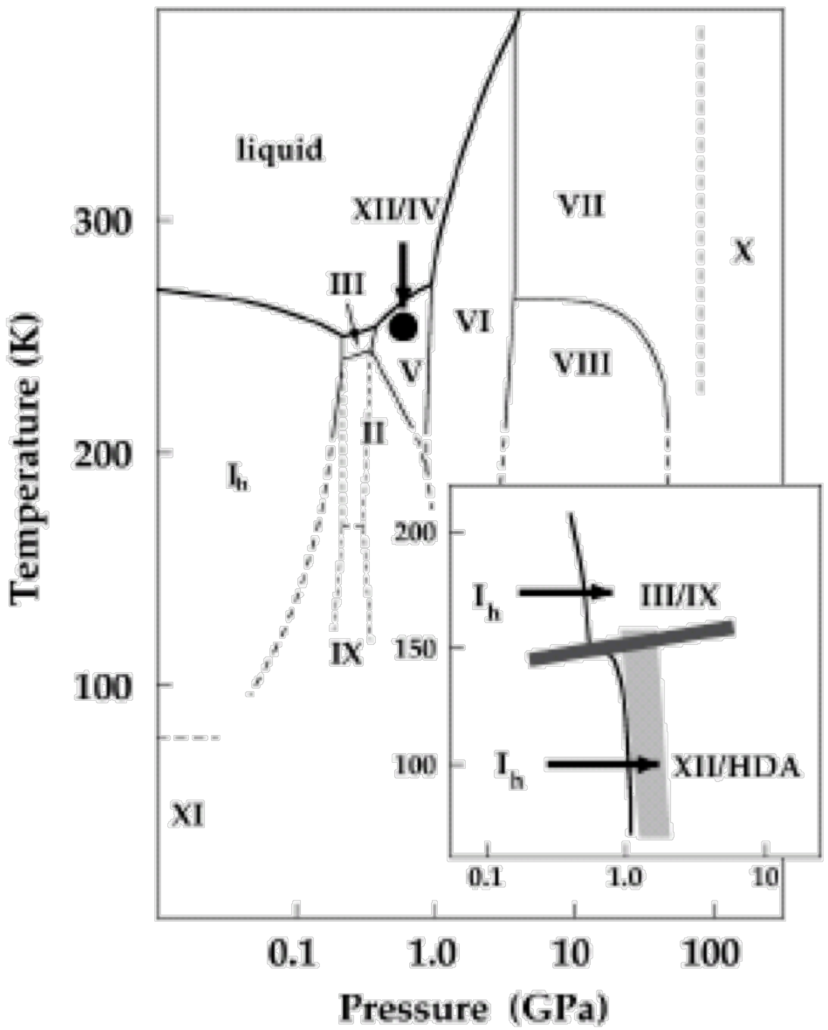
Georg Ehlers: Energy Selection

Beware of Other Useful Complementary Techniques



Anatomy of a Spectrometer: Q ⟷ The Scope of a Lens





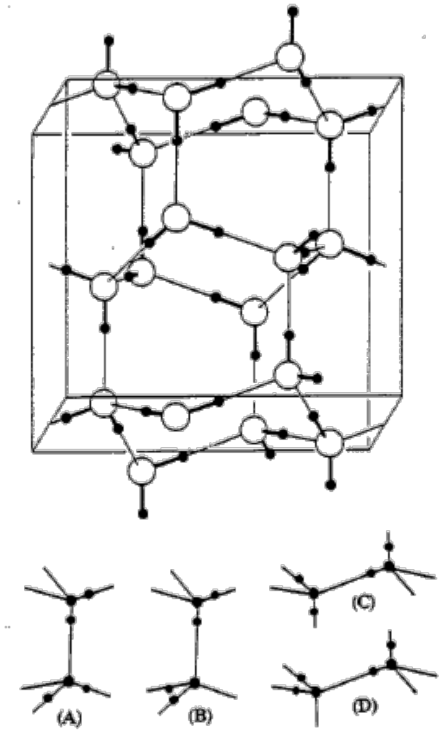
The 13(?) known phases of water

A substance (commonplace but very complex) connected to life, to planet Earth, and to the cosmos.

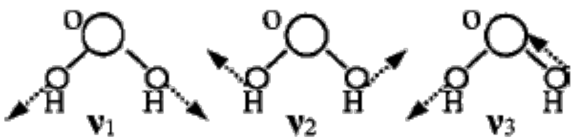
- In our bodies - we are aqueous being
- In cells – adsorbed, confined, embedded, … proteins, lipid bilayers, DNA, …
- In the environment – hydrologic cycle from supercooled droplets in clouds to surface & underground water, ice and to evaporated vapor
- In our civilization – societies' wellbeing and advancement in technology

Chen & Loong (2006)

Dynamics of Water: From Protons to Molecules to H-Bonded Network



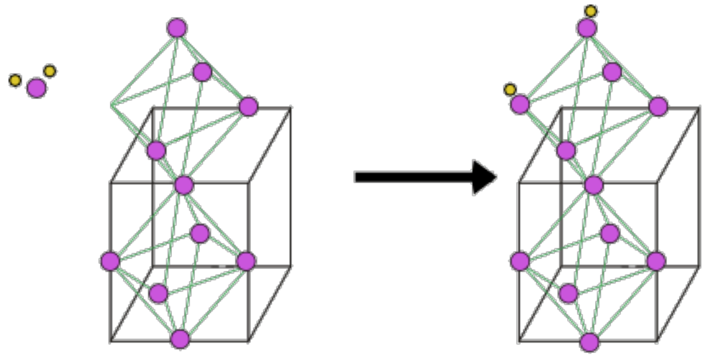
Ice Ih ($P6_3/mmc$): The four possible orientation of molecular pairs => hydrogen bonds



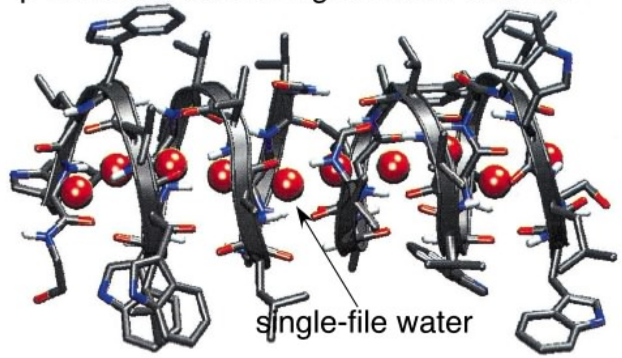
Schematic illustration of the bending, v2 , and stretching, v1 and v3, modes in water molecule

proton conductors

$$H_2O(g) + V_O^{\bullet\bullet} + O_O^X \rightarrow 2OH_O^{\bullet}$$



β-helix structure of a gramicidin channel



Diffraction probes D-O, O-O correlations:

