Why Neutron Scattering

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Spin Ice

Spins constrained to local <111> axes

Water ice

Spin ice
Dynamics of Spin Ice

Above 40 K

\[ \Delta = 23 \text{ meV} \]

\[ \tau = \tau_0 \exp\left(\frac{\Delta}{k_B T}\right) \]

\[ S(Q,t) = A \exp\left(-\frac{t}{\tau}\right) \]

Ehlers et al., PRB 73, 174429 (2006).
Fe – Pnictide Superconductors

LaFeAsO

SrFe$_2$As$_2$

de la Cruz et al., Nature 453, 899 (2008)
Phase Diagram of CeFeAsO$_{1-x}$F$_x$

Spin Resonance in Fe(Se$_{0.4}$Te$_{0.6}$)

Qiu et al., (2009)
A magnetic “resonance” in YBaCuO at about 41 meV, is widely viewed to be central to high temperature superconductivity.

Neutron scattering revealed a magnetic resonance was observed in an “electron-doped” superconductor PLCCO (Pr$_{0.88}$LaCe$_{0.12}$CuO$_{4-d}$) at 11 meV. 

Water

\[ D = D_0 \left( \frac{T}{223} - 1 \right)^{1.82} \]

\[ C_P \sim \left( \frac{T}{T_s} - 1 \right)^{-0.26} \]


Water in Confinement

Thermodynamic measurements suggest that supercooled water should undergo a fragile-to-strong transition between two liquid phases at around 228 K. However, supercooled bulk water reaches its homogeneous nucleation point and crystallizes into ice at 235 K.

Vogel-Fulcher-Tammann law

\[ \tau = \tau_o \exp\left[\frac{D T_o}{(T - T_o)}\right] \]

The anomalies in the thermodynamic quantities also indicate the possible existence of a low-temperature critical point near this transition temperature, but at somewhat elevated pressure.

Water in Confinement

More than 800 million metric tons of Portland cement are produced each year.

Tricalcium silicate (Ca$_3$SiO$_5$) is the most important and abundant component of Portland cement.

Dicalcium silicate (Ca$_2$SiO$_4$) is the second most abundant component.

These two components typically account for approximately 80 wt.% of Portland cement.

\[
BWl = \frac{Green + Blue}{Green + Blue + Red}
\]

Thomas et al., J. Am. Ceram. Soc. 84, 1811 (2001)
Kinetics of the Hydration of Cement

The main hydration reaction occurs over 24-48 hours. There are 3 periods.

Quasielastic Scattering from C3S-C2S Mixtures

Data is fit to kinetic models.

$A$ is the amount of product that would have been formed if the “nucleation and growth” regime had continued to $\infty$ time.

$D_i$ is the effective diffusion constant that controls the reaction in the “diffusion limited” regime.

Neutron Vibrational Spectroscopy

Understanding the binding of hydrogen is critical to developing effective materials for H storage.

Vibrational spectroscopy using neutrons is preferentially sensitive to those modes involving H motions.

Neutron spectra can easily be modeled using first principles calculations.

NaAlH$_4$
LiBH$_4$ releases H during decomposition

Li$_2$B$_{12}$H$_{12}$ is a stable intermediate

Metal-Organic Framework (MOF) Materials

MOF’s consist of metal oxide clusters linked by organic linkers

– High surface area materials
– Crystalline nano-porous material with tunable pore size by changing the organic linker
– Functionality of the linker can also be varied

As synthesized sample: $[\text{Mn(DMF)}_6]_3[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{H}_2\text{O})_{12}]_2 \cdot 42\text{DMF} \cdot 11\text{H}_2\text{O} \cdot 20\text{CH}_3\text{OH}$

After desolvation: $[\text{Mn(DMF)}_6]_{1.5}[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{DMF})_{12}]$

After solvent exchange and desolvation, a new material can be formed with molecular formula: $\text{Mn}_{1.5}[(\text{Mn}_4\text{Cl})_3\text{BTT}_8]$
H₂ is treated as a super atom with double occupancy. Fourier difference plot is used to visualize the initial position of H₂.
What is the Physical Picture?

