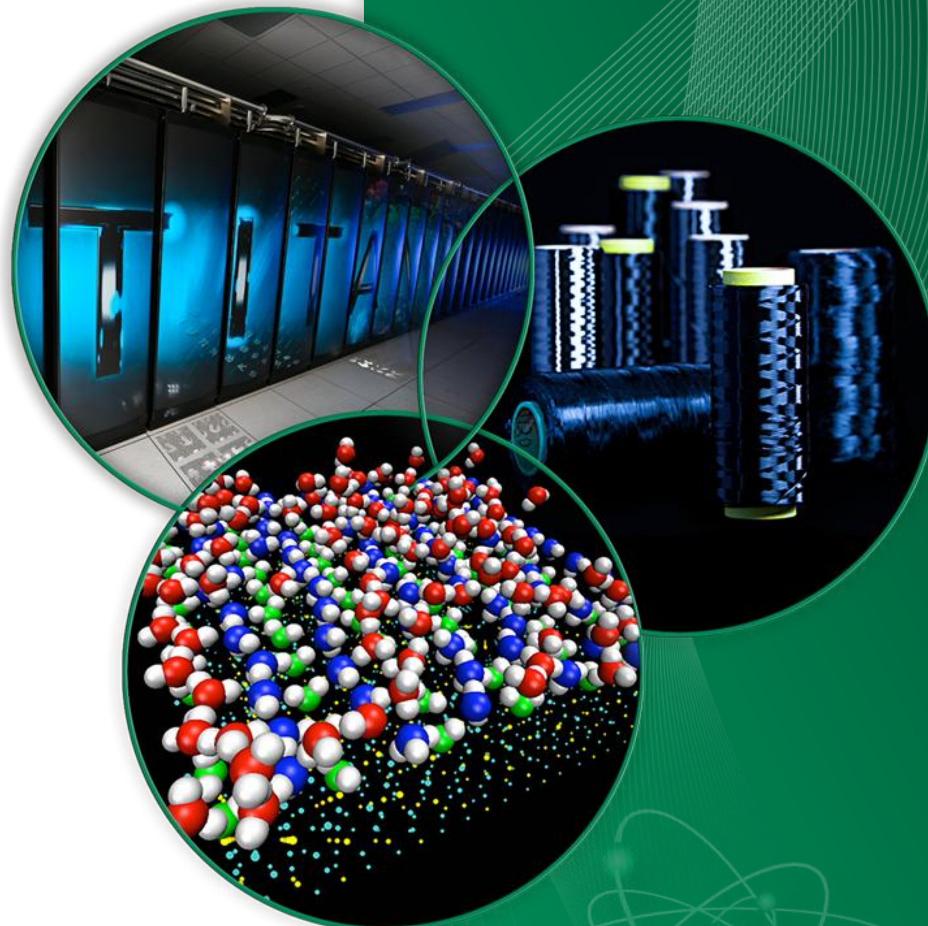
Quasielastic neutron scattering, neutron backscattering technique, BASIS and beyond



Part I: quasielastic neutron scattering

Eugene Mamontov

Neutron Sciences Directorate
Oak Ridge National Laboratory

Erice School “Neutron Science and Instrumentation”
July 4 – July 13, 2018

Inelastic neutron scattering in just one slide

Measure scattering intensity as a function of *Q* and ω

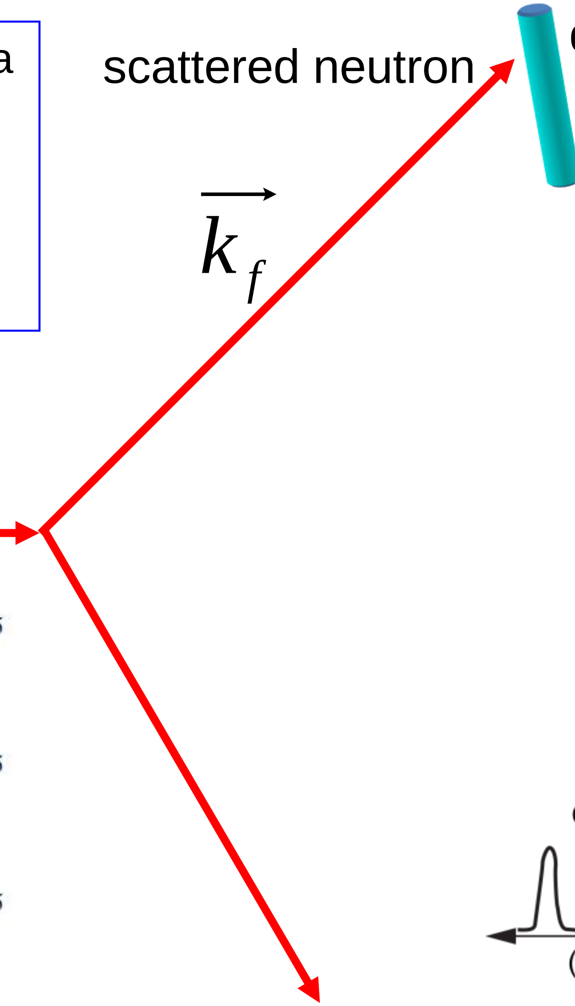
$\omega = 0$ –> elastic

$\omega \neq 0$ –> inelastic

ω near 0 –> quasielastic

$\vec{k}_i$

incident neutron

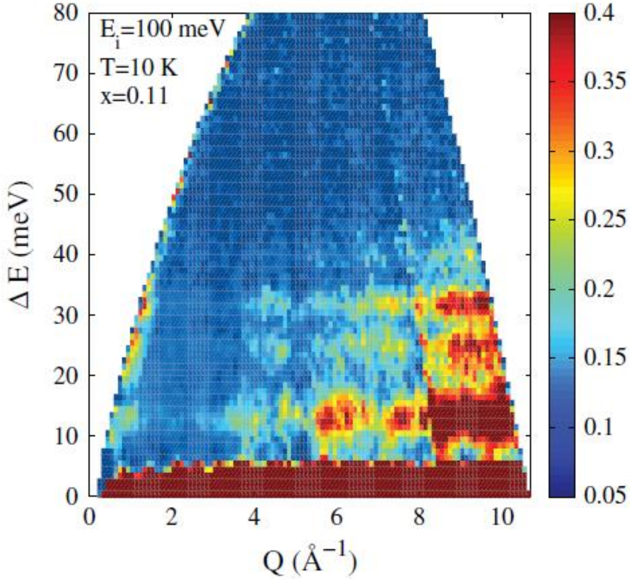


$$\text{Neutron momentum}: k = \frac{2\pi}{\lambda}$$

$$\text{Neutron energy}: E = \frac{(\hbar k)^2}{2m_n}$$

$$\text{Momentum transfer}: \vec{Q} = \vec{k}_i - \vec{k}_f$$

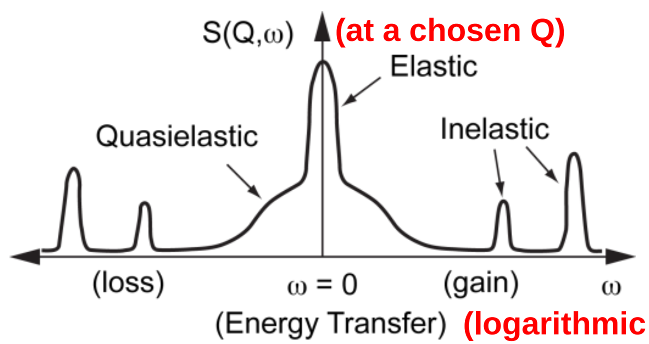
$$\text{Energy transfer}: \hbar\omega = E_i - E_f$$



PRL **101**, 157004 (2008) PHYSICAL REVIEW LETTERS week ending 10 OCTOBER 2008

Phonon Density of States of $LaFeAsO_{1-x}F_x$

A. D. Christianson,[1] M. D. Lumsden,[1] O. Delaire,[2] M. B. Stone,[1] D. L. Abernathy,[1] M. A. McGuire,[1] A. S. Sefat,[1] R. Jin,[1] B. C. Sales,[1] D. Mandrus,[1] E. D. Mun,[3] P. C. Canfield,[3] J. Y. Y. Lin,[2] M. Lucas,[2] M. Kresch,[2] J. B. Keith,[2] B. Fultz,[2] E. A. Goremychkin,[4,5] and R. J. McQueeney[3]



Quasielastic neutron scattering (QENS) is a special case of inelastic neutron scattering with small energy transfers, usually probing diffusion and relaxation phenomena

There are few QENS-capable spectrometers in the US…

Scattering technique is not the same as neutron instrumentation technique

Quasielastic neutron scattering concerns small energy transfers between neutrons and the sample

Backscattering is a special high energy-resolution technique often used for QENS…not the only one

In principle, QENS data can be collected on any inelastic spectrometer… even a triple-axis!

Backscattering spectrometers – specifically designed for QENS, disk chopper spectrometers – often can be used for QENS too

