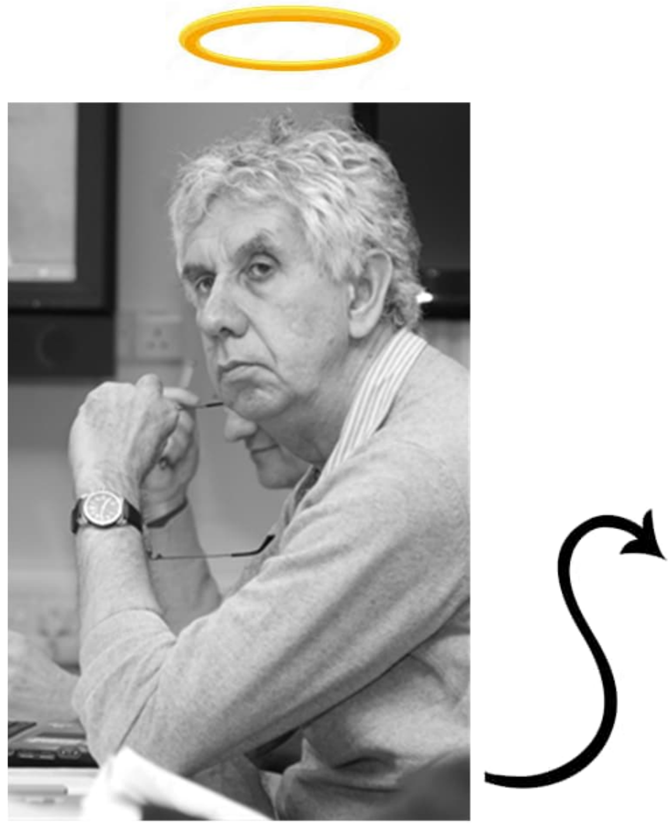
High Energy Neutron Scattering

Oxford School of Neutron Scattering 2024

“It’s the simplest bloody form of neutron scattering!”

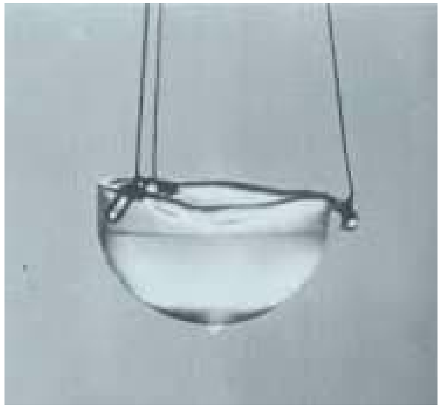
Jerry Mayers

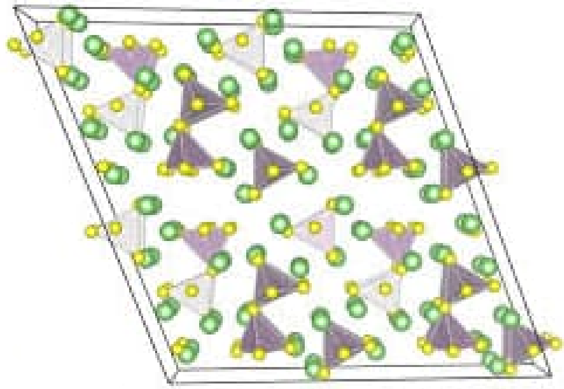


High energy neutrons (by our standards)

- High energy neutron scattering is one of the ‘newer’ experimental techniques.
- Spallation sources produce an intense flux of high energy neutrons which we can generally describe as fast or epithermal
- Broadly we characterize fast neutrons as those with energies >1MeV, and. Epithermal neutrons >0.5eV. From a scattering perspective, we are interested in **the eV-keV range**.

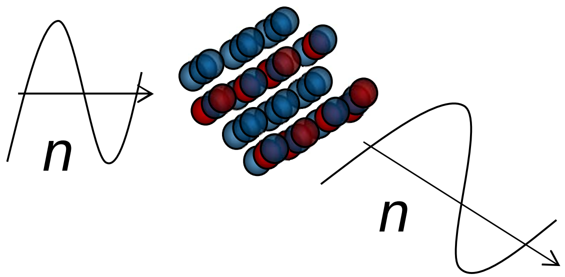
The kind of things we measure...

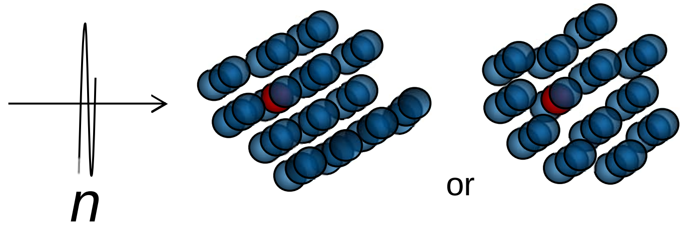




High Energy Concepts

- What difference does high incident energy make to neutron scattering?
- First consider an imaginary diffraction experiment for E_i = 1 eV (blackboard).
- High energies → large $\mathbf{k}_i$ → high $\mathbf{Q}$ (particularly inelastic processes)





For epithermal neutron scattering, all scattering is single atom scattering = **incoherent**.

Correlation Functions

- Some reminders from previous lectures:
- Within spectroscopy we (generally) express measurements in terms of the response function $S(\mathbf{Q},\omega)$

$$S(\mathbf{Q},\omega) = \frac{k_i}{k_f}\frac{d^2\sigma}{d\Omega dE_f}$$

- We can also express this as the time Fourier transform of the intermediate response function, $I(\mathbf{Q},t)$

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} I(\mathbf{Q},t)\ \mathrm{exp}(-i\omega t)\ \mathrm{d}t$$

$$\begin{tikzcd}
 & S(\mathbf{Q},\omega) \arrow[dl, Leftrightarrow] \arrow[dr, Leftrightarrow] & \\
G(\mathbf{r},t) \arrow[rr, Leftrightarrow] & & I(\mathbf{Q},t)
\end{tikzcd}$$

Correlation Functions

- When we look at high energy neutrons, we need to be careful with how we deal with $I(\mathbf{Q}, t)$

$$I(\mathbf{Q}, t) = \underbrace{I_{jj}(\mathbf{Q}, t)}_{\text{Incoherent terms only}} = \underbrace{\left\langle \exp\left[-i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0)\right]\exp\left[i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(t)\right]\right\rangle}_{\text{Correlations between an atom at time } t \text{ and } t\,=\,0}$$

- For low energy incoherent scattering (QENS)

$$\boxed{\textbf{CLASSICAL} \quad \left\langle \exp\left[-i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0)\right]\exp\left[i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(t)\right]\right\rangle = \left\langle \exp\left[-i\mathbf{Q}\cdot\left\{\hat{\mathbf{r}}_j(0)-\hat{\mathbf{r}}_j(t)\right\}\right]\right\rangle}$$

$$\Big\Downarrow \; FT$$

$$G(\mathbf{r}, t) = \frac{1}{(2\pi)^3}\frac{1}{N}\sum_j \int_{-\infty}^{\infty} \left\langle \exp\left[-i\mathbf{Q}\cdot\left\{\hat{\mathbf{r}}_j(0)-\hat{\mathbf{r}}_j(t)\right\}\right]\right\rangle \exp(-i\mathbf{Q}\cdot\mathbf{r})\,\mathrm{d}^3\mathbf{Q}$$

$$\Big\Downarrow \; Etc.$$

Quantum vs Classical

- High energy neutron scattering can't be considered as classical
  - Neutron energies are 'high' (wrt ...?)
  - Neutron wavelengths are 'small' (wrt ...?)