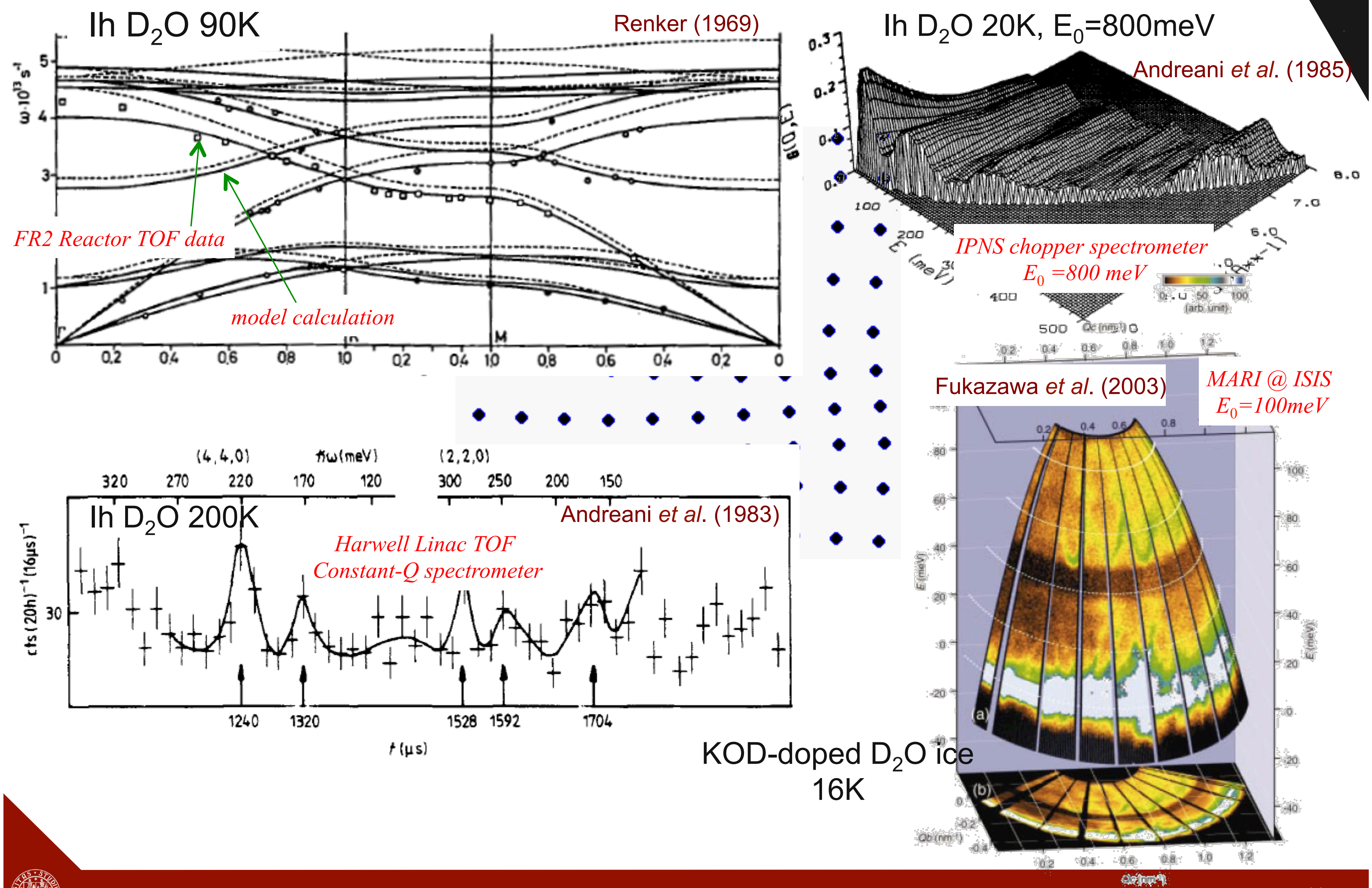
- ***tiny changes in g(r)***

Inelastic coherent scattering measures collective motions

Inelastic incoherent scattering probes single-particle (protons, molecules, protons)

- ***large spectroscopic changes ~50cm^{-1}***

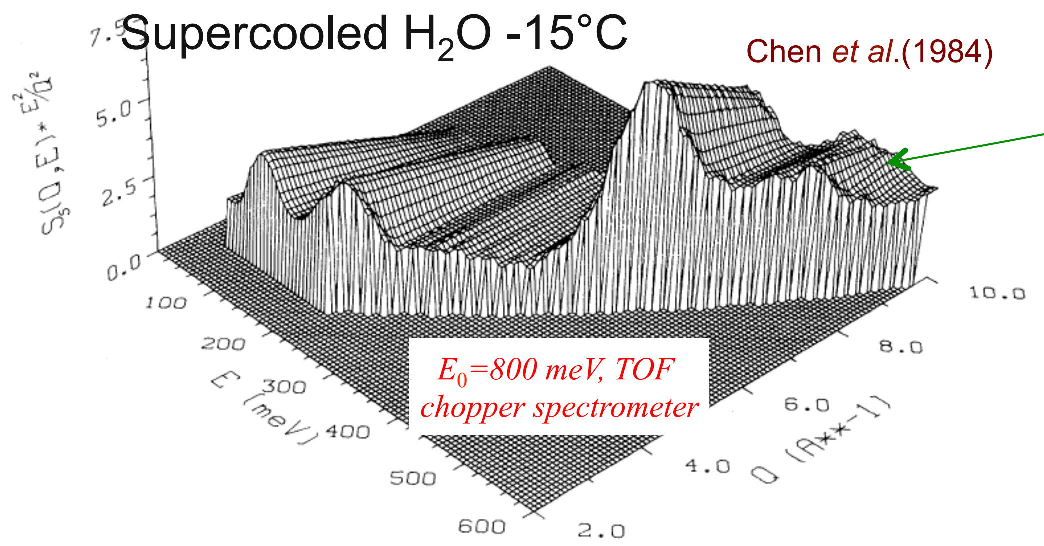
Coherent Scattering - Phonons in D_2O Ice



Instrument Configurations & Data Interpretation

- ✧ Instrumentation, see Andreani Erice (2014) lectures
- ✧ Many phenomenological models and microscopic theories of lattice dynamics since Born and Huang (1954)
- ✧ Nowadays, molecular-dynamics (MD) computer simulations and first-principles quantum mechanical treatments, e.g., DFT approach, are common.

Incoherent Scattering – Supercooled Water



Proton density scattering function

Neutron(scattering density)-weighted phonon density of States (NWDOS)

$$G(E) = \frac{2\bar{m}}{\hbar^2}\left\langle \frac{e^{2W(Q)}}{Q^2}\frac{E}{n(E)+1}S(Q,E)\right\rangle \approx \bar{M}\sum_i \frac{c_i\sigma_i}{m_i}F_i(E)$$

concentration (c_i), *scattering cross section* (σ_i), *mass* (m_i)

True partial DOS of the i^{th} component ($F_i(E)$)

True DOS

$$g(E) = \frac{\sum_i c_i F_i(E)}{\sum_i c_i}$$

Thermodynamics:
internal energy, entropy, heat capacity,…
& the counterparts from magnetic scattering

Sample Environment to Accommodate Extreme Conditions

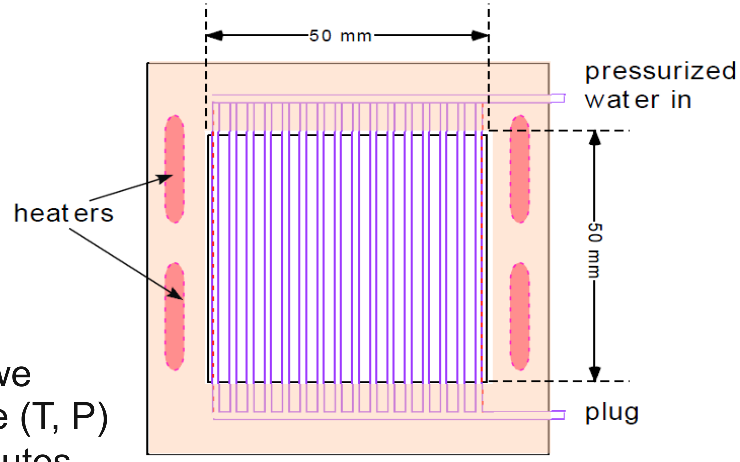
Neutron spectroscopy provides a microscopic understanding of thermodynamic and transport properties, including critical phenomena, of almost all condensed matter systems:

A primary objective of good spectrometers

supercritical water

- ✧ T up to ~500°C
- ✧ P ~30 MPa

H_2O in thin channels in plana geometry within a Ti cell



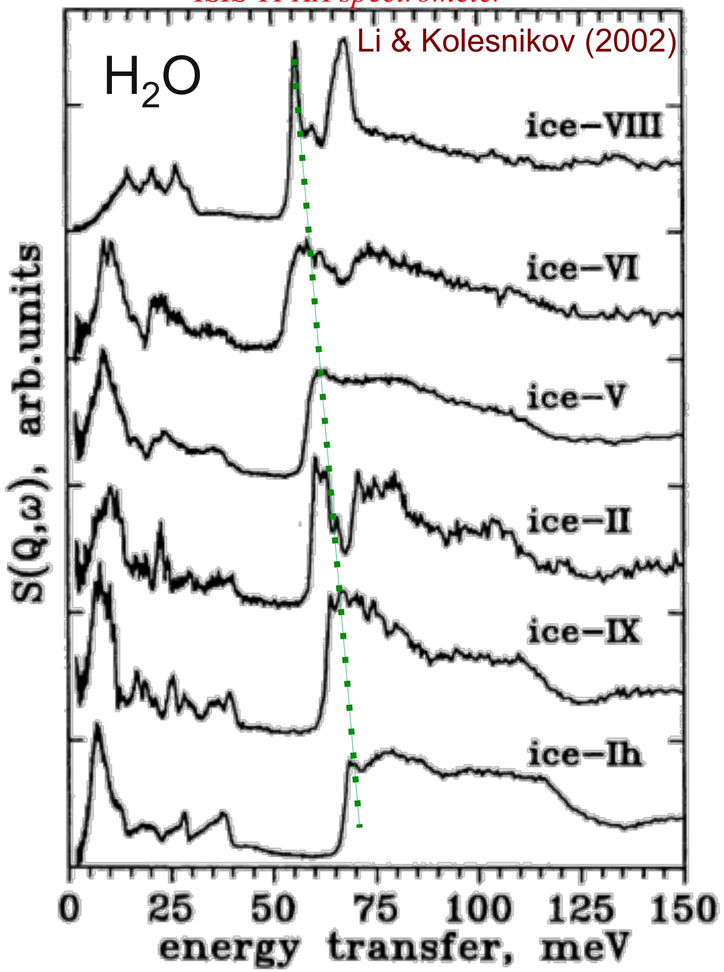
Scientist: Simple stuff, by the way, we want to be able to change (T, P) instantly,….okay, in 5 minutes.
Engineer: What?
Scientist: We already waste 300,000 good neutrons in 5 minutes!

Sample cell kindly designed and fabricated by SNS engineers at the request of C. Andreani *et al*.

- ✧ Minerals in Earth's mantle and outer core
- ✧ Chemical interactions, e.g., instantaneous explosion
- ✧ Mechanical failure: e.g., fracture dynamics

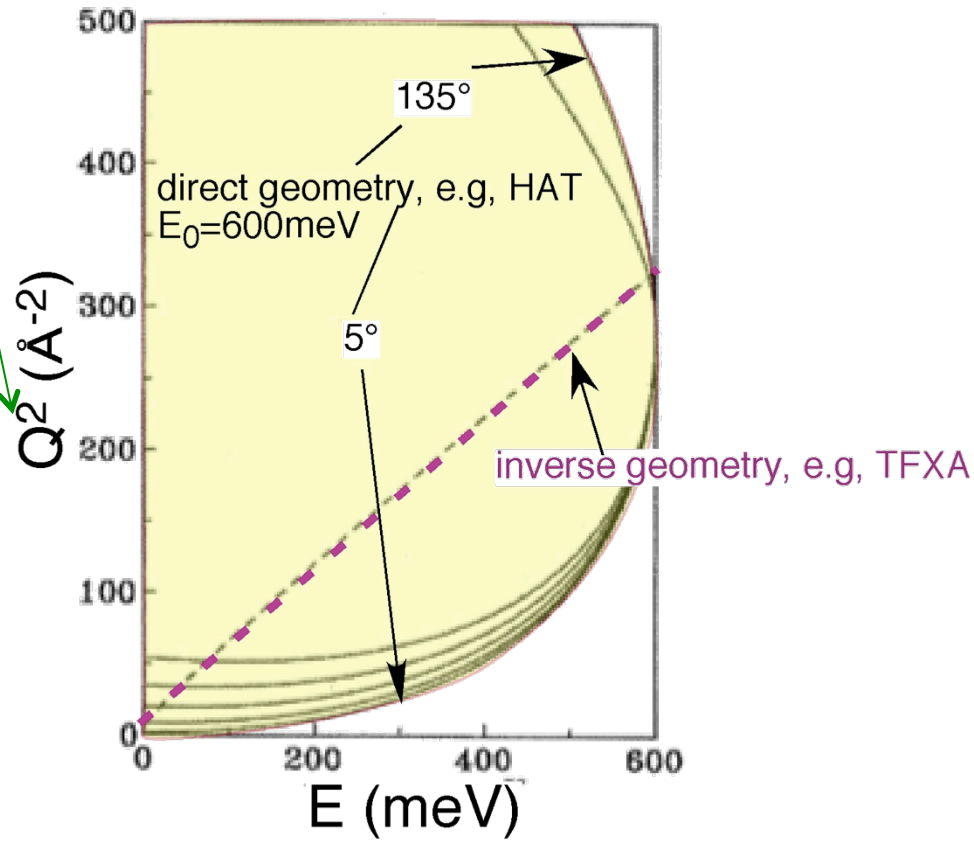
Inelastic Scattering is Very Revealing

ISIS TFXA spectrometer

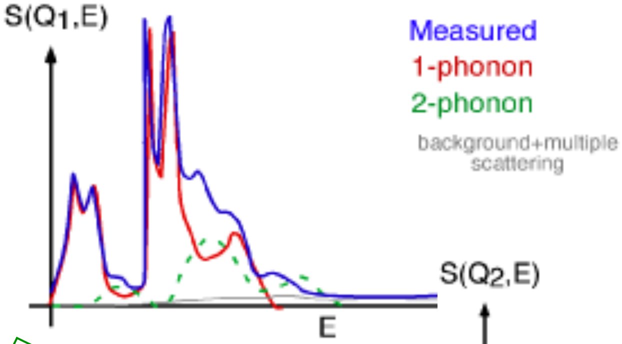


But be aware of the (Q,E)-coverage!

1-phonon intensity ~ Q^2



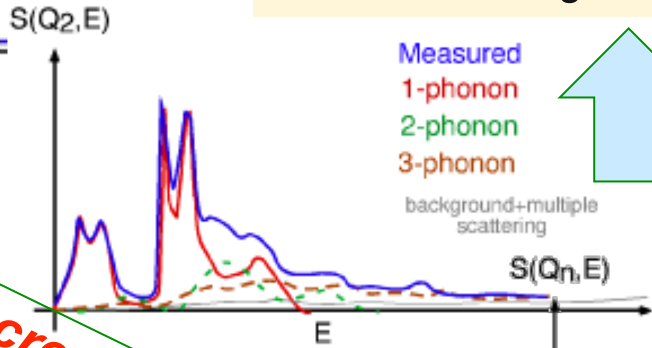
Different INS Regimes Require Tailored Spectrometers



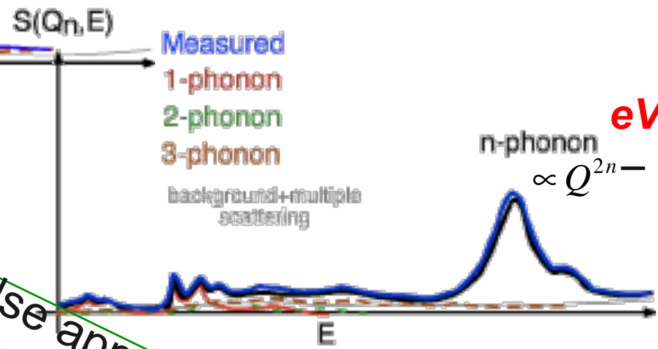
In order to better interpret the multi-phonons & to connect to thermodynamic properties via the harmonic approximation, we need to reach high E at small Q.