Disk Chopper Spectrometer (DCS), NIST Center for Neutron Research

High Flux Backscattering Spectrometer (HFBS), NIST Center for Neutron Research

Cold Neutron Chopper Spectrometer (CNCS), SNS, ORNL

Backscattering Spectrometer (BASIS), SNS, ORNL

...because of the stringent energy resolution requirements

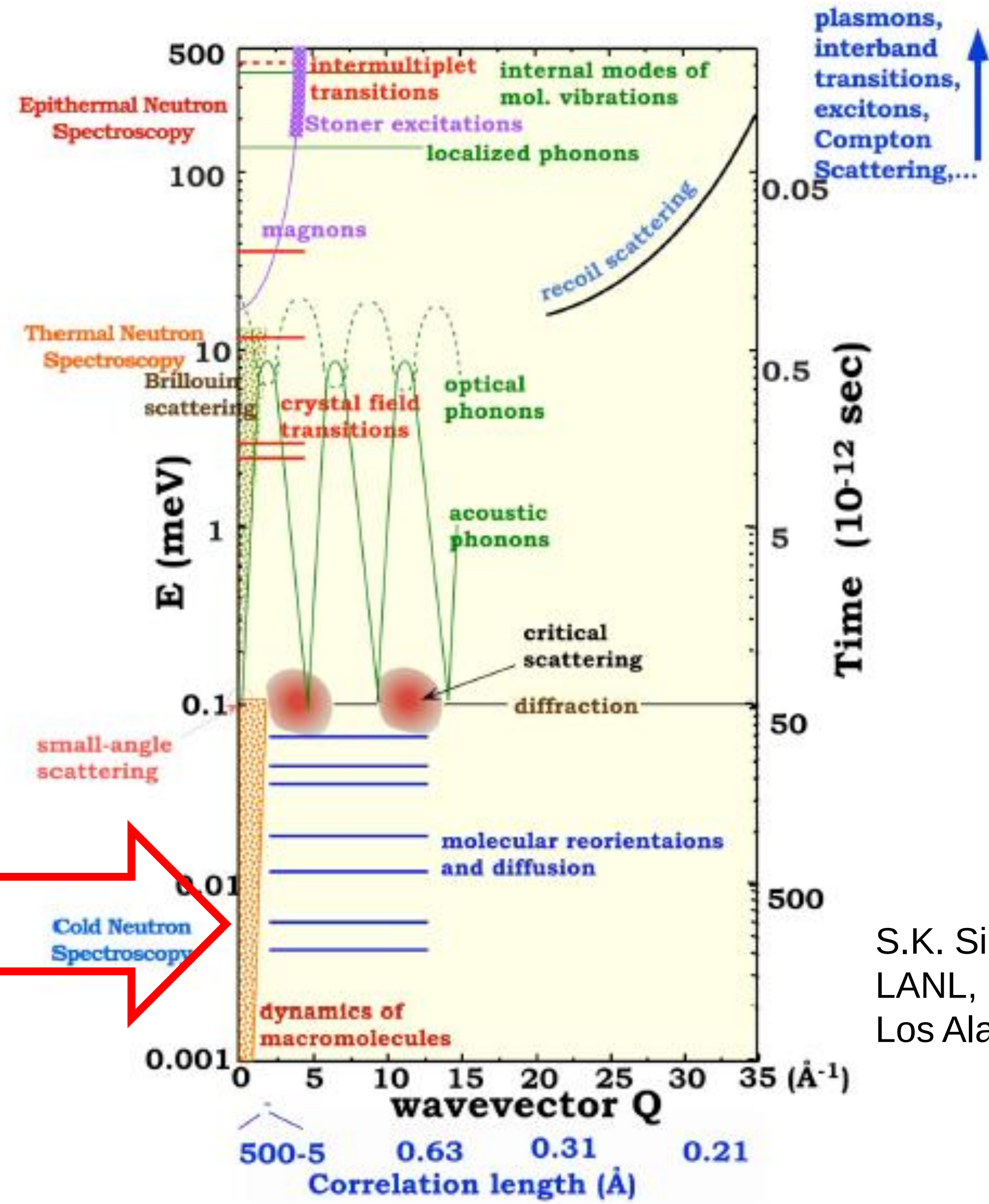
1 meV ~ 8 cm^{-1} ~ 1 ps
1 μeV ~ 0.008 cm^{-1} ~ 1 ns

sub-ps (vibrations)

$$\tau = \tau_0 \exp(E_a/T)$$

ns (diffusion jumps)

YOU ARE HERE

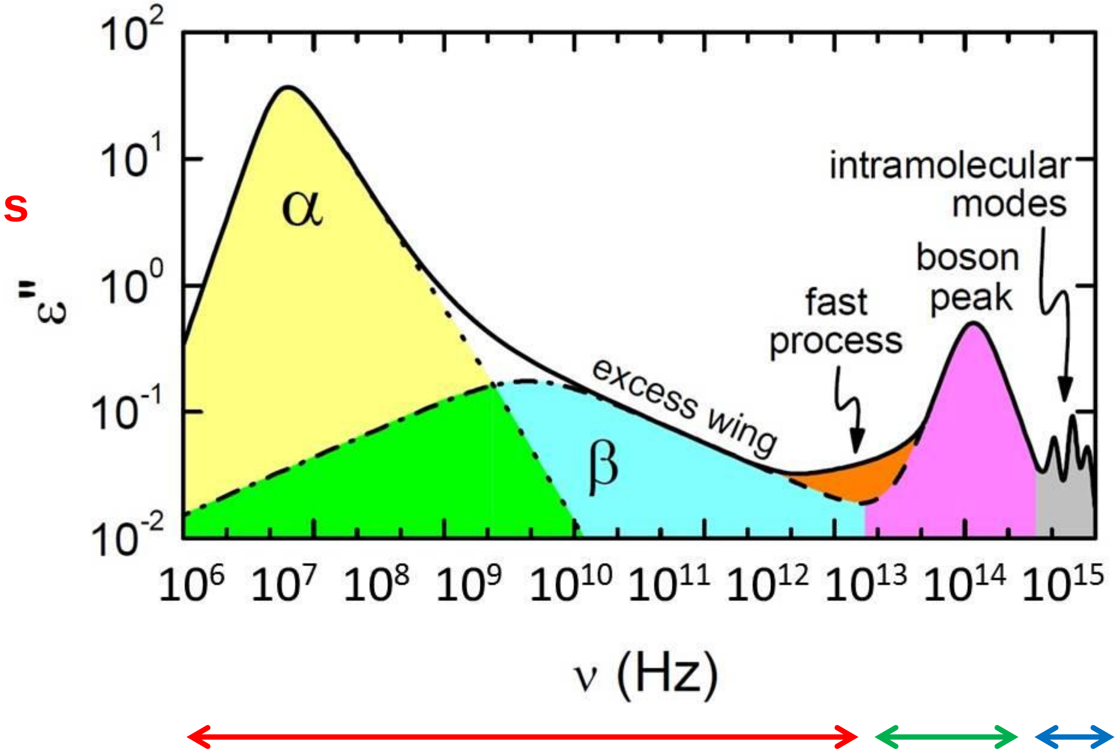


S.K. Sinha, 1985, LANL, LA-10227-C, Los Alamos, p.346

Hard vs. soft matter dynamics (a slide for spectroscopists)

Think of inelastic neutron scattering as a typical spectroscopic technique, but with a sensitivity to H and spatial information accessible through Q-resolution capabilities

1 meV ~ 8 cm^{-1} ~ 1 ps
1 μeV ~ 0.008 cm^{-1} ~ 1 ns



Relaxations: usually specific to soft matter (but could be, e.g., due to diffusion in solid)

Temperature dependence: strong

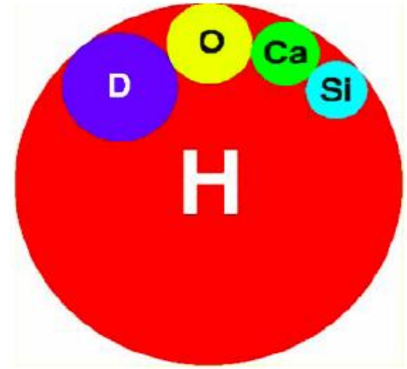
QENS needs both a high energy resolution and a wide dynamic range

Vibrations are always present

Mostly thermal population changes

Quasielastic scattering: simplest example to explain the signal Q-dependence - diffusion

$$S_{inc}(Q,E)=\int I_{inc}(Q,t)e^{i\frac{E}{\eta}t}dt=\int\int(G_{self}(r,t)e^{-iQr}dr)e^{i\frac{E}{\eta}t}dt$$



Total neutron scattering cross-section

Hydrogen dwarfs all the other elements due to its huge incoherent scattering cross-section:

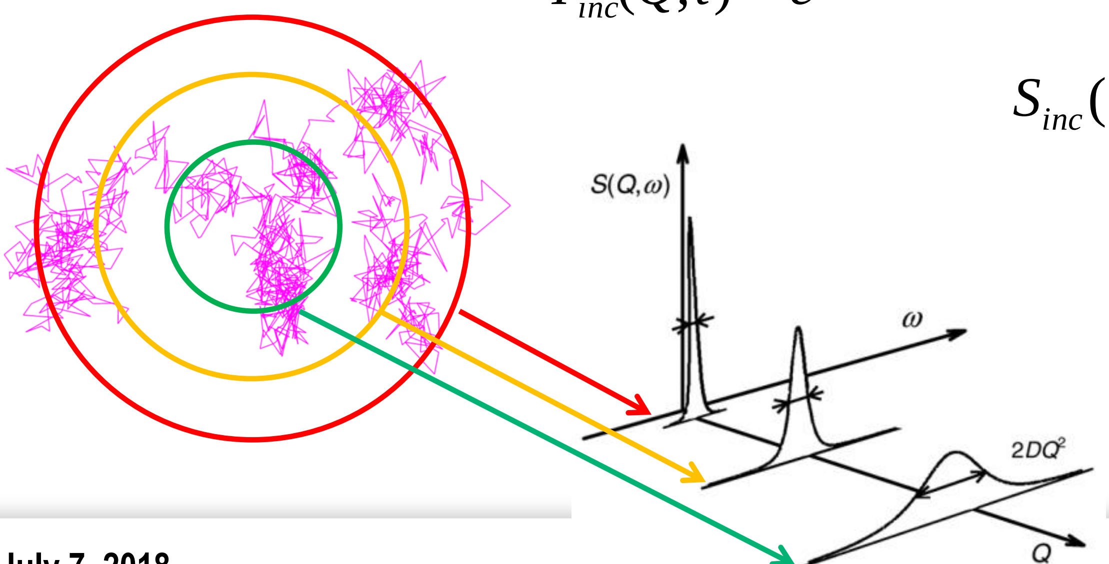
σ_{coh} = 1.76 barn, σ_{inc} = 80.26 barn

Simplest case: Fickian diffusion with a diffusion coefficient *D*

$$G_{self}(r,t)=\frac{e^{\left(-\frac{r^2}{4Dt}\right)}}{(4\pi Dt)^{3/2}}$$

$$I_{inc}(Q,t)=e^{-tDQ^2}$$

$$S_{inc}(Q,E)=\frac{1}{\pi}\frac{\eta DQ^2}{(\eta DQ^2)+E^2}$$



In an experiment, we'll see a Lorentzian QENS signal with Q-dependent HWHM

More realistic "jump" diffusion description (usually for "associated" fluids)

Atom/molecule occupies a position for a period of time τ, then quickly jumps to a new position

The HWHM, Γ(Q), is no longer ηDQ^2

$$\Gamma(Q) = \frac{\eta}{\tau_T}\left(1 - \frac{\sin(Qr)}{Qr}\right)$$

Well defined jump length r (where $D = \langle r^2 \rangle / 6\tau$) (powder-averaged)

Often describes hydrogen behavior in solids very well

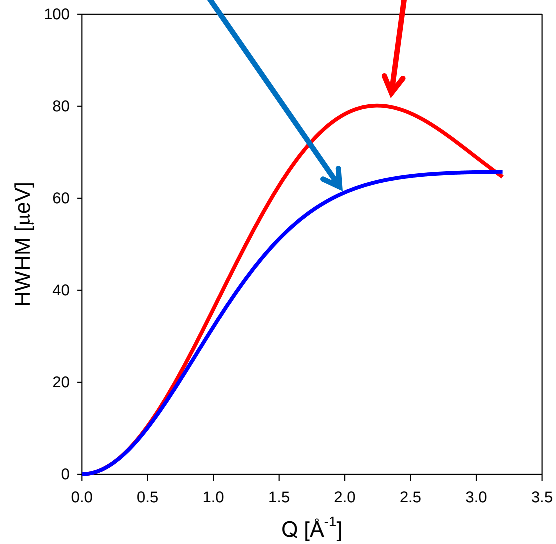
$$\Gamma(Q) = \frac{\eta}{\tau_T} \frac{\int_0^\infty \left(1 - \frac{\sin Qr}{Qr}\right) P(r)dr}{\int_0^\infty P(r)dr}$$