- In general, $\hat{\mathbf{r}}_j(0)$ and $\hat{\mathbf{r}}_j(t)$ **don't commute**
  - Heisenberg operators contain the Hamiltonian

$$\langle \exp[-i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0)]\exp[i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(t)]\rangle \neq \langle \exp[-i\mathbf{Q}\cdot\{\hat{\mathbf{r}}_j(0)-\hat{\mathbf{r}}_j(t)\}]\rangle$$

$$= \left\langle \exp[-i\mathbf{Q}\cdot\{\hat{\mathbf{r}}_j(0)-\hat{\mathbf{r}}_j(t)\}]\exp\left[\frac{1}{2}\left[\hat{\mathbf{r}}_j(0),\hat{\mathbf{r}}_j(t)\right]\right]\right\rangle$$

commutator

Baker-Campbell-Hausdorff relation

$$\exp A \exp B = \exp(A+B)\exp\left(\frac{1}{2}[A,B]\right)$$

The Impulse Approximation

- We still need to have an idea of what $\hat{\mathbf{r}}_j(t)$ is for epithermal scattering

- For this we use the Impulse Approximation
  - The energy transfer and $\mathbf{Q}$ are *sufficiently* high that only the shortest times need to be considered.
  - A particle travels freely for a *sufficiently* short time.
  - Equivalently: the final state of the system is irrelevant.

$$\hat{\mathbf{r}}_j(t) \cong \hat{\mathbf{r}}_j(0) + \frac{t}{M_j}\widehat{\boldsymbol{p}_j}$$

We have expressed $\hat{\mathbf{r}}_j(t)$ in terms of $\hat{\mathbf{r}}_j(0)$ and the particle **momentum** operator, $\widehat{\boldsymbol{p}_j}$.

The Impulse Approximation

- Let's plug this into $I_{jj}(\mathbf{Q},t)$:

$$I_{jj}(\mathbf{Q},t) = \left\langle \exp\left[-i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0)\right]\exp\left[i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(t)\right]\right\rangle$$

$$= \left\langle \exp\left[-i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0)\right]\exp\left[i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0) + \frac{it}{M_j}\mathbf{Q}\cdot\widehat{\boldsymbol{p}_j}\right]\right\rangle$$

$$= \left\langle \exp\left[\cancel{-i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0) + i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0)} + \frac{it}{M_j}\mathbf{Q}\cdot\widehat{\boldsymbol{p}_j}\right]\exp\left[\frac{1}{2}\left[-i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0), \cancel{i\mathbf{Q}\cdot\hat{\mathbf{r}}_j(0)} + \underbrace{\frac{it}{M_j}\mathbf{Q}\cdot\widehat{\boldsymbol{p}_j}}_{[\mathbf{r},\mathbf{p}]\,=\,i\hbar}\right]\right]\right\rangle$$

Position operators commute

$$\boxed{I_{jj}(\mathbf{Q},t) = \left\langle \exp\left[\frac{it}{M_j}\mathbf{Q}\cdot\widehat{\boldsymbol{p}_j}\right]\right\rangle \exp\left(\frac{i\hbar t Q^2}{2M_j}\right)}$$

The Impulse Approximation

$$I_{jj}(\mathbf{Q}, t) = \boxed{\left\langle \exp\left[\frac{it}{M_j}\mathbf{Q}\cdot\mathbf{p}_j\right]\right\rangle} \exp\left(\frac{i\hbar t Q^2}{2M_j}\right)$$

Weighted average of the exponential term taken over all $\boldsymbol{p}$ for the particle.

$$\boxed{\int n(\mathbf{p}_j)\exp\left[\frac{it}{M_j}\mathbf{Q}\cdot\mathbf{p}_j\right]d\mathbf{p}}$$

Expressed in terms of the momentum distribution $n(\mathbf{p}_j)$

$$I_{jj}(\mathbf{Q}, t) = \int n(\mathbf{p}_j)\exp\left[\frac{it}{M_j}\mathbf{Q}\cdot\mathbf{p}_j + \frac{i\hbar t Q^2}{2M_j}\right]d\mathbf{p}$$

The Impulse Approximation

- Let's FT to the scattering function, $S(\mathbf{Q}, \omega)$:

$$I_{jj}(\mathbf{Q}, t) = \int n(\mathbf{p}_j) \exp\left[\frac{it}{M_j}\mathbf{Q} \cdot \mathbf{p}_j + \frac{i\hbar t Q^2}{2M_j}\right] d\mathbf{p}$$

$$S(\mathbf{Q}, \omega) = \int \int n(\mathbf{p}_j) \exp\left[\frac{it}{M_j}\mathbf{Q} \cdot \mathbf{p}_j + \frac{i\hbar t Q^2}{2M_j}\right] \exp(-i\omega t)\, d\mathbf{p}\, dt$$

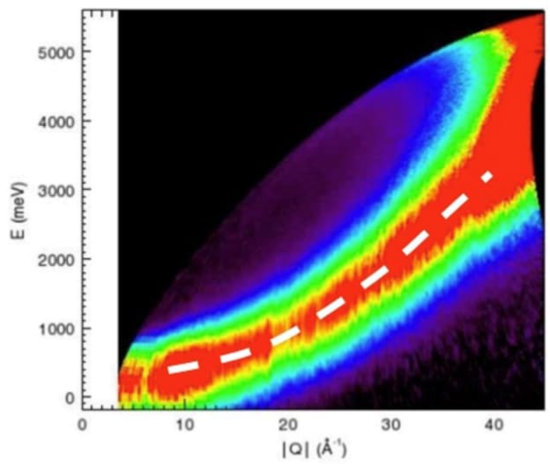
$$\boxed{S(\mathbf{Q}, \omega) = \int n(\mathbf{p}_j)\, \delta\left(\hbar\omega - \frac{\hbar^2 Q^2}{2M_j} - \frac{\hbar}{M_j}\mathbf{Q} \cdot \mathbf{p}_j\right) d\mathbf{p}}$$

DONE!