Dynamic behavior of a single particle renormalized in a many-body systems

- momentum distribution
- kinetic energy
- Bose condensate in quantum fluids



phonons
collective motions
increasing Q & E
Impulse approximation
single-particle response

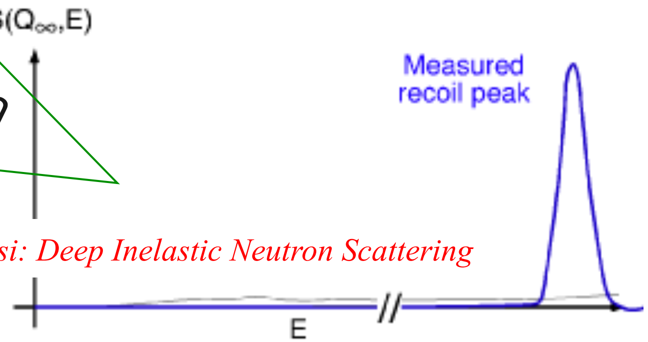


n-phonon $\propto Q^{2n}$

eV-Spectrometer – Deep inelastic scattering

Characterization of fast sounds in fluids and solids

Neutron Brillouin Scattering – To reach Q-values connecting the light-scattering data with high resolution.

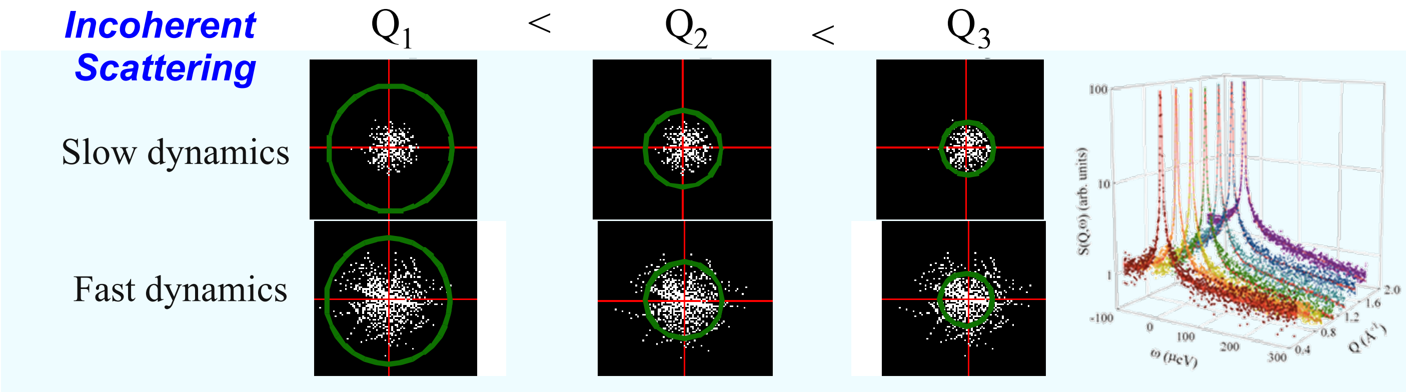


Roberto Senesi: Deep Inelastic Neutron Scattering

I look forward to hearing new capabilities of the proposed TOF instrument.

Quasielastic Neutron Scattering (QENS)

For stochastic processes such as diffusion that do not have well-defined discrete energy levels of excitation, the QENS intensities tend to pile up underneath the elastic peak. The nature of the dynamics manifests itself in the Q-dependence of the intensity. Spectrometers are built to accomplish specific dynamic ranges and resolutions, demanding for a suite of QENS instruments. Recalling:



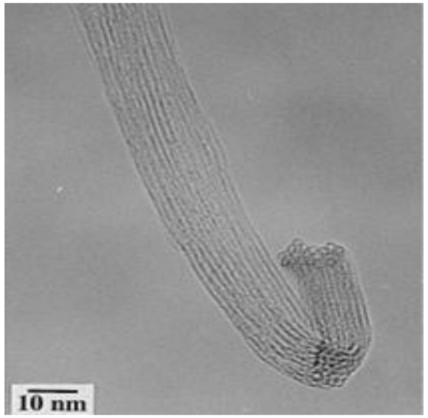
Of special importance is the ***Intermediate Scattering Functions*** which can measured directly by spin-echo spectroscopy (*Roger Pynn's talk*)

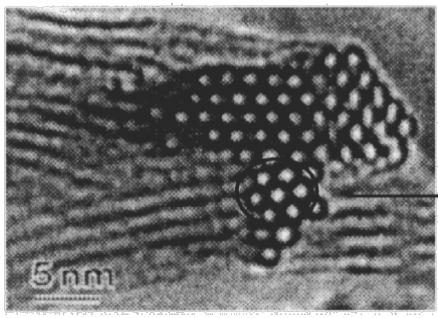
$$I^{dd'}\left(\vec{Q},t\right) = \sum_{\substack{l\in d\\ l'\in d'}} \left\langle \exp\left(-i\vec{Q}\cdot\vec{r}_l(0)\right) \exp\left(i\vec{Q}\cdot\vec{r}_{l'}(t)\right)\right\rangle$$

$$I_s^{d}\left(\vec{Q},t\right) = \sum_{l\in d} \left\langle \exp\left(-i\vec{Q}\cdot\vec{r}_l(0)\right) \exp\left(i\vec{Q}\cdot\vec{r}_l(t)\right)\right\rangle$$

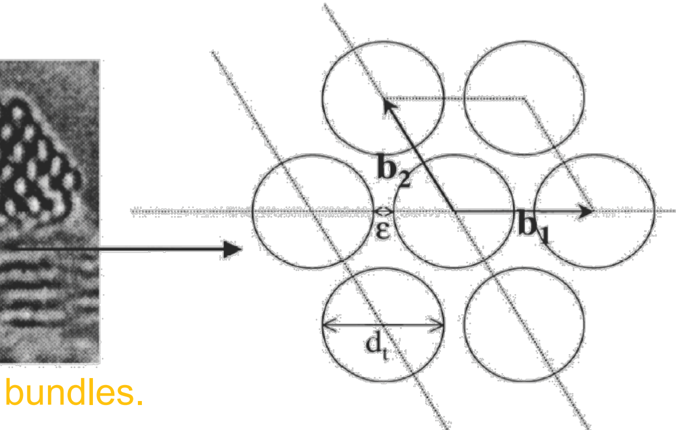
Anomalously Soft Dynamics in Nanotube-Confined Water (n-Water)

- ✧ INS to measure the NWDOS of n-water in comparison with bulk Ih-ice
- ✧ High-resolution INS to determine the mean-squared displacements of hydrogen atoms as a function of temperature and pressure (from $\ln\left[I^{el}(Q)\right] = -\left\langle u_H^2 \right\rangle Q^2$)
- ✧ QENS to characterize the anomalous diffusion of water molecules in nanotubes
- ✧ DINS to study the proton zero point motion Reiter *et al.*(2006)





TEM picture of SWNT bundles.