If there is a distribution of jump length…

Often describes liquids such as water

$\Gamma(Q \to 0) = \eta DQ^2$

$\Gamma(Q \to \infty) = \eta / \tau_T$



$$\Gamma(Q) = \frac{\eta}{\tau_T}\left[1 - \frac{1}{1 + DQ^2\tau_T}\right]$$

For exponential distribution

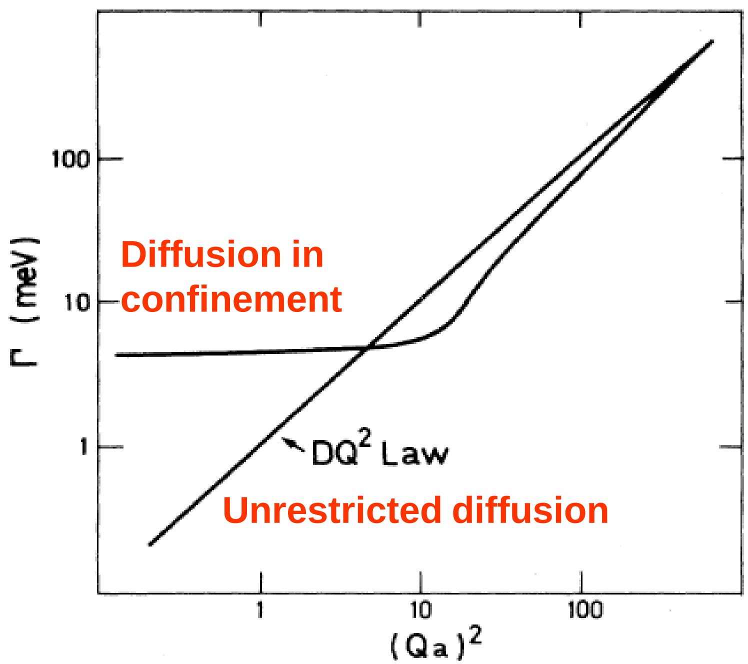
$$\Gamma(Q) = \frac{\eta}{\tau_T}\left[1 - \exp(-DQ^2\tau_T)\right]$$

For Gaussian distribution

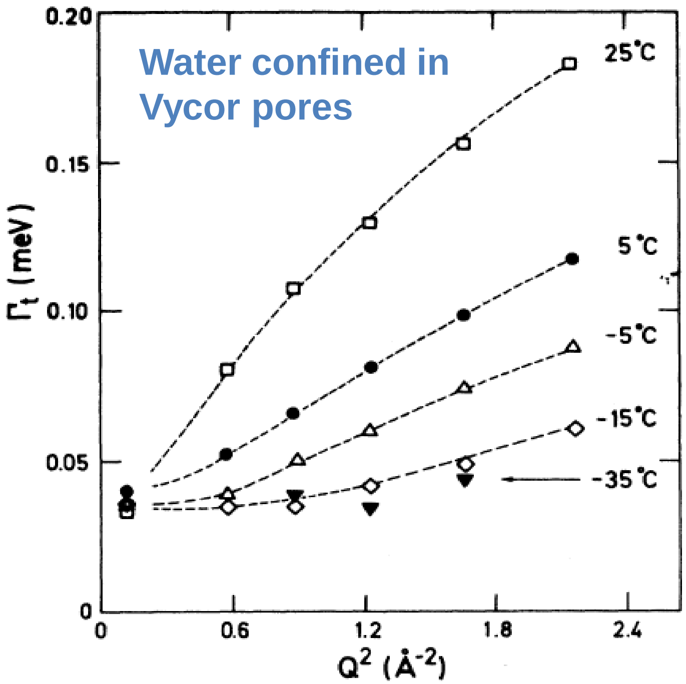
From the data fits, we get D, τ, $\langle r^2 \rangle$

What if the diffusion process is localized is space: The effect on the QENS signal broadening

- Examples: liquids in nano-cavities, hydrogen hopping back and forth between the interstitial sites



Volino and Dianoux, Mol. Phys. 41, 271 (1980)



Bellissent-Funel et al., Phys. Rev. E **51**, 4558 (1995)

Common feature: diffusing molecules cannot penetrate the borders of the pore. This effect is evident at low Q that corresponds to large distances: no more DQ^2 law!

For example, for diffusion in a sphere of radius a, HWHM = $4.33D/a^2$ for $0 < Qa < 3.3$

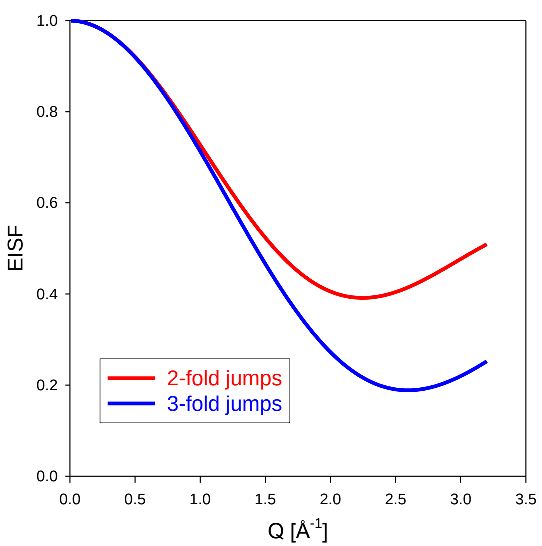
What if the diffusion process is localized is space: Some of the scattering signal becomes elastic

- Examples: liquids in nano-cavities, hydrogen hopping back and forth between the interstitial sites

Then there is an elastic scattering due to "spatial restriction"

Practical definition of EISF: Elastic Incoherent Structure Factor = Elastic/(Elastic+Quasielastic)

Physical meaning: EISF(Q) measured in an experiment with an energy resolution ΔE is a probability that, after a time $\sim(\eta/\Delta E)$, the moving particles still resides inside a box of $\sim 1/Q$ size

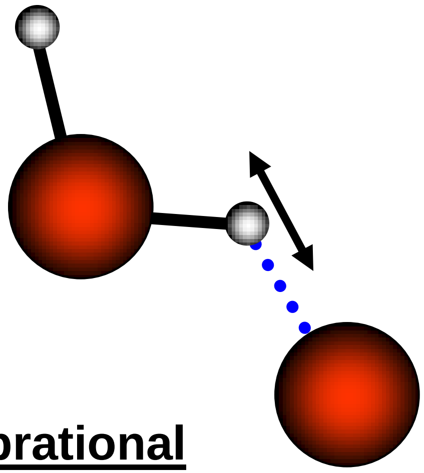


Measuring EISF(Q) is a great way to deduce the geometry of the corresponding restricted motion!

But EISF(Q) may depend on the energy resolution of the experiment – beware!

From the data fits, we get the characteristic size and (sometimes) geometry of the confinement

A textbook example: molecular motions in water

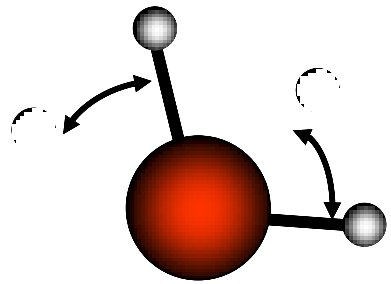


Vibrational

(harmonic oscillation)

$\langle u^2 \rangle^{1/2}$

Debye-Waller



Reorientational

(isotropic rotation)

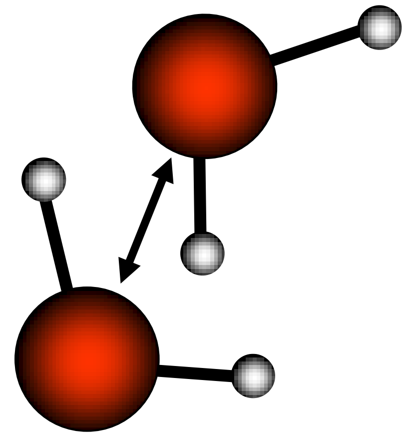
Localized motion: *EISF=j_0^2(Qa)*

τ_r

Rotational Correlation Time

r_g

Radius of Gyration



Jump Translational

Non-localized motion: no EISF

D_t

Translational Diffusion Constant

τ_t

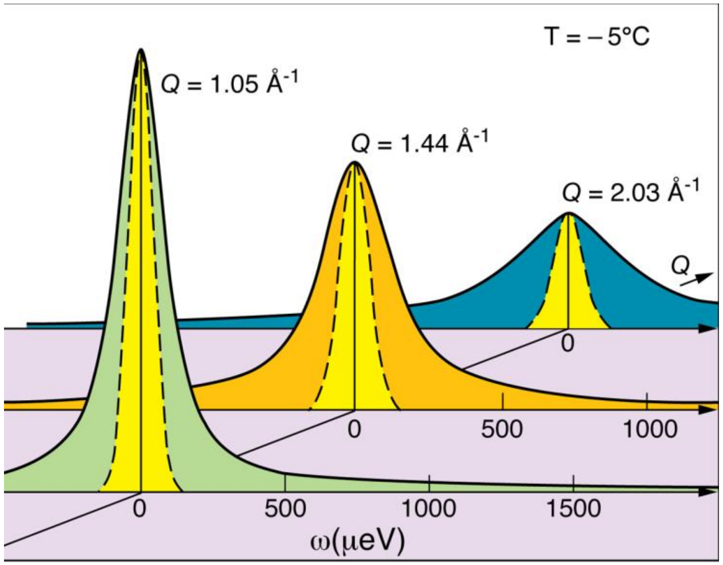
Residence Time

l

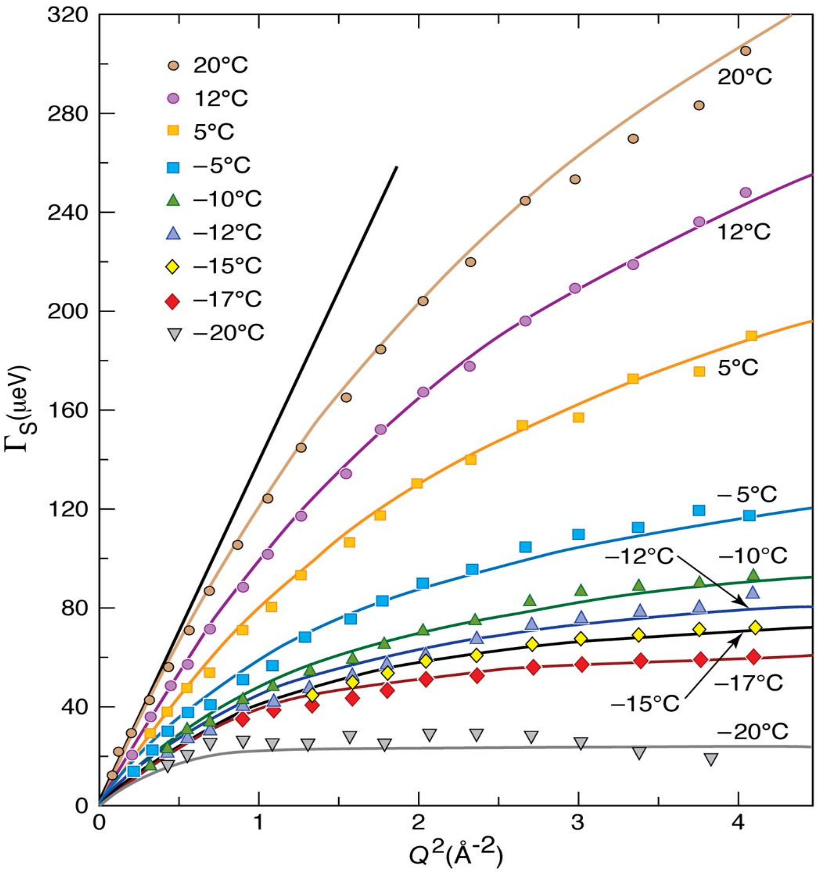
Mean Jump Distance

$$\boxed{S(Q,\omega) = e^{-\langle u^2 \rangle Q^2/3}\, T(Q,\omega) \otimes R(Q,\omega)}$$