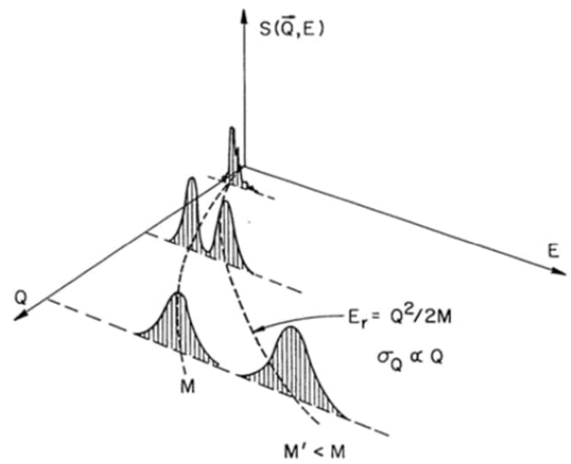
almost

$S(\mathbf{Q}, \omega)$ in eV Scattering

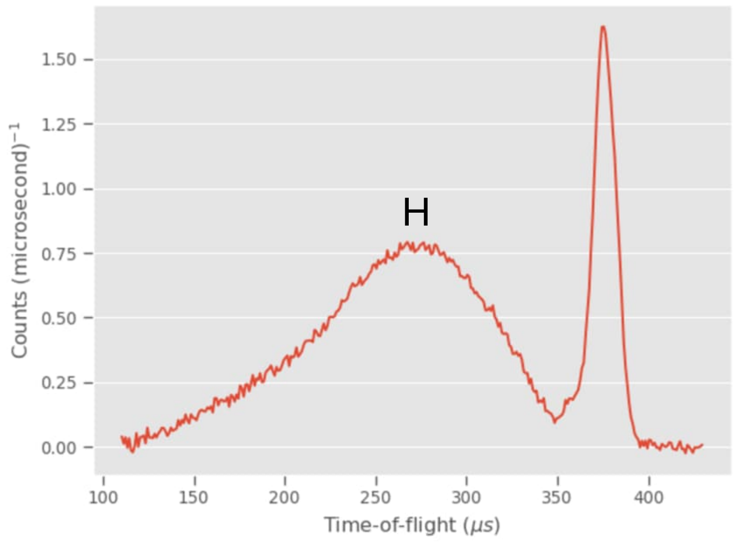
$$S(\mathbf{Q},\omega) = \int n(\mathbf{p}_j)\,\delta\left(\hbar\omega - \underbrace{\frac{\hbar^2 Q^2}{2M_j}}_{\textit{Recoil Energy}} - \underbrace{\frac{\hbar}{M_j}\mathbf{Q}\cdot\mathbf{p}_j}_{\textit{Spectroscopic broadening}}\right) d\mathbf{p}$$

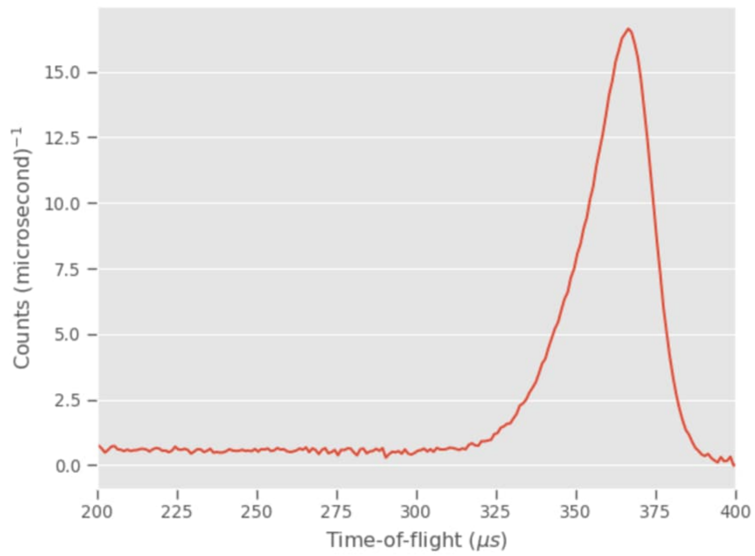


- eV neutron scattering gives us access to atomic momentum distributions, $n(\mathbf{p}_j)$, with each unique mass contributing to $S(\mathbf{Q},\omega)$ as a single peak centred on its (stationary) recoil energy.
- The peak width is determined by $\mathbf{Q}$ and $\mathbf{p}_j$.



Forward vs Backwards Scattering





- The neutron is slightly heavier than the proton
  - No proton signal in backscattering, but we see deuteron scattering in both forward and backscattering.
- Recoil energies rapidly converge for M>7amu
  - backscattering usually involves trying to decompose a broad feature into its component mass signals.

The silly bit.

- Unfortunately, we don't work in $S(\mathbf{Q},\omega)$… This annoys other spectroscopists.

$$S(\mathbf{Q},\omega) = \int n(\mathbf{p}_j)\,\delta\left(\hbar\omega - \frac{\hbar^2 Q^2}{2M_j} - \frac{\hbar}{M_j}\mathbf{Q}\cdot\mathbf{p}_j\right)d\mathbf{p}$$

Detector-by-detector (Q)

$$y_M = \frac{M_j}{\hbar^2 Q}\left(\hbar\omega - \frac{\hbar^2 Q^2}{2M_j}\right)$$

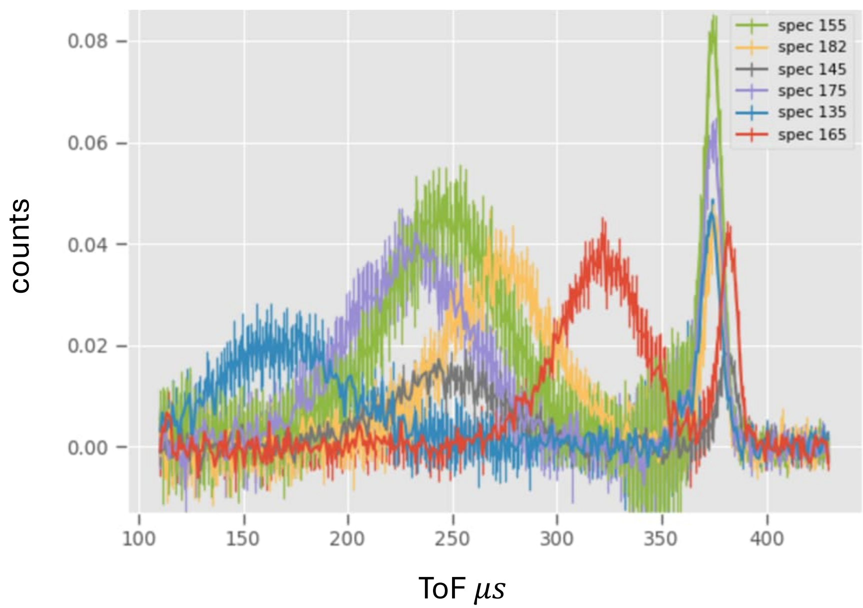
All detectors can be collapsed onto the same $J(y,\widehat{\boldsymbol{q}})$

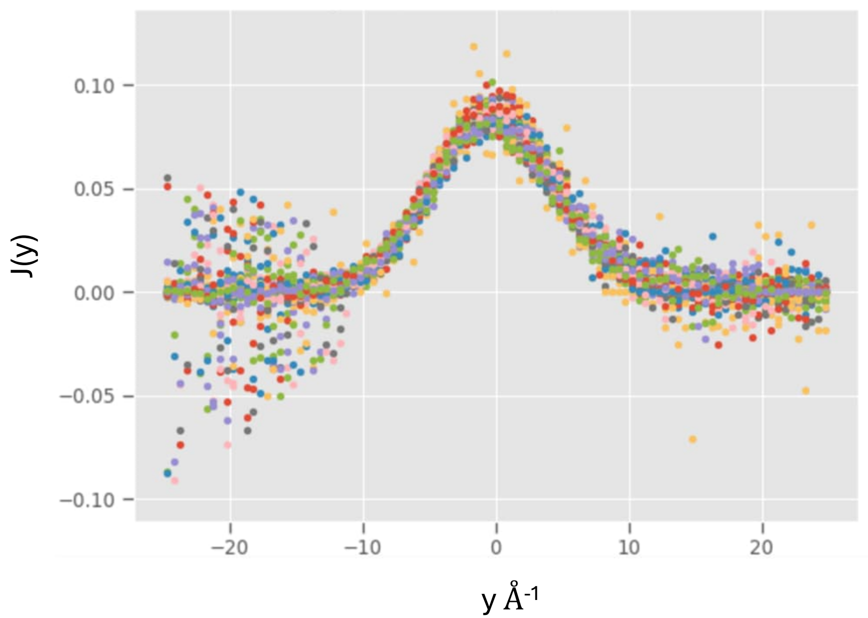
$$S(\mathbf{Q},\omega) = \frac{M_j}{Q}J(y,\widehat{\boldsymbol{q}}) \quad \text{where} \quad \boxed{J(y_M,\widehat{\boldsymbol{q}}) = \int n(\mathbf{p}_j)\,\delta\left(\hbar y_M - \widehat{\mathbf{Q}}\cdot\mathbf{p}_j\right)d\mathbf{p}}$$

DONE!