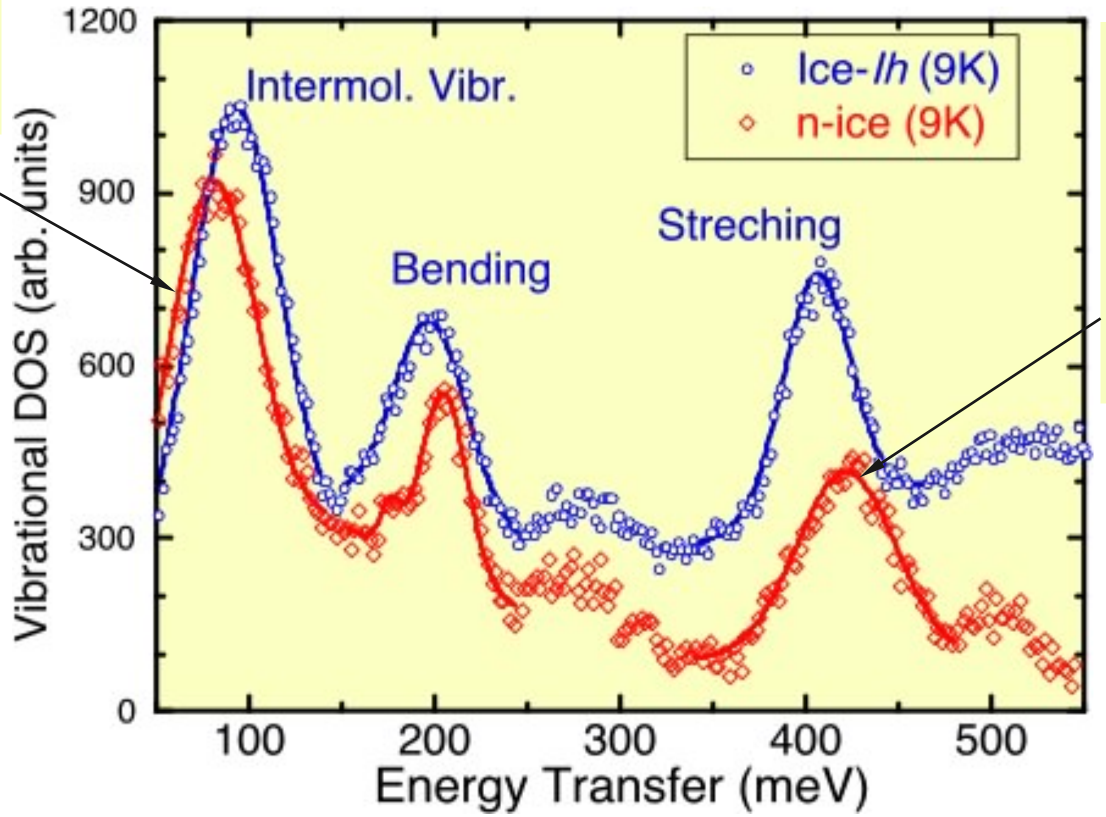
SWNT sample (m=3.8 g) with D≈14±1 Å, l~10 μm was produced by MER and characterized by HRTEM, TEM, SEM, Raman and ND measurements.
To fill the SWNT with water, the dry SWNT sample was first exposed to saturated vapor from a water bath (1:1 weight ratio) at 110°C for 2 hours in an enclosed environment. The excess water adsorbed in the exterior of the nanotubes was then evaporated at 45°C. An optimal filling, in terms of H_2O/SWNT mass ratio was found to be 11.3%.

Study proton dynamics in nanotube-confined H_2O, referred to n-water or n-ice interchangeably.

Inelastic Scattering: To Reveal a Weakened Hydrogen-Bond Network

Inelastic neutron scattering measurements of hydrogen vibrational density of nanotube-ice.

Red shifts of intermolecular modes

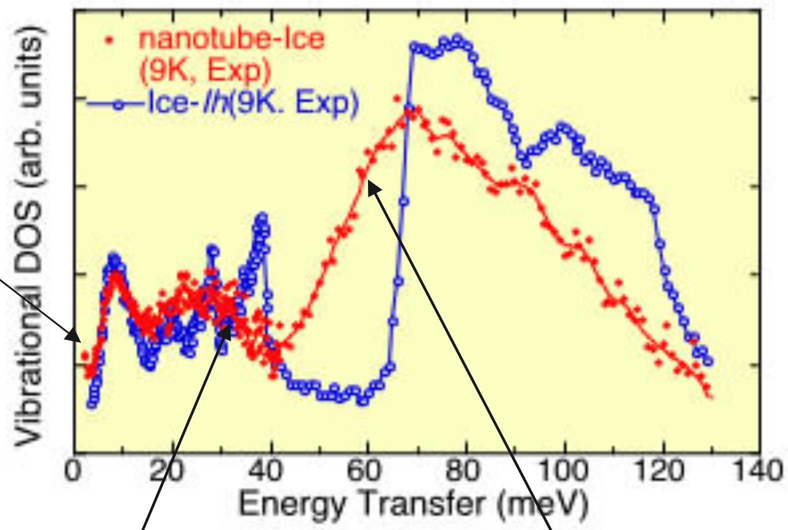


Blue shifts and broadening of intramolecular modes => Shorter $R_{O\text{-}H}$ covalent bonds and a longer intermolecular $R_{O\text{-}O}$ distance

Strong Renormalization of the Low-Energy Vibrational Density

Translation-like & optical modes

Librational Band



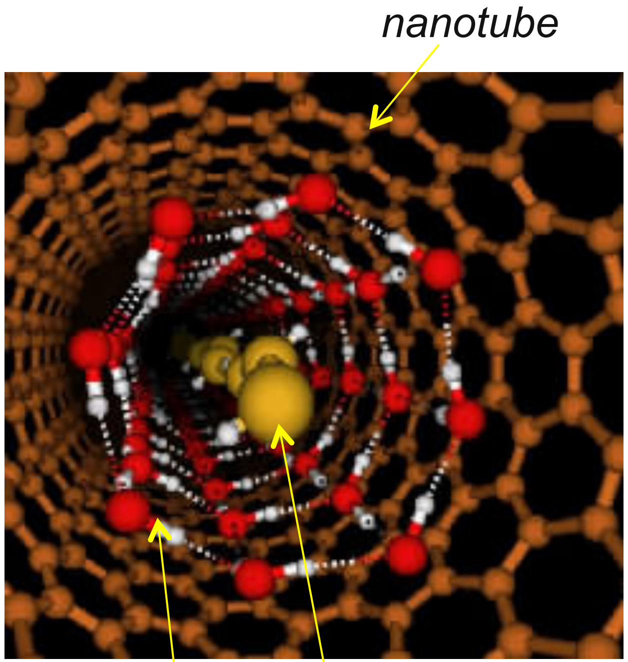
Boson-Peak-like large excess intensity appears below 5 meV