Supercooled bulk water



Data from Teixeira et al. (1985)



- **Translational Motion**

$$T(Q,\omega) = \frac{1}{\pi}\ \frac{\Gamma(Q)}{\Gamma^2(Q)+\omega^2}$$

- **Jump Diffusion**

$$\Gamma(Q) = \frac{D_t Q^2}{1+D_t Q^2 \tau_0} \text{ and } D_t = \frac{L^2}{6\tau_0}$$

Good example of translational jump diffusion

Γ (HWHM) is Q-dependent

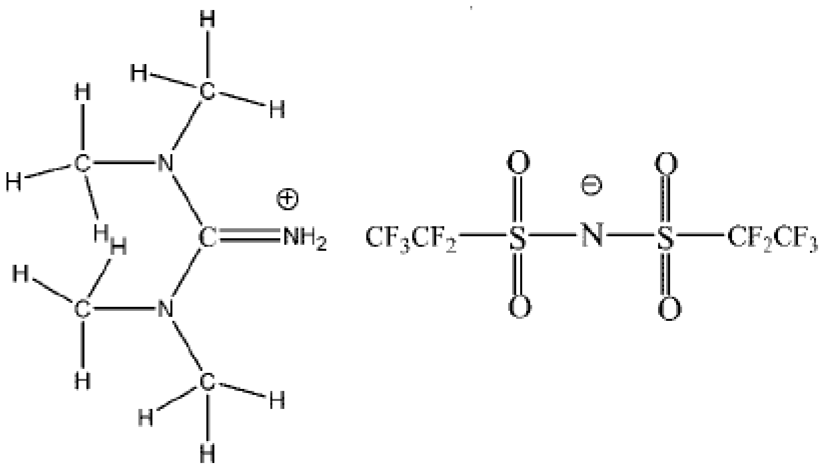
Low Q: $\Gamma = \hbar D Q^2$; High Q, $\Gamma = \hbar/\tau_O$

A practical example: a room-temperature ionic liquid

J. Phys. Chem. B **2009**, *113*, 159–169

Proton Dynamics in *N*,*N*,*N*′,*N*′-Tetramethylguanidinium Bis(perfluoroethylsulfonyl)imide Protic Ionic Liquid Probed by Quasielastic Neutron Scattering

Eugene Mamontov,*,† Huimin Luo,‡ and Sheng Dai§



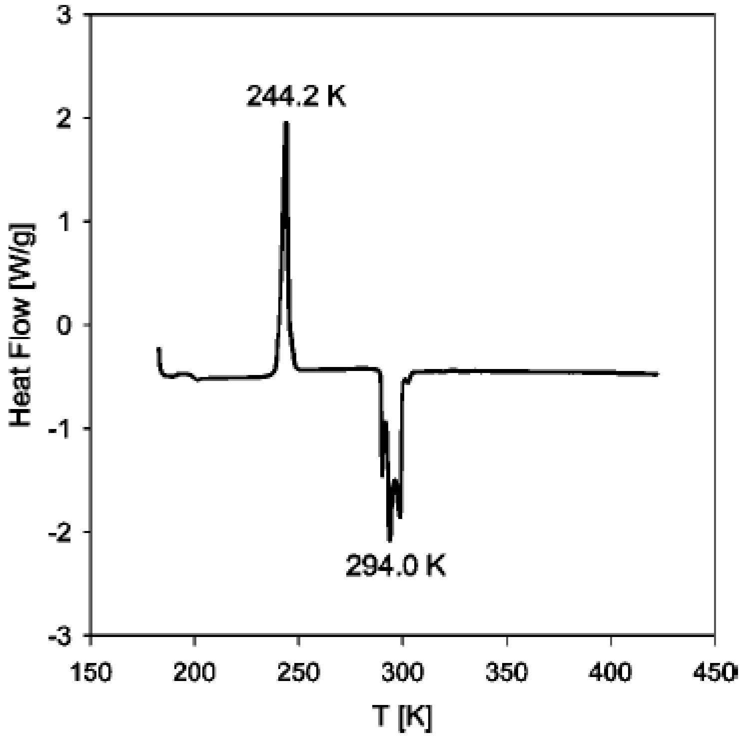
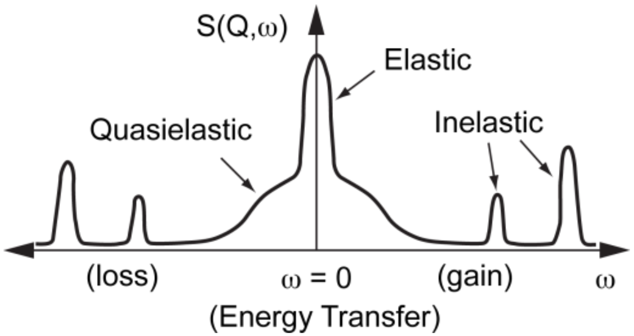
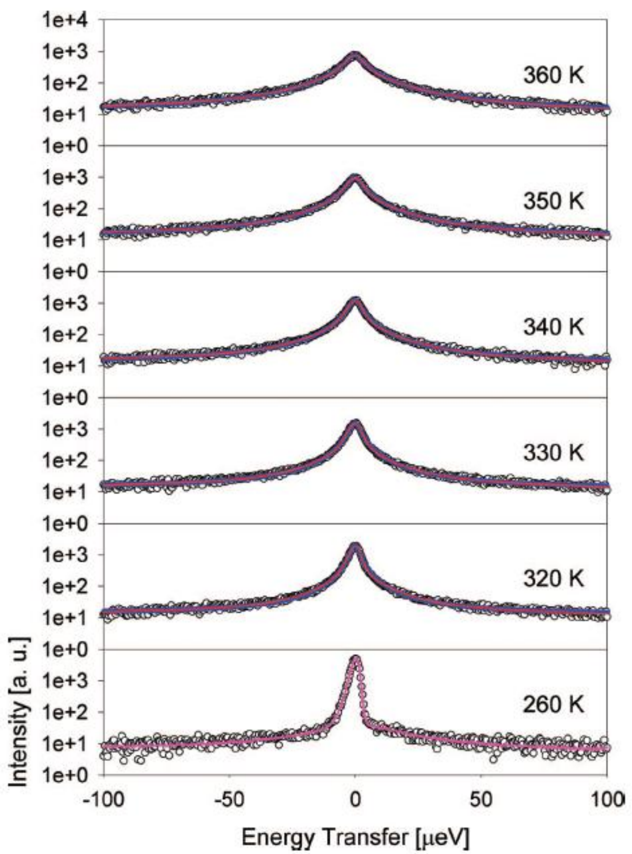
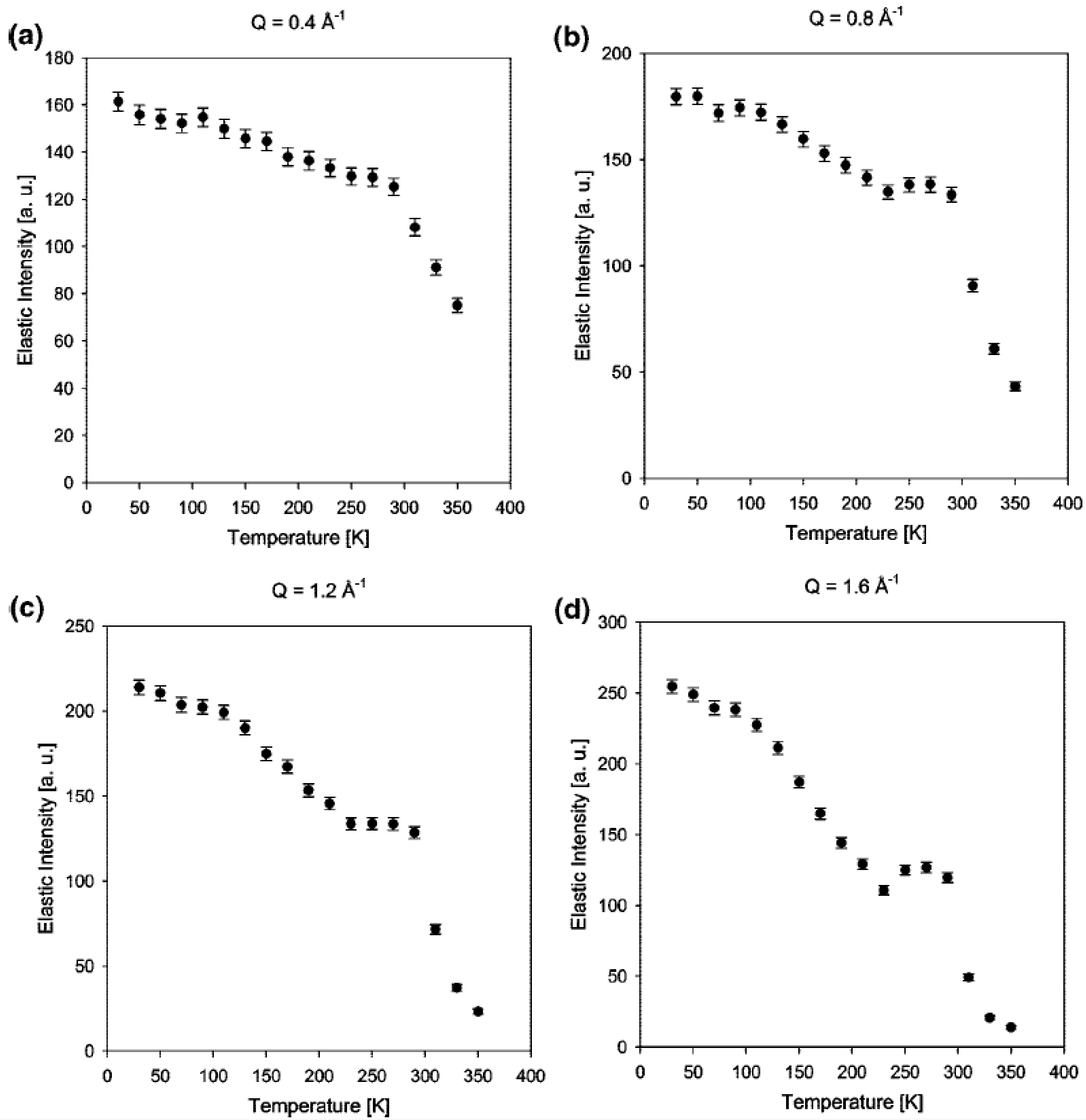


Figure 2. Differential scanning calorimetry measurement of $[H_2NC(dma)_2][BETI]$ taken on warming up at 2 K/min.