The silly bit.

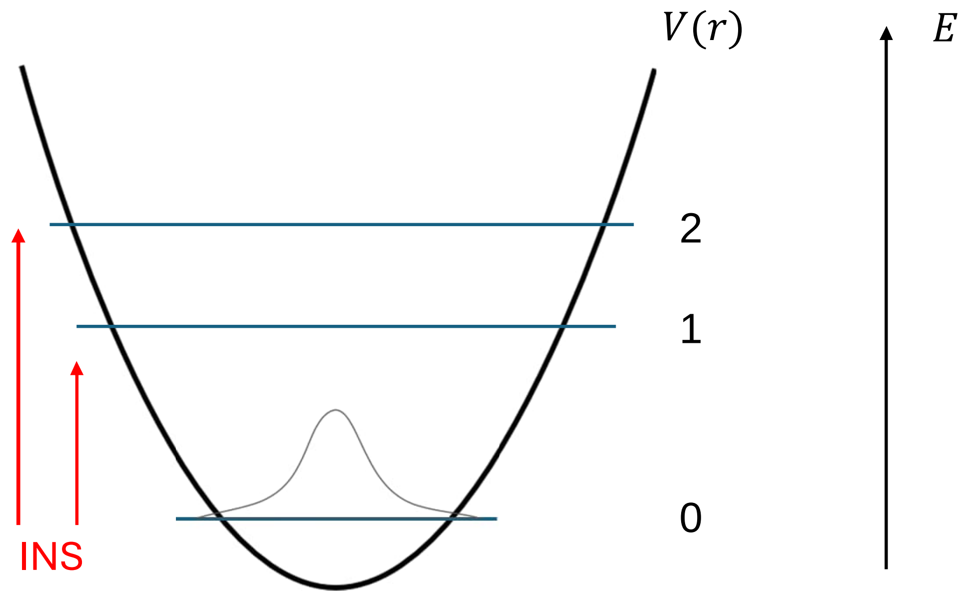
$$J(y_M, \widehat{\boldsymbol{q}}) = \int n(\mathbf{p}_j)\,\delta\big(\hbar y_M - \widehat{\mathbf{Q}} \cdot \mathbf{p}_j\big)d\mathbf{p}$$





Why do we care about $n(p)$?

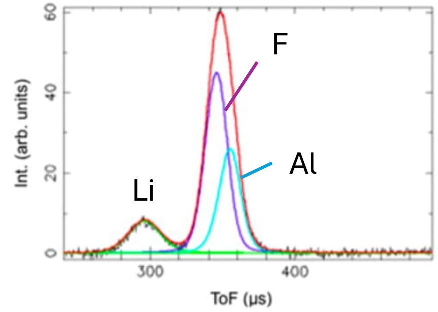
- A particle in a harmonic potential has a gaussian $n(p)$.
- A more tightly bound system has a broader $n(p)$.
- $n(p)$ examines the zero-point motion of the particle, unlike conventional INS.
- The shape of $n(p)$ reflects anharmonicity in the potential.



Example: Harmonic Solid LiF

- For an atom harmonic potential/Gaussian $J(y_M)$ there is a simple relationship between the gaussian width, σ_M, and the atomic kinetic energy: E_K.

$$J(y_M) = \frac{1}{\sqrt{2\pi\sigma_M^2}} \exp\left(-\frac{y_M}{2\sigma_M^2}\right), \qquad E_K = \frac{3\hbar^2\sigma_M^2}{2M}$$



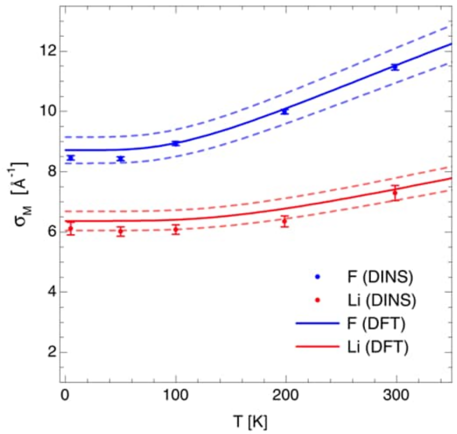
$\sigma_{Li}^T = 1.40\ b$

$\sigma_F^T = 4.02\ b$

$\sigma_{Al}^T = 1.50\ b$

- σ_M is also directly calculable from an atom-projected density of states:

$$\sigma_M^2(T) = \frac{M}{\hbar^2}\int D(\omega)\frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2k_BT}\,d\omega$$



Example: Nuclear Quantum Effects

- The proton is light, and sometimes we need to look beyond a harmonic model, or for situations where H/D behave differently (an extreme being proton delocalisation).
- The shape of $J(y)$ is sensitive to any anharmonicity, but is an even function.
  - We can take a set of orthogonal polynomial functions and expand the gaussian term to account for kurtosis etc.

$$J(y_M) = \frac{1}{\sqrt{2\pi\sigma_M^2}} \exp\left(-\frac{y_M}{2\sigma_M^2}\right) \left[1 + \sum_n \frac{C_n}{2^{2n} n!} H_{2n}\left(\frac{y_M}{\sqrt{2}\sigma_M}\right)\right]$$

  - We rarely need to go over C_4 terms (a simple kurtosis).

Example: ~~Water~~ Weak Quantum Fluid

- The neutron community is delightfully obsessed with water, for which there is no shame and has in no way diverted attention from other interesting scientific problems.

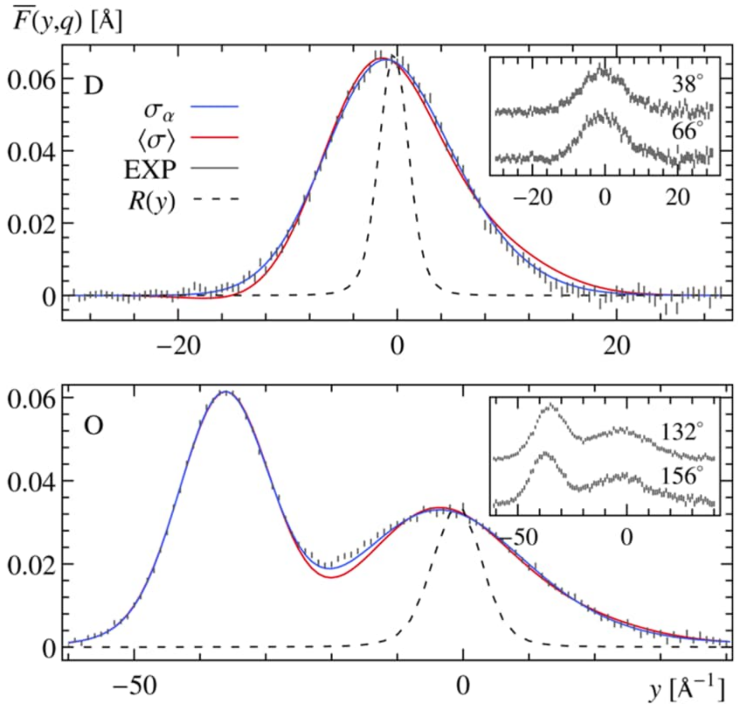
- ~~The community has now reached consensus~~