Large modification of the translation-like and optical modes

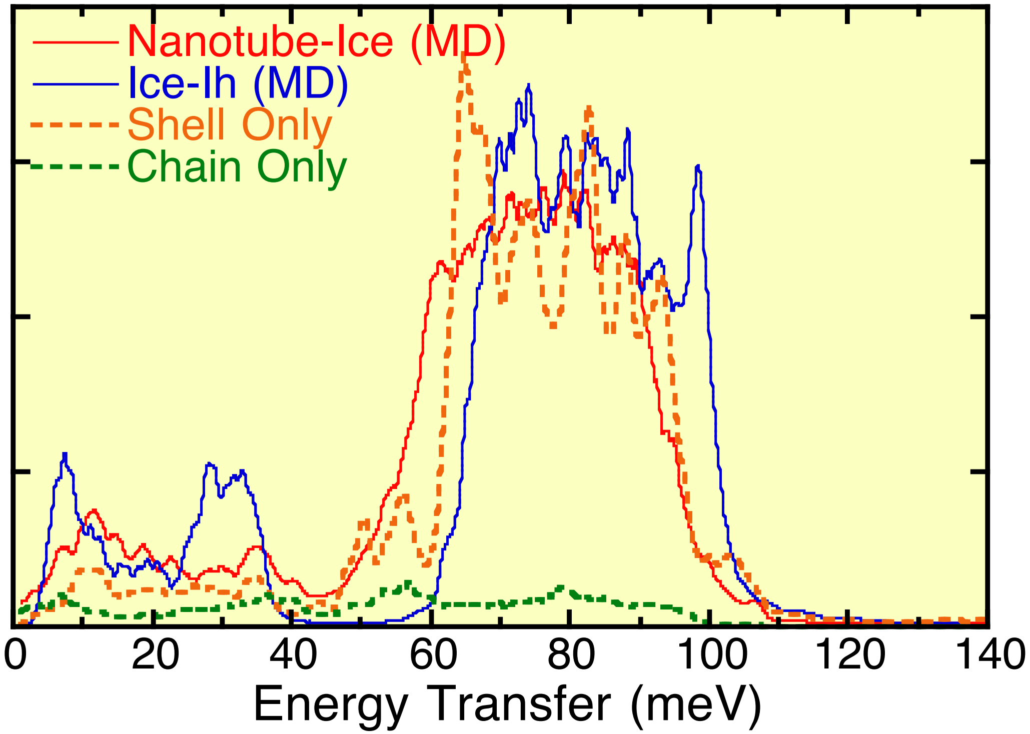
Significant shift of librational band to lower energies.

Interpret INS Data by MD Simulations

- ✧ Identify a "shell + chain" structural model of nanotube-water
- ✧ Calculate the contributions to vibrational DOS by the shell & chain



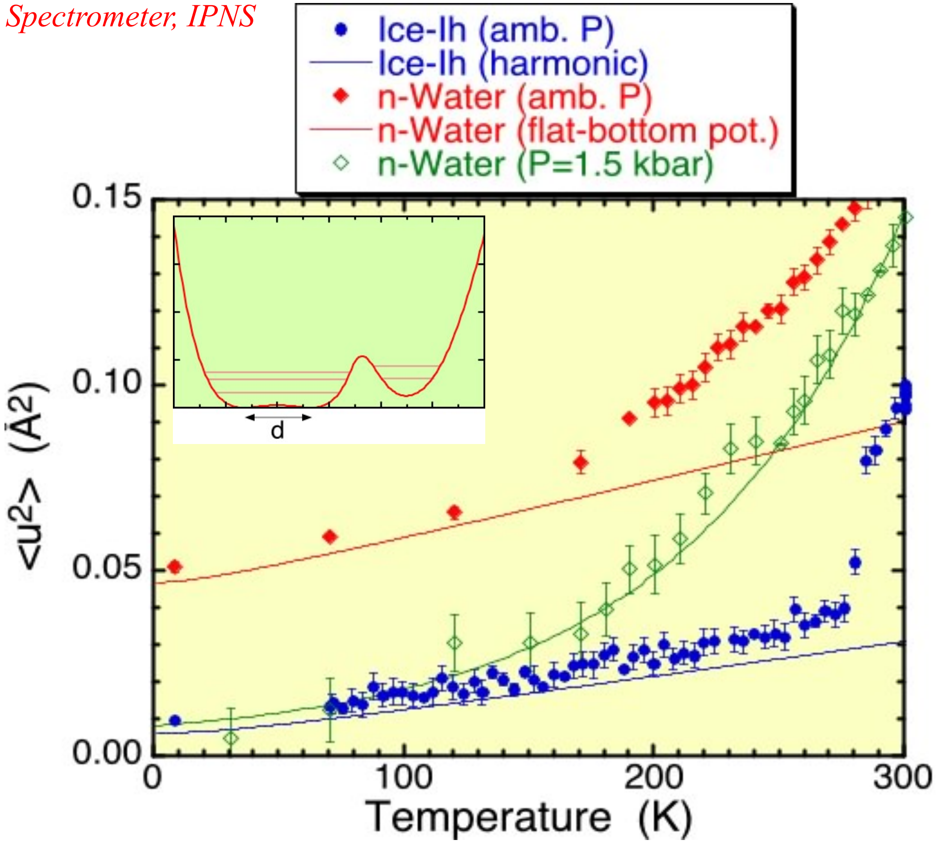
The "shell+chain" structure



Anomalously Soft Dynamics in Nanotube-Water

High-resolution INS permits the determination of the mean-squared displacements of hydrogen atoms as a function of temperature and pressure

HRMECS Chopper Spectrometer, IPNS



- Nanotube-water under pressure $<u_H^2>$ below 100K is reduced drastically to values comparable to those in ice-Ih. At higher temperatures it rises very rapidly above the ice-Ih value. Data show no abrupt transition near 273K.

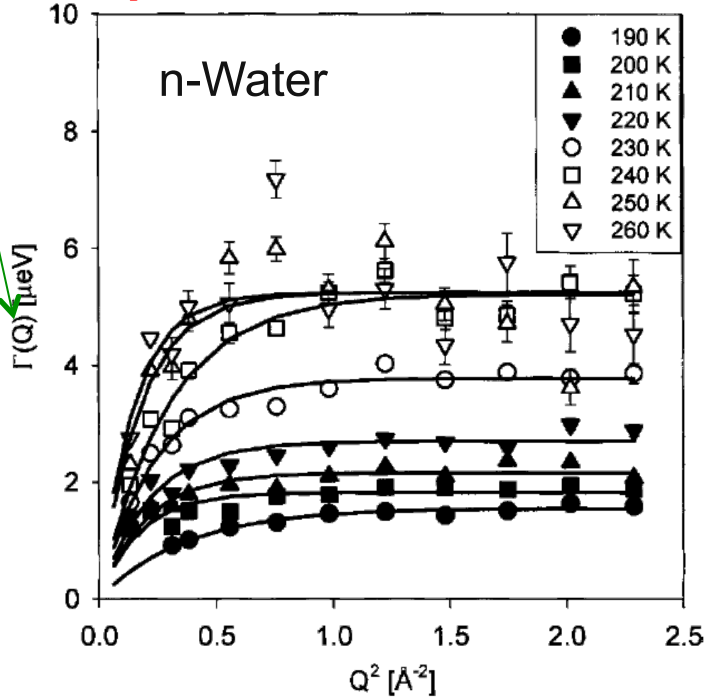
Water confined in nanotubes exhibits properties intermediate of the liquid and solid states that are different from those of all known phases of water-ice.

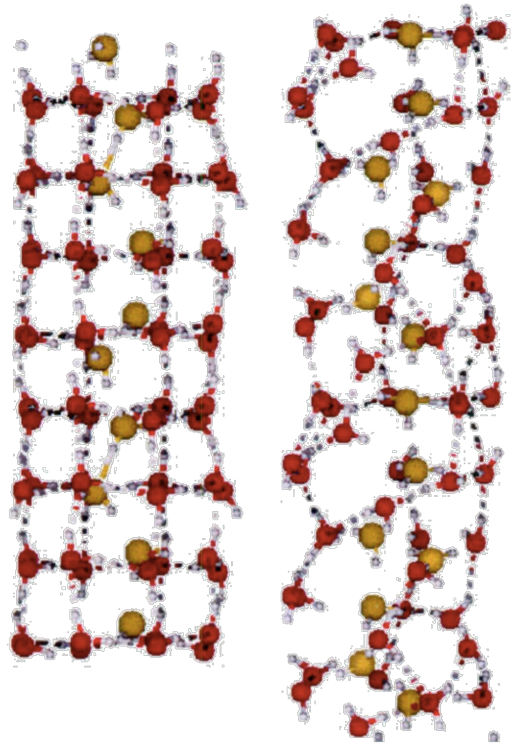
QENS Study of Diffusion of Water Molecules in Nanotubes