A diagnostic tool: elastic intensity scan

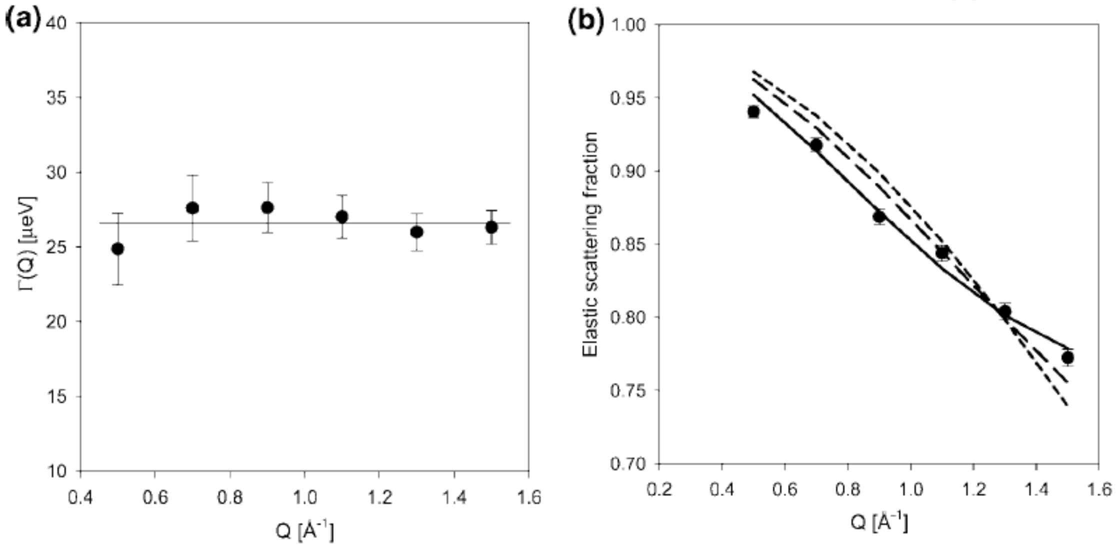






Methyl group rotation in the solid phase, or something else?

$$EISF_{apparent} = x_{immobile} + (1 - x_{immobile}) EISF$$



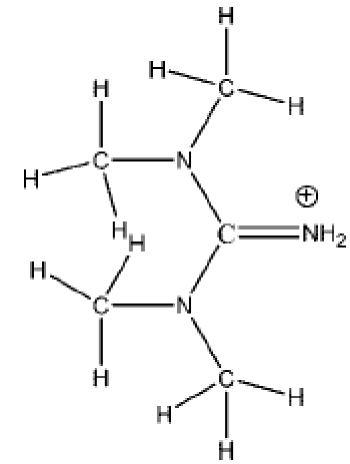


Figure 6. Parameters of the 260 K data fits obtained using eq 2 and 3. (a) Hwhm of the Lorentzian QENS broadening with a Q-independent fit. (b) Total measured elastic scattering fraction, $(x + (1 - x)\mathrm{EISF})$, where x is a parameter in eq 2, and its best fits obtained using EISF described by eq 4 while x was fixed to zero (short-dashed line), EISF described by eq 4 while x was allowed to vary (solid line), and EISF described by eq 5 while x was allowed to vary (long-dashed line).

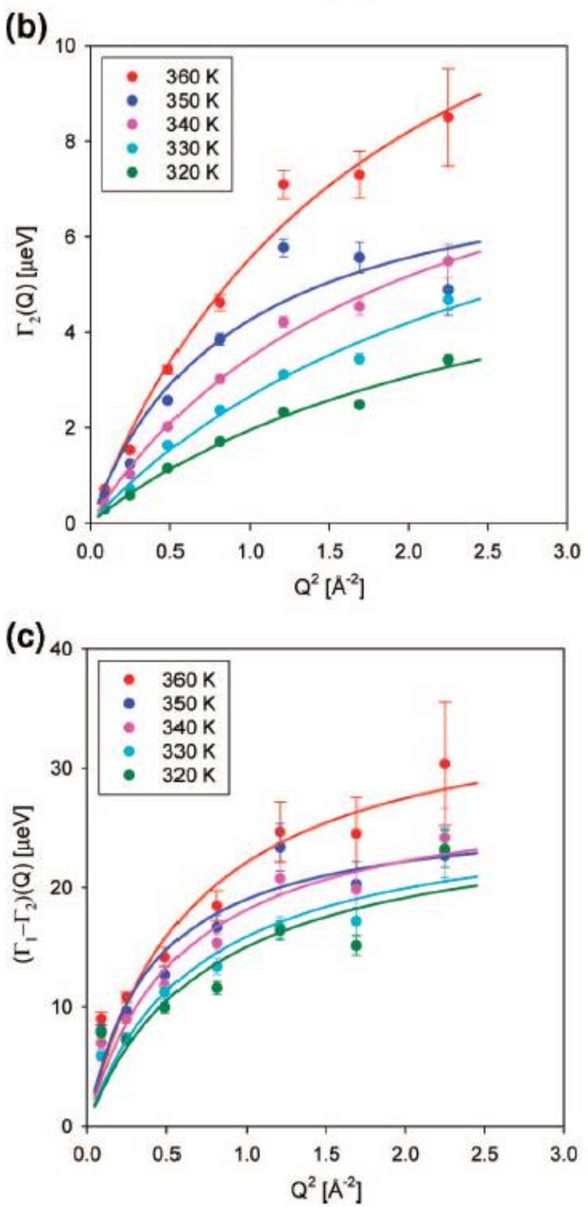
$$\mathrm{EISF}(Q) = (1 + 2j_0(Qr\sqrt{3}))/3$$

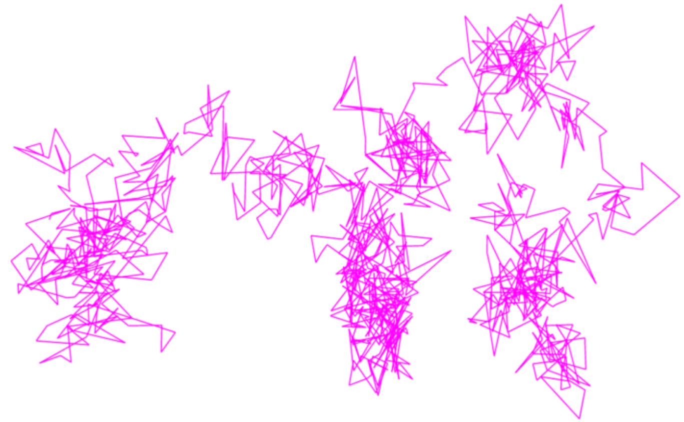
- Methyl group rotation model with a known value r = 1 Å does not work well, even when allowed for adjustable immobile fraction

$$\mathrm{EISF}(Q) = j_0^2(QR_1)$$

- A generic “diffusion on a sphere” model works well when allowed for adjustable immobile fraction, yielding r = 1.6 Å

Liquid phase: two-component fits and what they mean





At short times, a particle moves inside a transient cage made of the nearest neighbours…

…then eventually breaks the cage to perform a translational diffusion jump

$$S(E) = T_1(E) \otimes T_2(E)$$

$$S(E) = (1-p)\frac{1}{\pi}\frac{((\hbar/\tau_1)+(\hbar/\tau_2))}{E^2+((\hbar/\tau_1)+(\hbar/\tau_2))^2} +$$

This parameter, *p*, is actually EISF(Q) for those “caged” motions, yielding the cage size

$$p\frac{1}{\pi}\frac{(\hbar/\tau_2)}{E^2+(\hbar/\tau_2)^2}$$

Then we can summarize all the processes we have seen

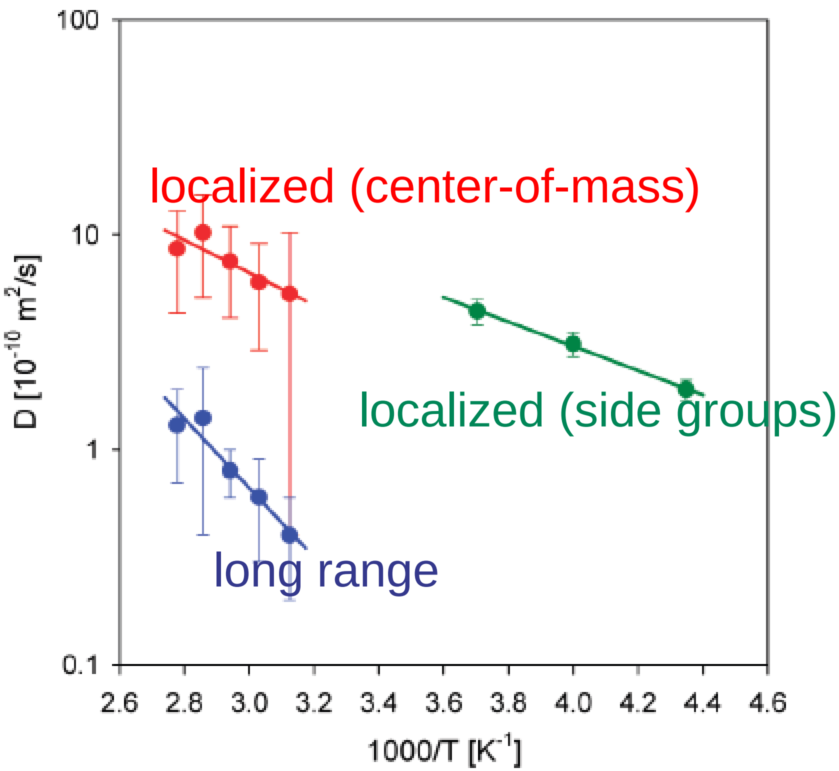
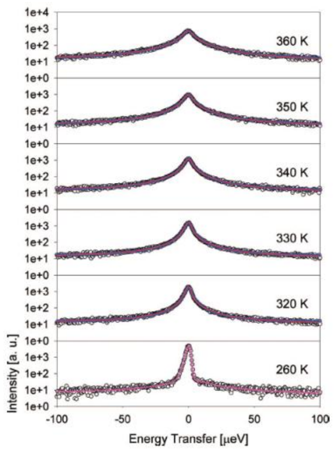
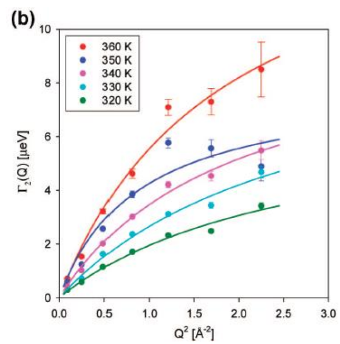


Figure 10. Temperature dependence of the diffusion coefficients describing a long-range translational diffusion process in the liquid phase (blue), a localized translational diffusion process in the liquid phase (red), and a localized process which is present in solid and liquid phases (green).