1. Metal Hydride

2. Kubas complex

3. Two dimensional rotor

4. Three dimensional rotor
Hydrogen Rotational Transitions

Para has a nuclear spin $I=0$. This constrains $J$ to be even.

Ortho has a nuclear spin $I=1$. This constrains $J$ to be odd.

Transition between ortho and para species can occur through flipping the nuclear spin.

Energy

$E_J = B J(J+1)$, $B_{\text{H}_2} = 7.35 \text{ meV}$

Para
$\begin{align*}
I &= 0 \\
J &= 0
\end{align*}$

Ortho
$\begin{align*}
I &= 1 \\
J &= 1
\end{align*}$

Transitions

Neutron Transitions

J=2

Photon Transitions

J=0

J=1

J=3

(Neutron energy loss)
p-H$_2$ in HKUST-1

$I(Q) \propto e^{-Q^2<u^2>/3} j_1(d_{HH} Q / 2)^2$

$d_{HH}=0.74$ Å

At ~5K, $<u^2>$ of p-H$_2$ =0.48 Å$^2$

C.M. Brown et al., Nanotechnology 20, 204025 (2009)
$p-H_2$ in HKUST-1

$J = 0$ to $J = 1$, $m = \pm 1$

9.7 meV

$J = 0$ to $J = 2$, $m = \pm 2$

36.1 meV

$J = 0$ to $J = 1$, $m = 0$

37.3 meV

In-plane phonons

$\hbar \omega_x = 9.6$ meV

$\hbar \omega_y = 13.4$ meV

Out-of-plane phonons

$\hbar \omega_z = 22.9$ meV

C.M. Brown et al.,
Nanotechnology 20, 204025 (2009)
<u^2> and Proteins

The dynamic transition in <u^2> correlates with the onset of enzymatic activity.


The viscous nature of glycerol retards onset of anharmonicity. The low-temperature “harmonic” region shows that glycerol stiffens the formulation.

Tsai et al., Biophys. J. (2000)
QENS & Protein Preservation

HRP and YADH preserved in trehalose with small dilutions of glycerol (trehalose with 0, 5, 10, 15, and 20 % glycerol by mass)


- Small additions of glycerol to trehalose greatly suppresses $<u^2>$
- Neutron scattering predicts long term enzyme stability
  $\Rightarrow$ pharmaceutical preservation
The dynamics of solvent molecules controls the dynamic transition in RNA as well as proteins.
Contrast Variation using Deuteration

Contrast Matching - reduce the number of phases “visible”

\[ \rho_{\text{solvent}} = \rho_{\text{core}} \]

or

\[ \rho_{\text{solvent}} = \rho_{\text{shell}} \]

(shell visible)

(core visible)

The two distinct 2-phase systems can be easily understood
Phospholipid Membranes
Relaxation rate of $S(Q, t)$

\[ \Gamma \propto \sqrt{\frac{k_B T}{\kappa} \frac{k_B T}{\eta}} Q^3 \]
Temperature Dependence of $\kappa$
Vesicles with Cholesterol

- Presence of cholesterol
- 50%
- 33%
- 0%

Temperature $T/°C$ and relative parameter $\kappa$
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The NCNR Has 25 Operating Neutron Beam Instruments Tailored to Specific Needs …

www.ncnr.nist.gov
Expansion Activities

- New Cold Source
- Construction
- Instrument development
- Beam delivery
- Reactor reliability enhancements
NCNR Expansion

Many sub-projects:
5 new capabilities
MACS relocation
instrument moves
software
guides/shields
cold source

Major areas of activity:
Construction
Cold source
Guide systems
Shield systems
Instruments
Control room upgrade

guide hall addition

confinement building

existing guide hall
Neutron methods are extremely versatile

Which type of instrument might be useful in your research?

dan@nist.gov

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