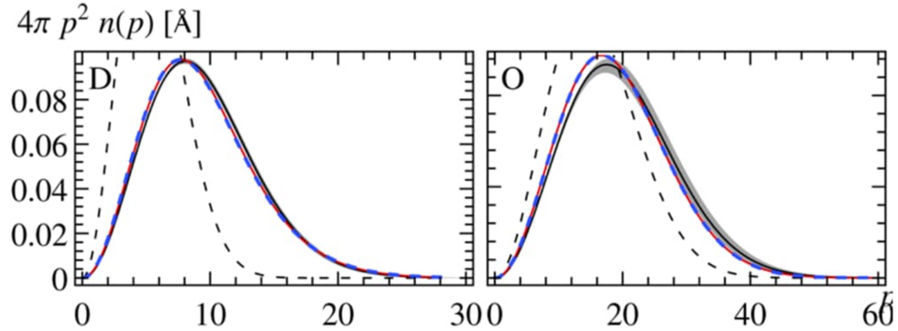
- The stronger a hydrogen bond is, the less harmonic the potential and the less Gaussian is $n(p)$.

- DINS gives a direct experimental probe as to how important nuclear quantum effects are, so is water a quantum liquid?

Example: ~~Water~~ Weak Quantum Fluid

- D, like H, is separable from other masses in forward scattering, meaning we can compare measurements on H_2O and D_2O.

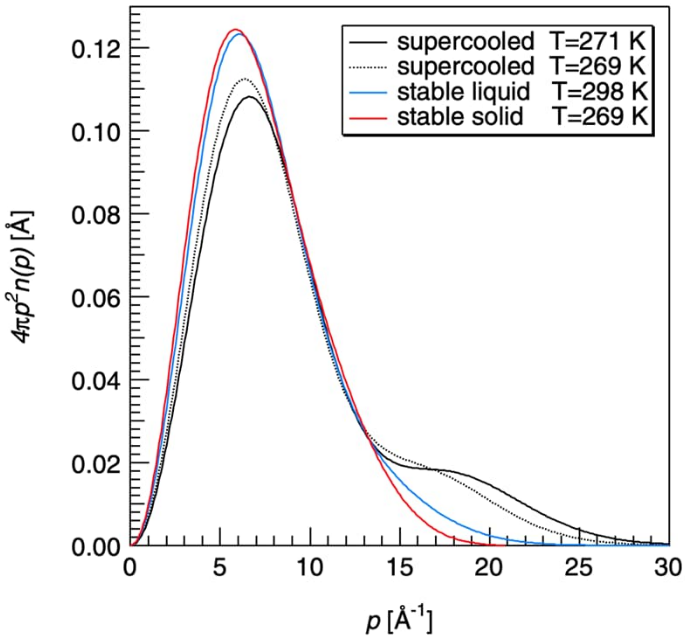




- Sophisticated path integral molecular dynamics simulations reproduce well experimental $n(p)$ for both D and O.
- Growing evidence exits that on melting the $\langle E_K \rangle$ perpendicular and parallel to the OD bond change in opposing directions.

Example: ~~Water~~ Weak Quantum Fluid

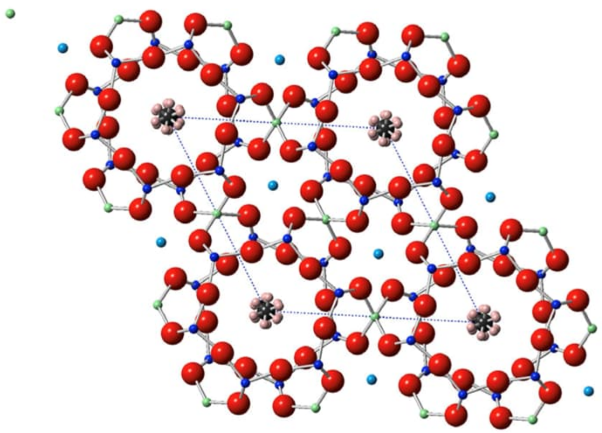
- There are some contentious results on supercooled (and even more contentious supercritical) water.
- The proton radial momentum distribution $4\pi p^2 n(p)$ shows an inflection. This can only happen in the case of a spatially delocalised proton.

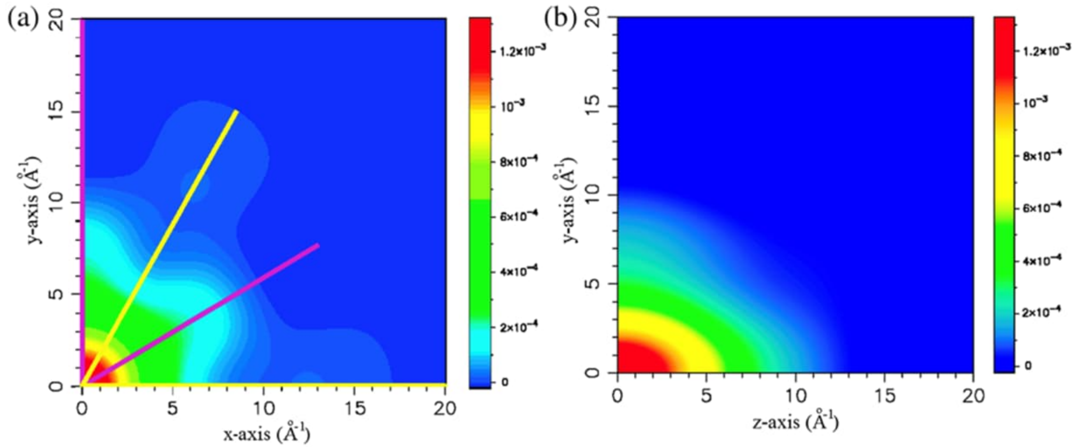


- No theoretical models can qualitatively reproduce this behaviour

Example: ~~Water~~ Less Weak Quantum Fluid

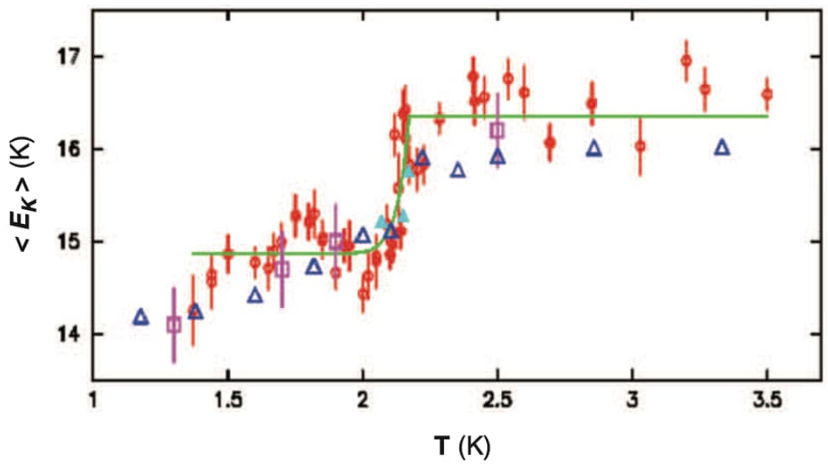
- There are not many DINS measurements on single crystal/aligned samples. Why is this?
- Co-aligning crystals of Beryl with 1D water channels in it allowed for identification of proton delocalisation perpendicular to the chain.
- This was backed up with the appearance of tunnelling peaks in INS measurements, and qualitatively with some ab initio work…