- At each temperature, collect the I(E) spectra at several Q values (simultaneously) and fit each spectrum with an appropriate model scattering function (a very important decision to make at this point)



- The so obtained HWHM(Q), EISF(Q), etc., are in turn fit with an appropriate model to obtain, e.g., the jump time (or similar parameters) at each temperature



- Make an Arrhenius plot of this parameter; analyze the temperature dependence

Quasielastic neutron scattering: Conclusion

- **QENS can elucidate microscopic diffusion dynamics through analysis of Q-dependence of signal broadening and the fraction of elastic vs. quasielastic scattering signal; this information is unobtainable by any technique other than MD**

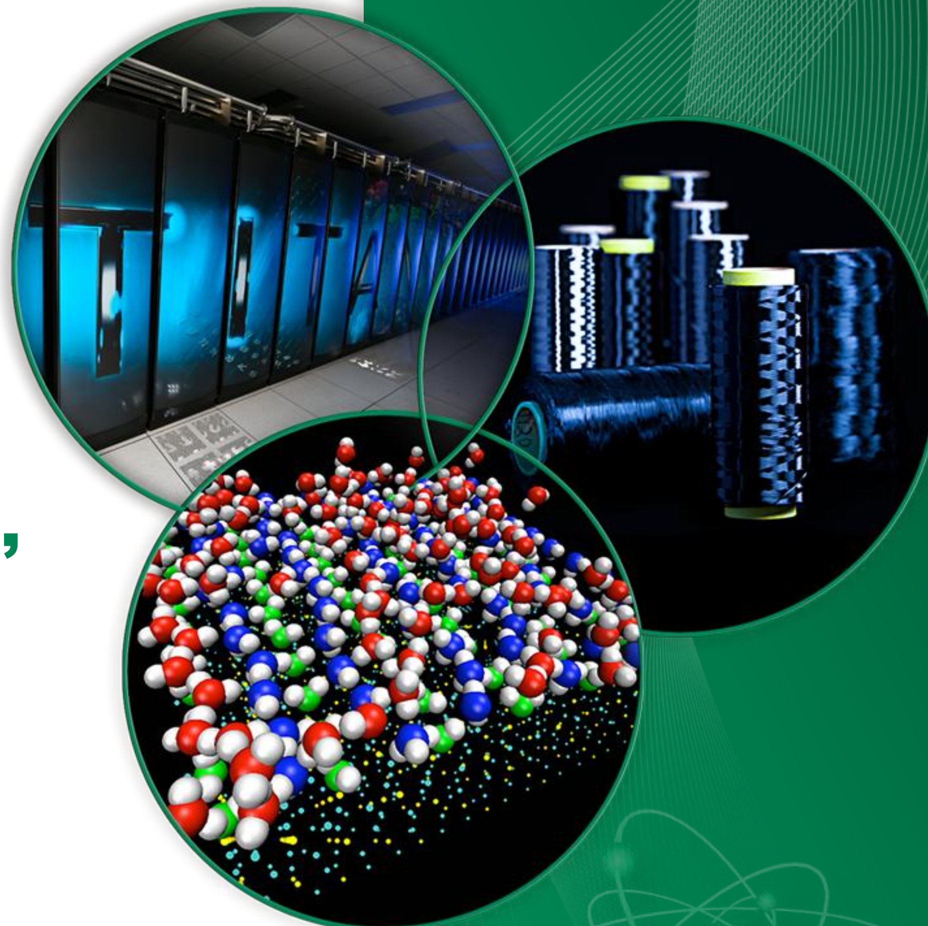
- **If your system exhibits diffusion/relaxation dynamics on pico- to nano-second time scale, QENS can likely help in you research efforts**

- **The power of QENS to elucidate microscopic diffusion dynamics is demonstrated best by a new generation spectrometer such as BASIS at SNS, ORNL because of its ability to probe several processes at once; see Part II for explanation of what it takes**

Acknowledgement

Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy

Quasielastic neutron scattering, neutron backscattering technique, BASIS and beyond



Part II: neutron backscattering technique, BASIS and beyond

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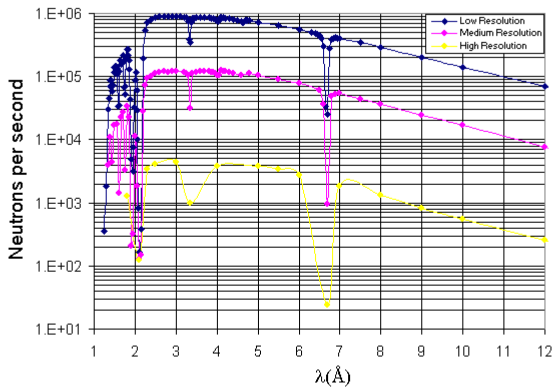
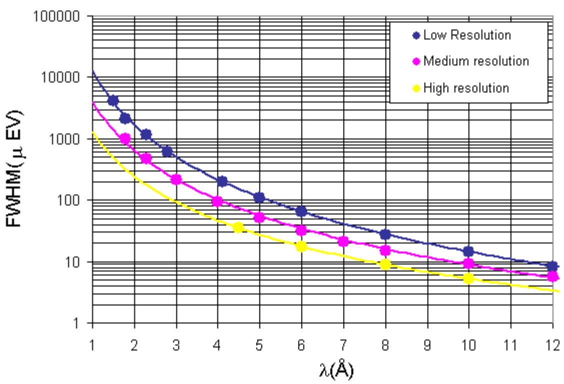
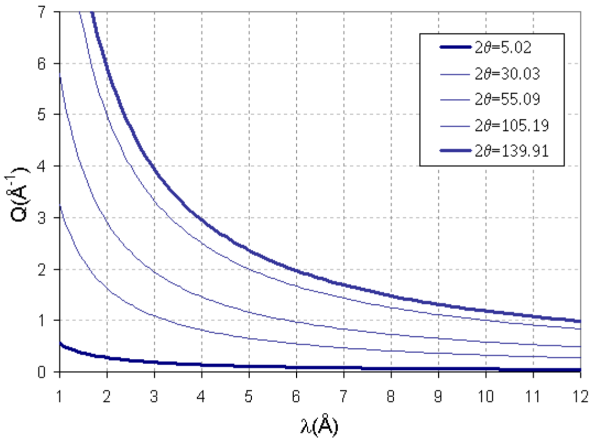
Quasielastic neutron scattering measurements do not absolutely require a backscattering spectrometer, but…

Some prominent quasielastic studies were even performed in the past on triple-axis spectrometers!

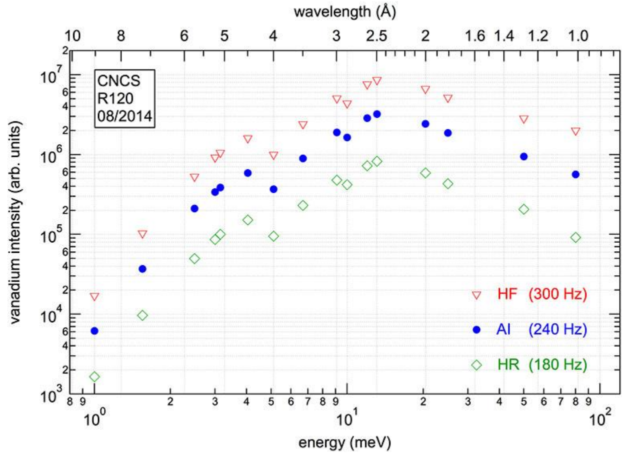
Direct-geometry TOF spectrometers are widely used for medium-resolution QENS measurements today, but they come with serious limitations

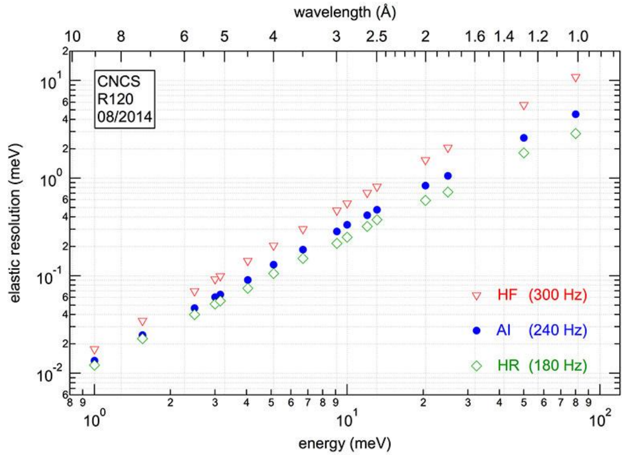






Very long incident wavelengths required for high resolution QENS come with intensity and Q-range problems





Disk Chopper Spectrometer, NCNR

Cold Neutron Chopper Spectrometer, SNS

Neutron backscattering: the limiting case of the [inverse geometry] crystal analyzer spectrometer for the best possible energy resolution

Whether a crystal analyzer spectrometer is TOF-based or on a steady source, the energy resolution of the analyzer crystals:

$$\delta E_f = 2E_f\left(\frac{\delta d}{d} + \cot\theta\delta\theta\right)$$

If a crystal analyzer spectrometer is TOF-based, then $E = E_i - E_f$, where E_f is fixed by analyzer Bragg reflection, E_i is determined from the TOF

The overall energy resolution then becomes:

$$\delta E = 2E\sqrt{\left(\frac{\delta d}{d} + \cot\theta\delta\theta\right)^2 + \left(\frac{\delta TOF}{TOF}\right)^2}$$

Long-wavelength neutrons

Small lattice constant spread

Backscattering conditions

Sharp neutron pulse, or long flight path

Building a TOF backscattering spectrometer: what's not negotiable?