HWHM of the quasielastic peak

Back-scattering Spectrometer, NIST

Mamontov *et al.*(2006)



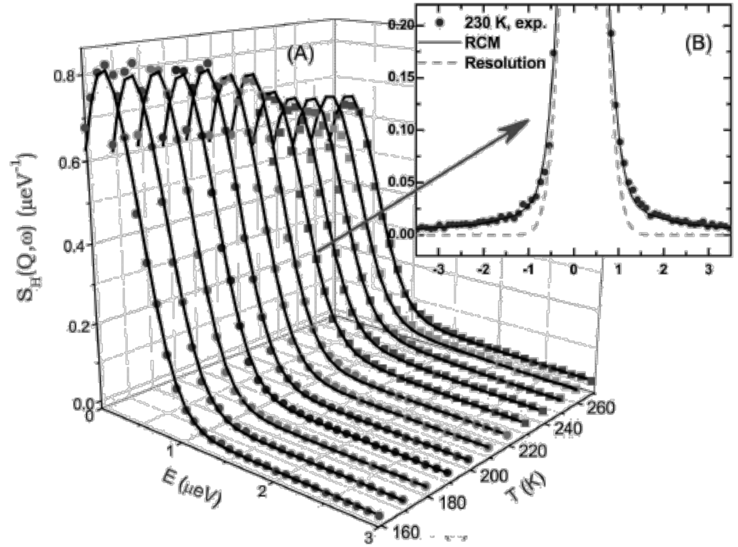


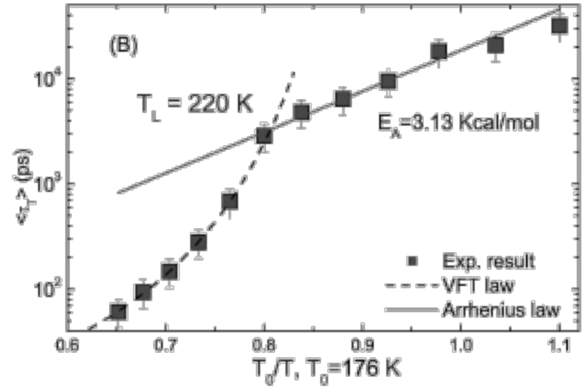
Neutron Spectroscopy Is NOT Enough to Tell a Good Story

- ✧ **Low-Q diffraction to confirm the confined geometry of water, i.e., inside the nanotubes**
- ✧ **Classical and quantum mechanical MD simulations to interpret the data**

A. I. Kolesnikov, J.-M. Zanotti, C.-K. Loong, P. Thiyagarajan *(Neutrons)* & C. J. Burnham *(MD)*

MCM-Confined water Chen et al. (2012)





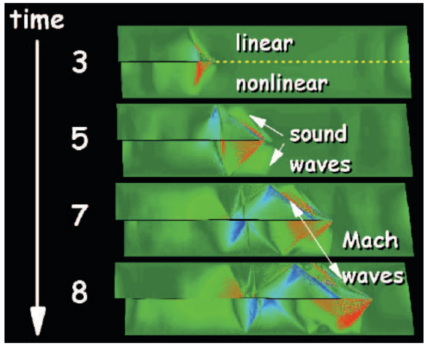
Neutron Spectroscopy: Challenges & Future Development

Materials: Stronger & tougher

Monitoring & warning capable

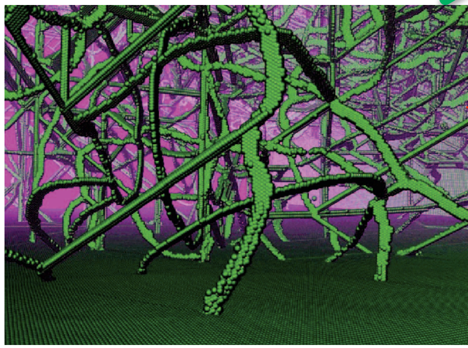
Self-repairable

Brittle: catastrophic bond breakage — Brittle ⟷ ductile transition — **Ductile: dislocations, slip planes**

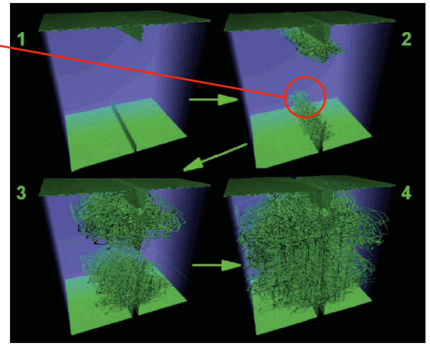


Longitudinal crack speed limited by the Rayleigh wave speed but transverse supersonic cracks occur.

- nonlinear properties
- anharmonic forces
- ballistic phonons
- crack blunting & bifurcation
- sessile dislocation



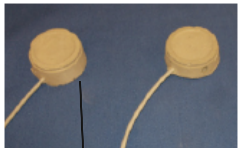
Only those atoms that have a cohesive energy less than 97% of the ideal bulk value are shown.

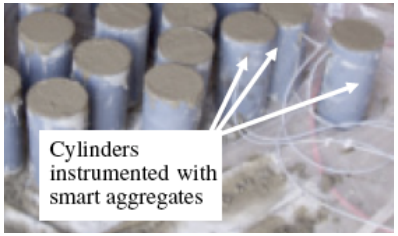


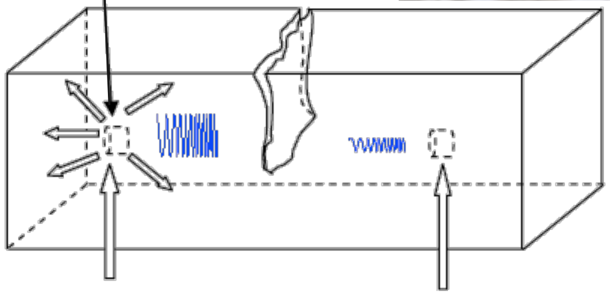
Abraham (2003)

The strength and fracture toughness can be tailored through manipulation of the structure and interfaces at nanoscale.

Song (2008)



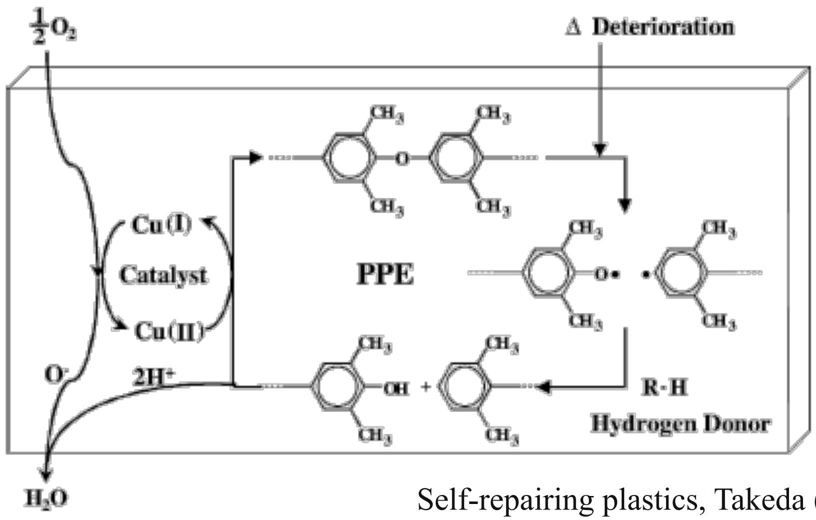




embedded actuator aggregate

embedded sensor aggregate

Crack generation causes rupture of the microcapsules that contain repairing agents and catalysts.