Example: Lambda Transition in He

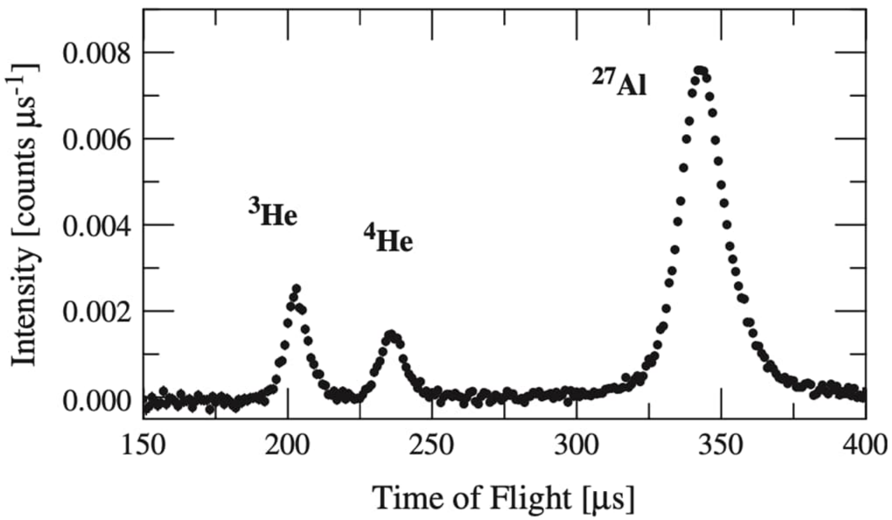
- There is a transition in liquid ^{4}He at 2.17 K called the lambda point, below which it is a superfluid.
- In the superfluid phase ^{4}He behaves as two liquids, one 'normal' and one frictionless (a Bose-Einstein condensate fraction).
- The condensate fraction should enter a zero-momentum state which should, in turn, reduce the average E_K.



- DINS quantified the condensate fraction in superfluid ^{4}He as 8.8 ± 0.3 %

Example: Lambda Transition in He

- Of course we don't need to just look at Bose fluids, we can also look at a Fermi fluid ^{3}He, or even mixes of Fermi-Bose systems ^{3}He-^{4}He… yay backscattering!

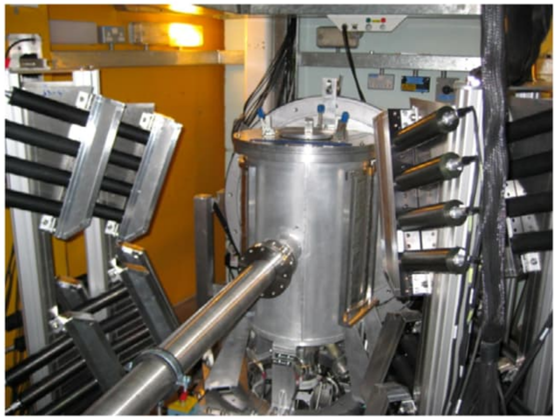


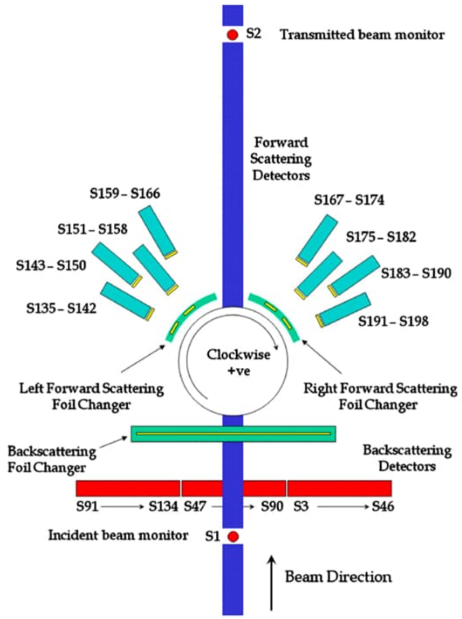
- ^{3}He is interesting because it is tremendously absorbing of thermal neutrons (not so much epithermal…), so there is little data *other than* DINS!
- It is an open question as to why DINS reproduces theoretical $n(p)$ lineshapes for ^{3}He or ^{4}He, but not ^{3}He-^{4}He mixes…

Instrumentation: VESUVIO

- Production of intense epithermal neutrons at spallation sources is only part of the epithermal story…
- We need to be able to fix E_i (direct geometry) or E_f (indirect geometry).
- We need to be able to detect high energy neutrons with suitable resolution.
- eV spectrometers (present and planned) are indirect geometry, for example the VESUVIO spectrometer at ISIS

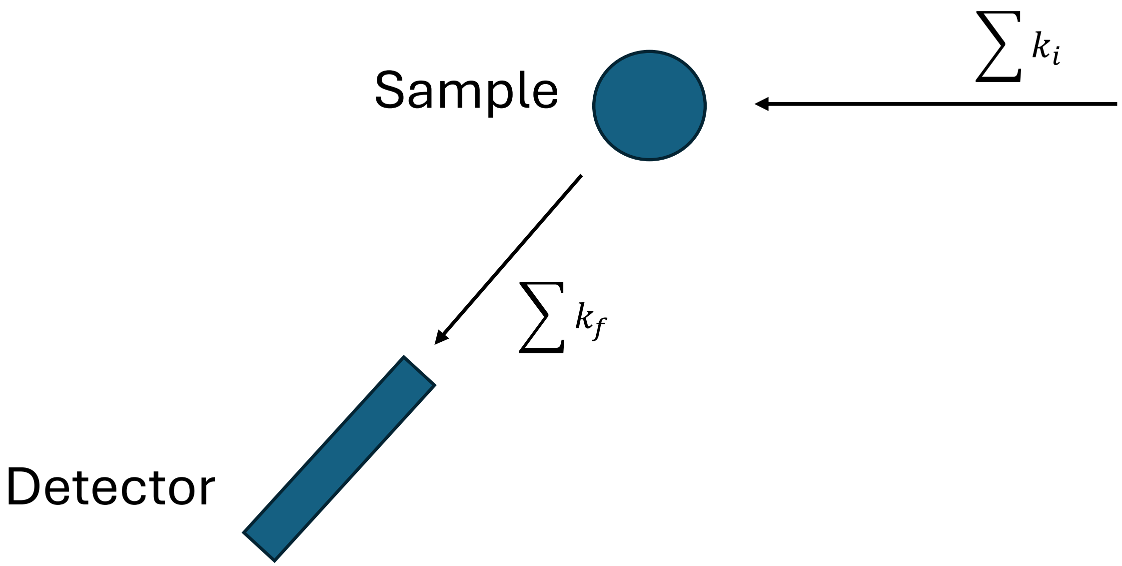
Looks like a normal spectrometer except for there being a lot of gold foil around the detectors…