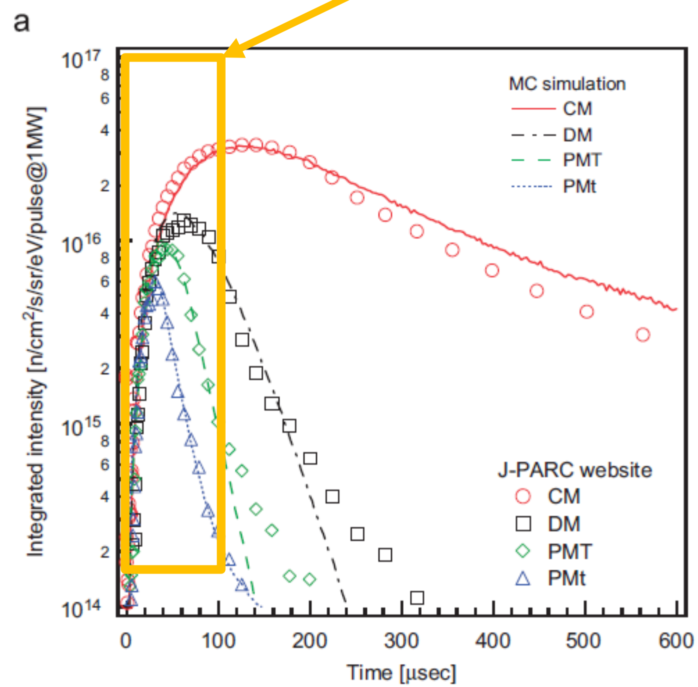
$$\delta E = 2E\sqrt{\left(\frac{\delta d}{d} + \cot\theta\,\delta\theta\right)^2 + \left(\frac{\delta TOF}{TOF}\right)^2}$$

Analyzer crystals with small (δd/d) in the backscattering position

Crystal plane	$\frac{\Delta\tau}{\tau}$	ΔE_{ext} (μeV)	λ (Å) for Θ = 90°
Si (111)	$1.86.10^{-5}$	0.077	6.2708
Si (311)	$0.51.10^{-5}$	0.077	3.2748
Ca F_2 (111)	$1.52.10^{-5}$	0.063	6.307
Ca F_2 (422)	$0.54.10^{-5}$	0.177	2.23
Ga As (400)	$0.75.10^{-5}$	0.153	2.8269
Ga As (200)	$0.157.10^{-5}$	0.008	5.6537
Graphite (002)	$12.10.10^{-5}$	0.44	6.70

https://www.ill.eu/other_sites/BS-review/index.htm

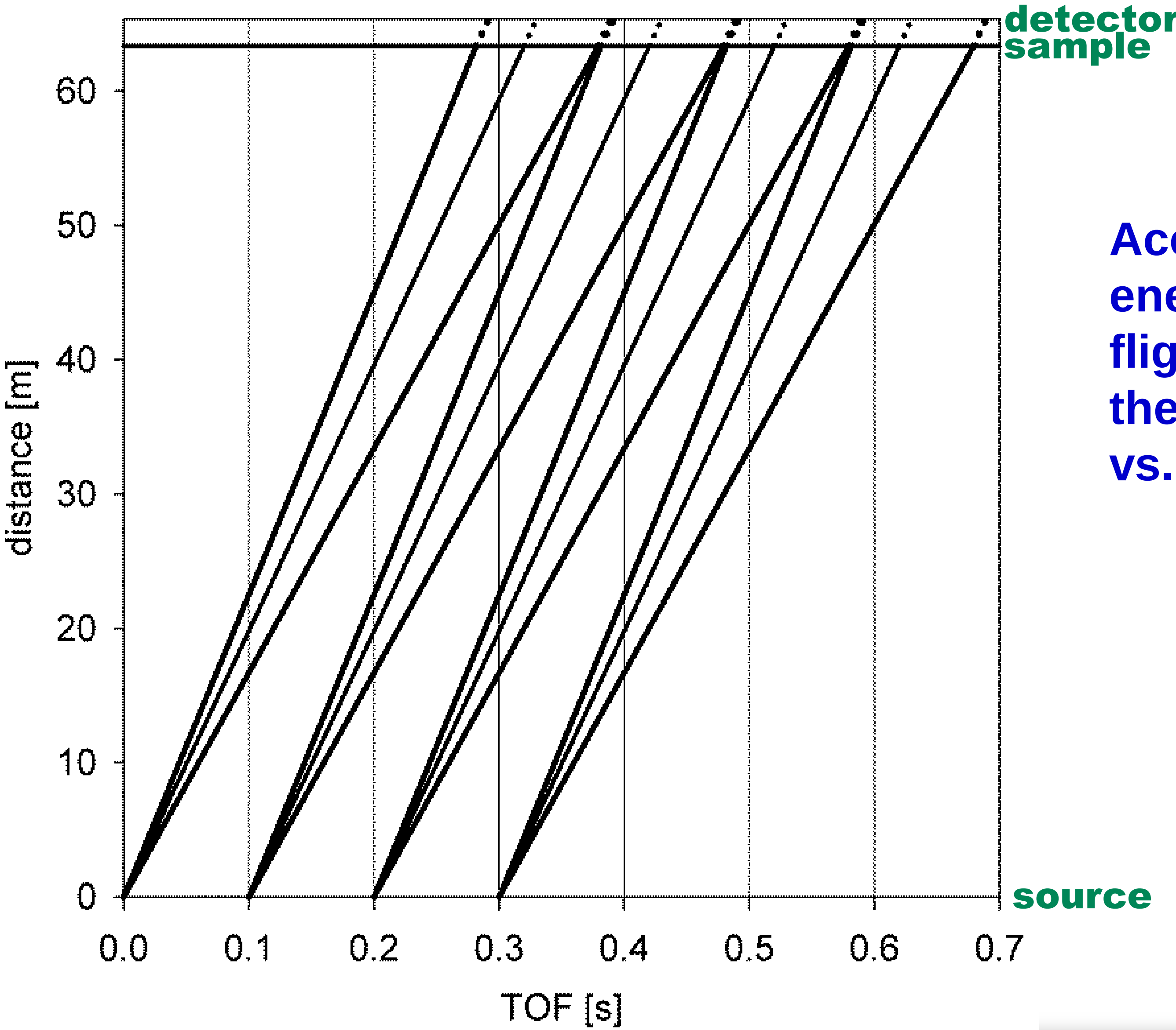
Relatively long flight path with a sharp pulse, either from a decoupled moderator, or a pulse-shaping chopper



The art of the possible: Because improving energy resolution kills counting statistics, why kill statistics for only a marginal resolution improvement? Hence one usually wants to match the resolution terms

Attainable energy resolution: Perfect crystals < Elastically bent perfect crystals < Mosaic crystals

Once the resolution has been worked out, what's negotiable?



Accessible range of energy transfers vs. flight path (needed for the desired resolution!) vs. source repetition rate

BASIS at SNS, ORNL, 11th year in the user program

REVIEW OF SCIENTIFIC INSTRUMENTS **82**, 085109 (2011)

A time-of-flight backscattering spectrometer at the Spallation Neutron Source, BASIS

E. Mamontov[a)] and K. W. Herwig
Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

(Received 1 June 2011; accepted 28 July 2011; published online 25 August 2011)

2008 7 Publications

2009 10 Publications

2010 16 Publications

2011 13 Publications

2012 30 Publications

2013 24 Publications

2014 23 Publications

2015 30 Publications

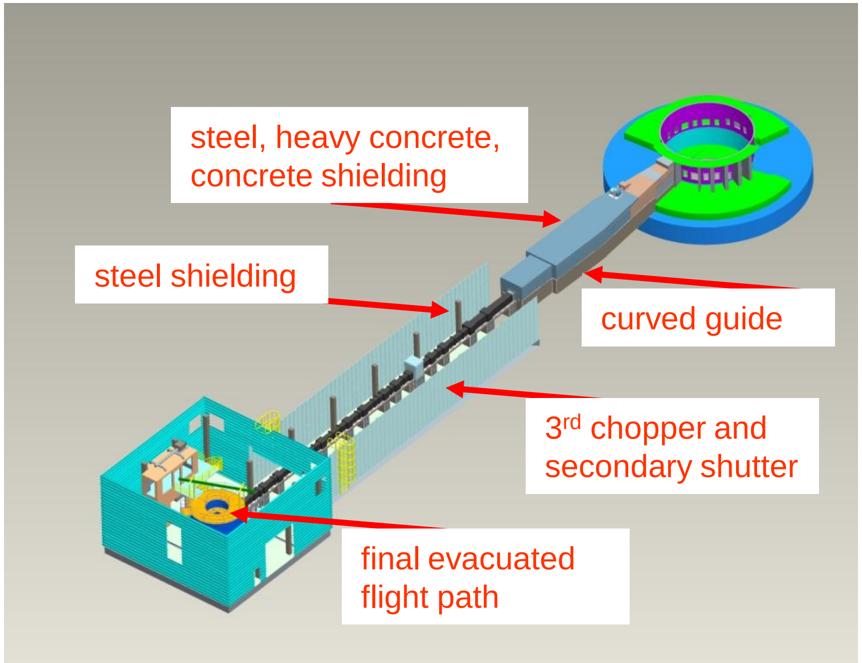
2016 37 Publications

2017 34 Publications

We must have done it about right!

TOF backscattering implementation, BASIS at SNS

- BAckscattering SIlicon Spectrometer is a high-energy resolution, wide-dynamic range inverted geometry neutron spectrometer built on BL2 and facing a decoupled supercritical hydrogen, centerline-poisoned moderator



- Incident Flight Path - 84 m moderator-sample position
  - Curved Guide: 10 cm wide x 12 cm tall, 1000 m radius of curvature, line-of-sight at 31 m
  - Straight Guide: 10 cm wide x 12 cm tall
  - Converging Funnel: last 7.7 m; exit 3.25 cm x 3.25 cm, stops 27.5 cm from sample
- Chopper System

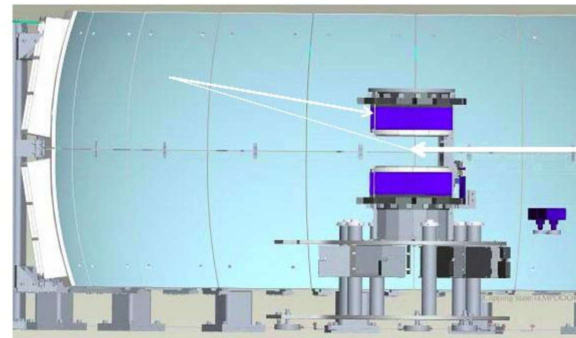
  - 3 bandwidth/frame overlap choppers at 7, 9.25 and 50 m

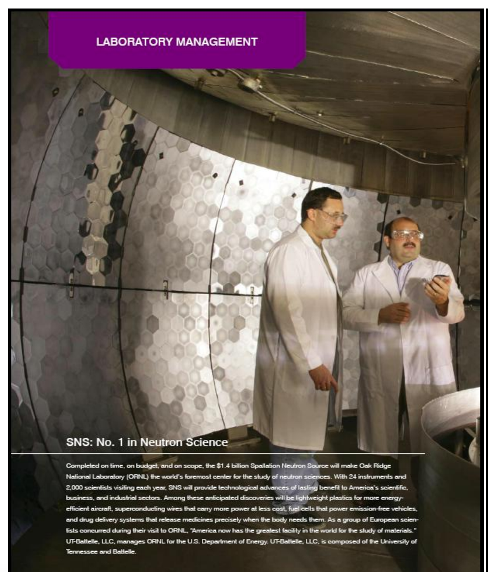
  - Operation at 60 (standard), 30, 20, 15, 12, or 10 Hz