Self-repairing plastics, Takeda (2003)

Materials: Continuing Endeavor

Crystals ⟷ **Glass** ⟷ **Liquid**

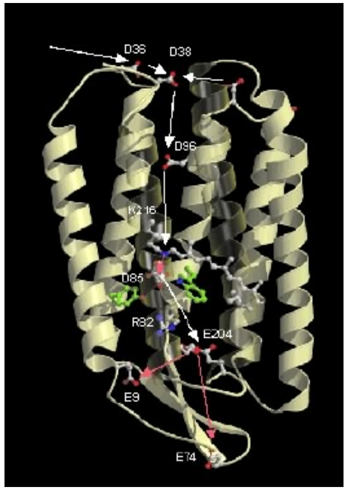
glass forming and glass transition

No fundamental theory, only phenomenological trea

C. A. Angell (2002)

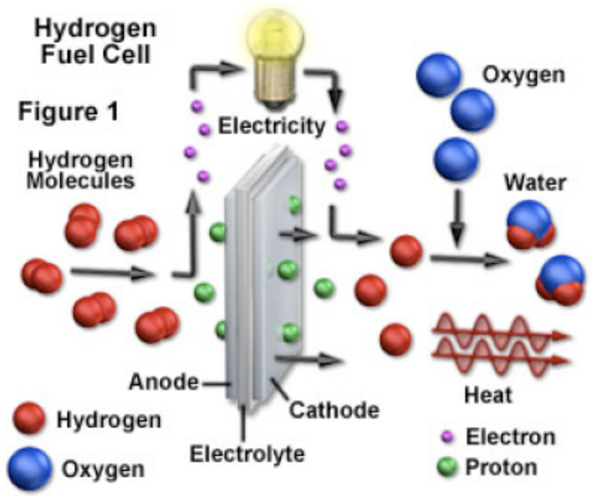
1. WHY IS THERE APENDING ENTROPY CRISIS FOR STRUCTURAL GLASSFORMERS AND NOT FOR OTHER GLASS TYPES?
2. WHY DO STRUCTURAL GLASSES EXHIBIT SUCH A RANGE OF FRAGILITIES?
3. WHY DO FRAGILE GLASSFORMERS OFTEN (BUT NOT ALWAYS) SHOW THE a–b BIFURCATION AT T_{a-b} AND WHY DOES T_{a-b} CORRESPOND TO T_C OF THE MODE COUPLING THEORY?
4. WHY DOES THE MEAN SQUARED PARTICLE DISPLACEMENT, MSD, MEASURED ON ps TIME SCALES, SHOW A BREAK AT OR NEAR T_G - WHERE THE ALPHA RELAXATION TIME IS 200s?
5. WHAT IS THE ORIGIN OF THE BOSON PEAK, AND THE RELATION BETWEEN THE BOSON PEAK, THE MOTIONS RESPONSIBLE FOR THE MSD BEHAVIOR DISCUSSED IN QU. 4, AND THE TWO-LEVEL SYSTEMS RESPONSIBLE FOR THE LOW TEMPERATURE SPECIFIC HEAT ANOMALIES?
6. WHY IS THE RELAXATION FUNCTION NON-EXPONENTIAL AT TEMPERATURES WHERE THE RELAXATION TIME IS NONARRHENIUS?
7. WHAT IS THE CONNECTION BETWEEN MICROHETEROGENEOUS DYNAMICS, SEEN IN COMPUTER SIMULATION STUDIES AT TEMPERATURES BELOW THE ONSET TEMPERATURE OF TWO-STEP RELAXATION, THE MICROHETEROGENEOUS DYNAMICS SEEN IN EXPERIMENTAL STUDIES NEAR T_G, AND THE NON-EXPONENTIALITY OF RELAXATION?
8. WHY DOES THE STOKES-EINSTEIN RELATION BETWEEN VISCOSITY AND DIFFUSIVITY IN SINGLE COMPONENT SYSTEMS BREAK DOWN NEAR AND BELOW THE CROSSOVER TEMPERATURE T_X (Tc,T_B)?
9. WHY ARE THE KINETICS OF ANNEALING (AGING, EQUILIBRATION) SO NON-LINEAR (STRUCTURE-DEPENDENT) FOR FRAGILE LIQUIDS?
10. WHY DOES THE EXCITATION OF THE STRUCTURAL DEGREES OF FREEDOM IN SOME OVERCONSTRAINED SYSTEMS (e.g. Si, Ge) BECOME FIRST ORDER IN CHARACTER, LIKE A WEAK MELTING TRANSITION?

Bacteriorhodopsin (bR): Renewable Energy Generator, Hydrogen Fuel Cells, Pattern Recognition, Holographic Data Storage, Biosensors, Artificial Retina

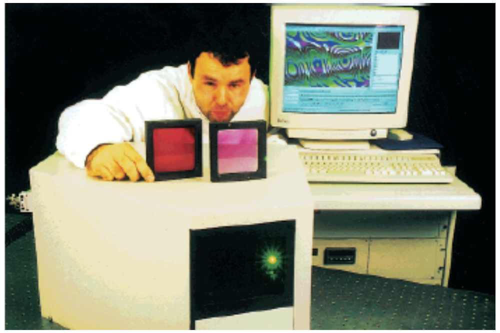


bR consists of 7 a-helices spanning across the double-layered lipid. Unlimited supply of PM from the ocean, extracted and purified by economical biotechnological techniques rather than by expensive synthesis. bR can function safely over a wide temperature range, up to ~120°C, and under extreme pH conditions.

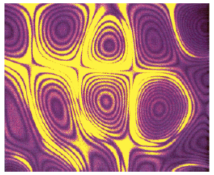
- **Photosynthetic, photoelectric**: Light sensitive, capable of pumping ~100 protons/sec/molecule using sun light - as renewable energy source for a hydrogen-based economy.

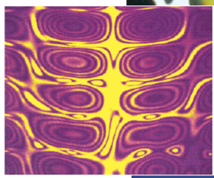


- **Photochromatic**: Information processing, pattern recognition, 2D/3D holographic data storage - as counterfeit-proof media, the next-generation nanoscale information storage a penny/10Mbyte with terabyte capacity.

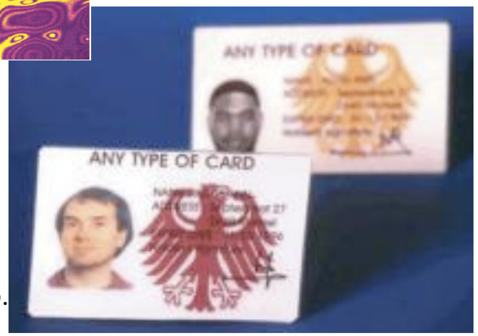


- **Bio-electronic**: light/radiation detectors, biosensors, devices - as crack/vibration monitors, artificial retina, medical diagnosis.





Neutron-scattering studies can provide insight into the mechanism of light-driven proton transport and other related properties.



Jobic (1981), Ferrand (1993), Lechner et al. (1994), Lehert et al. (1998), Hauess et al, (1994), Fitter et al. (1996), Zacccai (2000), Chen et al. (2003).

'It is and remains an inadequate instrument'

Ludwig van Beethoven

~1826 *The piano*

But if Wolfgang Mozart had lived to play Beethoven's piano, he would have been delighted by its many improvements.

*Today, many important materials cannot be studied effectively by neutrons. For example, novel systems relevant to **tribology** and **catalysis**,…*




In view of the continuing improvement and construction of powerful sources, I hope that young students, scientists & engineers will be like Mozart, enthusiastically exploring materials science to the fullest potential of the neutron (and muon) facilities. In the future they will continue improving these sources and methodologies as Beethoven did to the piano, maybe even demanding for yet another generation of new sources. (Jack Carpenter will tell us more in his second talk.)

Thank you!