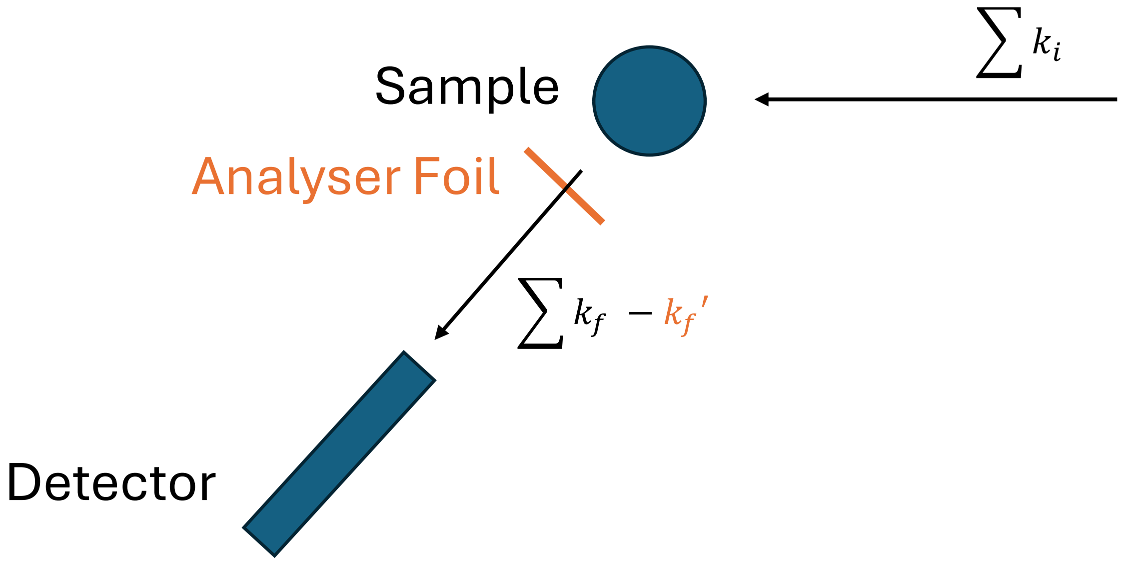
Instrumentation: E_f

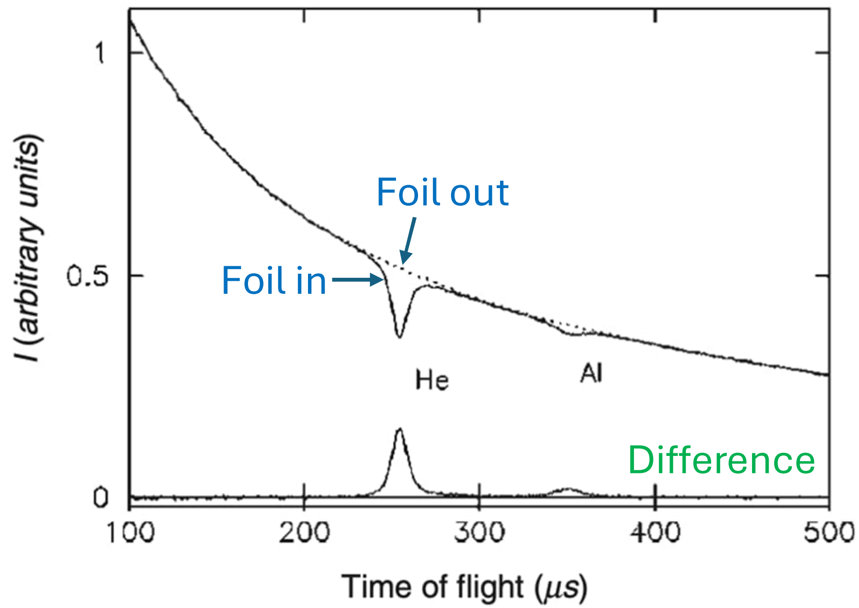
- Without an analyser, all scattered neutron energies are detected.



Instrumentation: E_f

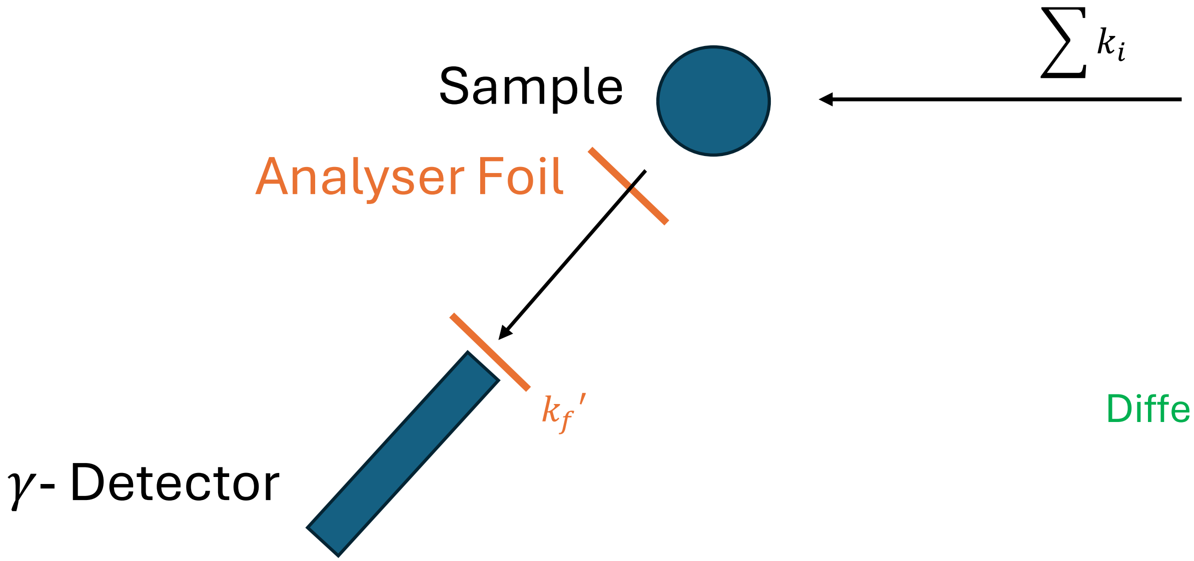
- A thin foil of Au uses a nuclear (n, γ)resonance at 4.9 eV to filter neutrons of this energy, the so called resonance filter method

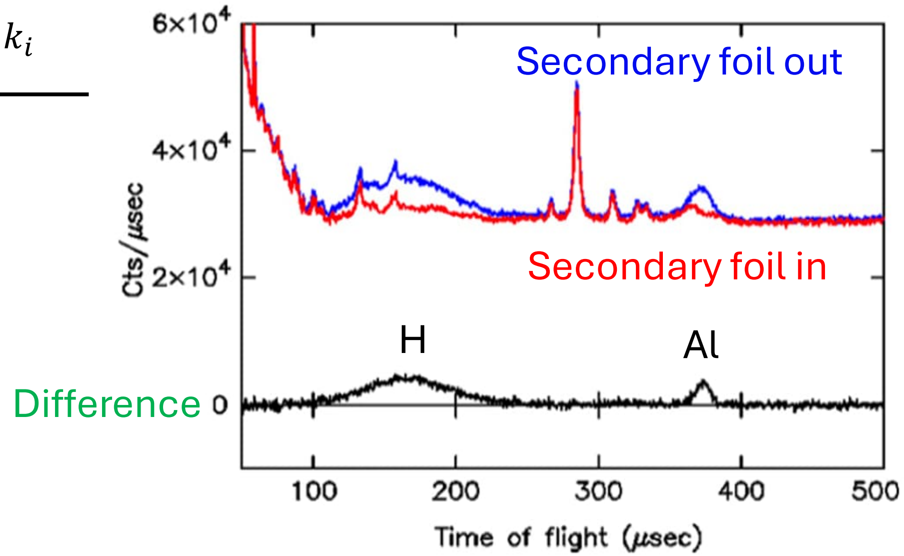




Instrumentation: E_f

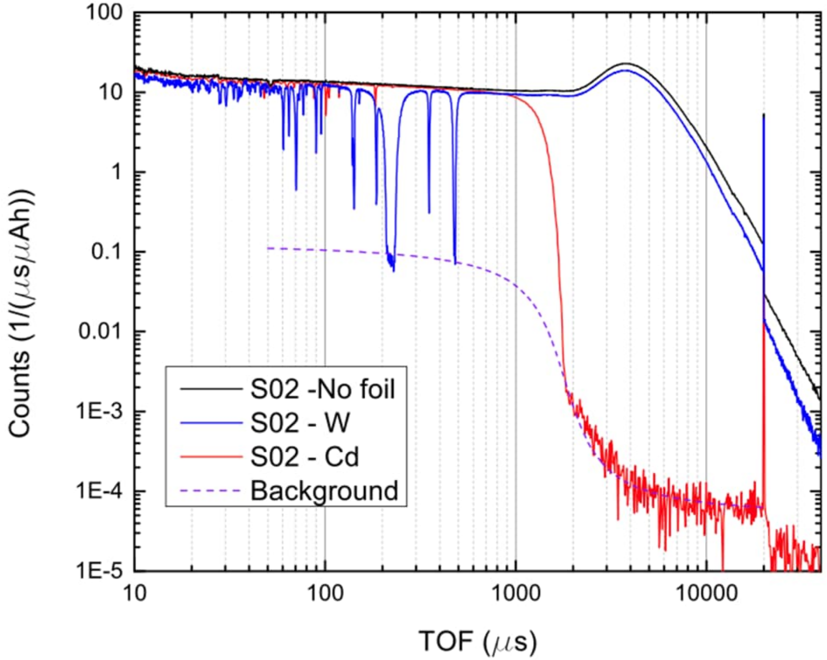
- A more modern implementation is to use γ-detectors instead of neutron detectors, the resonance detector technique. These detect the gamma cascade directly, and using a secondary foil still enables background removal.





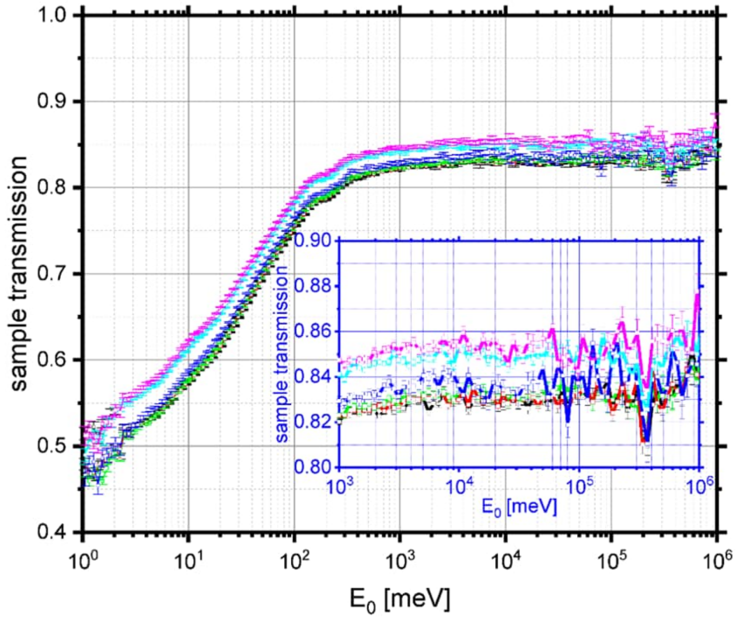
Neutron Transmission

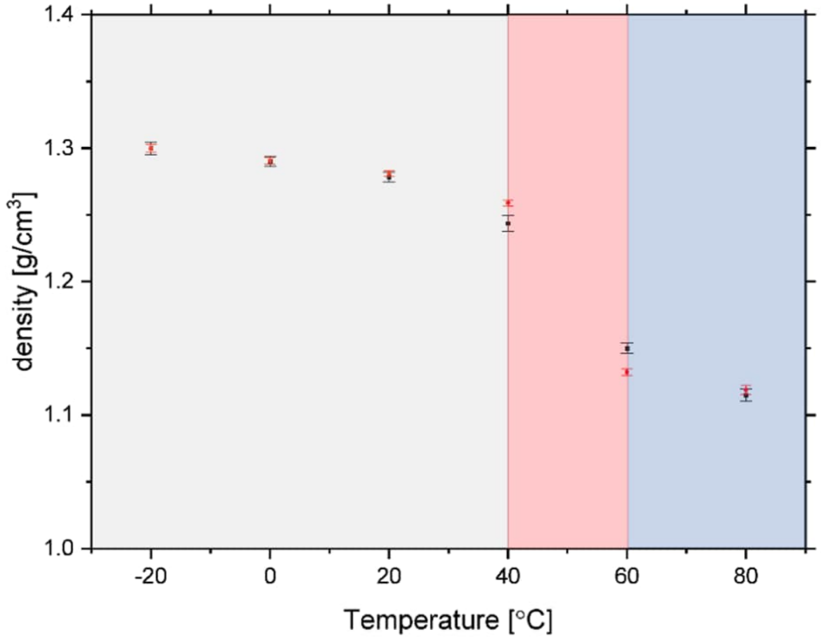
- The epithermal region is also of interest in neutron transmission.
- With the exception of γ-sources (resonances) neutron absorption drops off at high energies, so elements which absorb thermal neutrons such as Cd are not too problematic.



Neutron Transmission

- The epithermal region is also of interest in neutron transmission.
- The plateau at high energies is also a function of the number of atoms in the sample, so you can track things like changes in density across a glass transition.





Current Frontiers

- Epithermal scattering has moved towards more complex samples or problems in recent years.
    - Kinetic energies of M>4 amu in functional materials
    - Confined water or water in extreme environments (pressure in particular)
    - Low dimensional systems
- There are still open questions such as the shape of $n(p)$ for ^{4}He or ^{3}He, supercooled water and quantum delocalized protons.
- Can we take $n(p)$ and ‘invert’ it to extract V(r)?
    - Probably, assuming inversion symmetry and a few other approximations.

- The current epithermal instrument(s) were not designed for this, but to test things like y-scaling and extract light mass $\langle E_K \rangle$

Summary of Epithermal Scattering

- DINS/NCS measures $\langle E_K \rangle$ and $n(p)$ of single atoms.
- It is a direct probe of nuclear quantum effects and zero-point energy.
- It is a mass-selective technique which is unique to neutron scattering.
- Long runtimes and broadband measurements mean that complementary techniques can be done at the same time
  - Neutron diffraction
  - NRA/PGAA
  - Neutron transmission