  - Bandwidth (full choppers transmission) of about 0.5 Å at 60 Hz

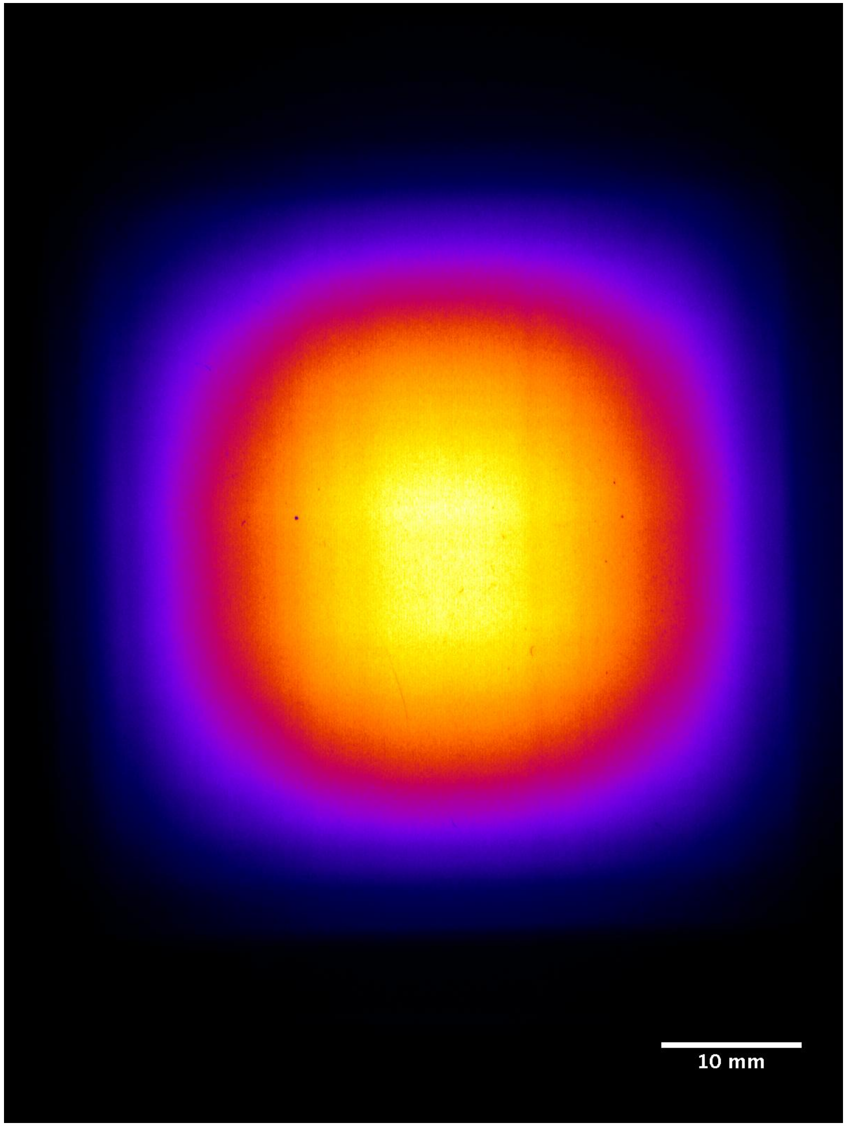
Evacuated Final Flight Path (aka tank)

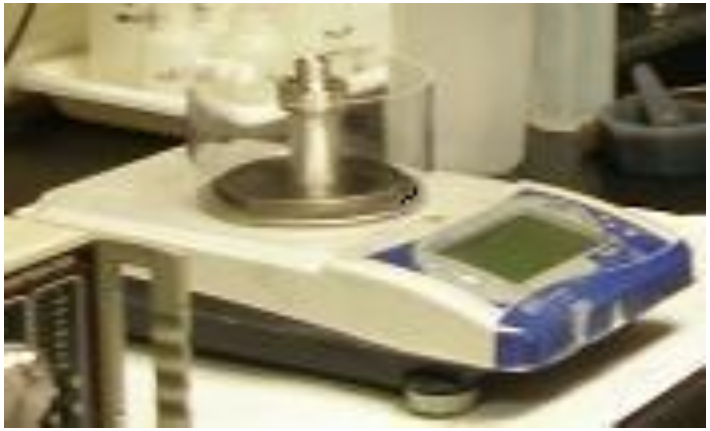
- Sample – nominal dimensions 3 x 3 cm^2
- Analyzer Crystals - Si (111): $\lambda_f = 6.267$ Å, $\delta d/d \sim 3.5 \times 10^{-4}$, 2.0 ster coverage (16 % of 4π).
- Radial Collimator – restricts analyzer view of the sample
- Final Evacuated Flight Path - 2.5 m sample - analyzer, ~ 2.23 m analyzer – detector
- Detector Choice – LPSD ^{3}He tubes





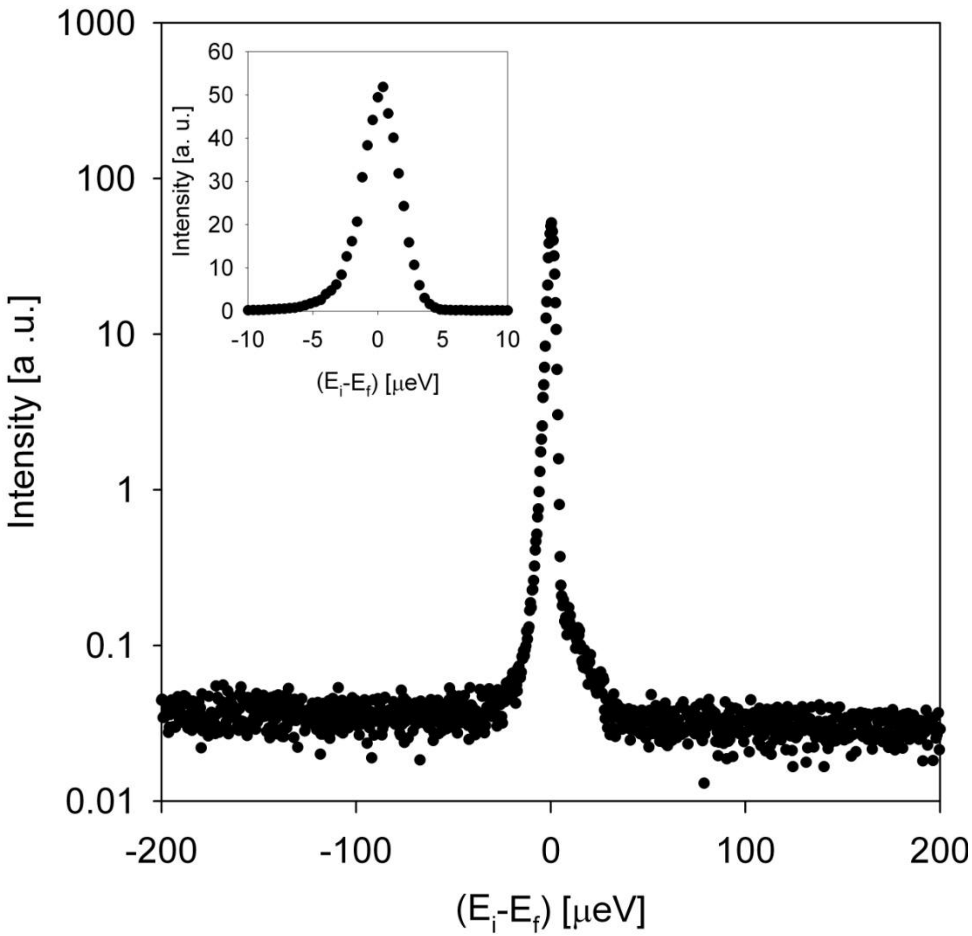
Beam at the sample position (6.3 Å)





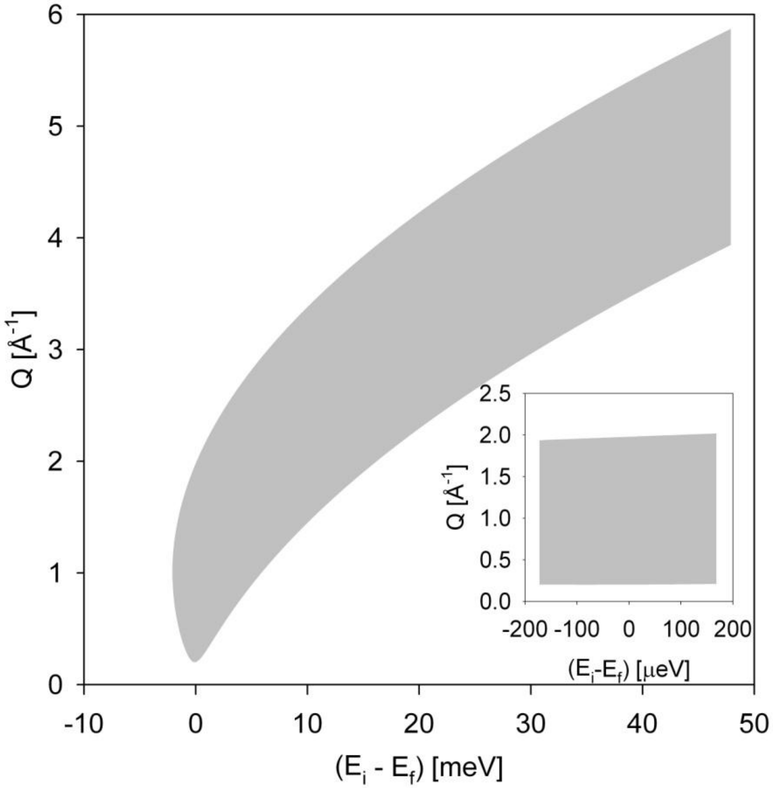
- Sample holders ID: 29.0 mm; cylindrical inserts can provide a gap as narrow as 0.05 mm

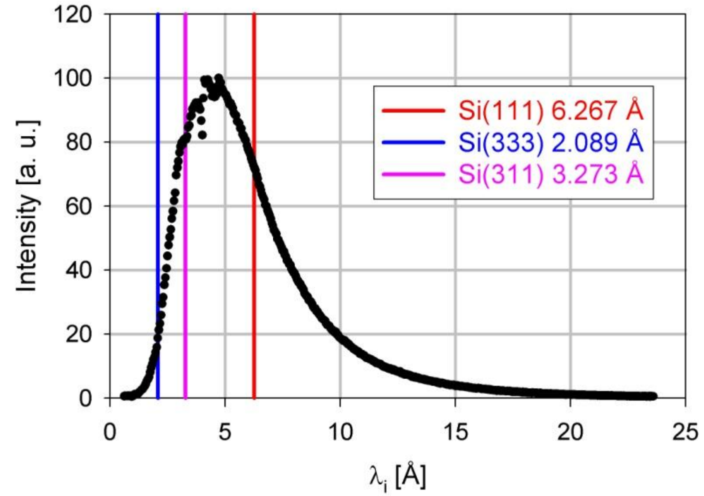
Annular vanadium, 94 % transmission

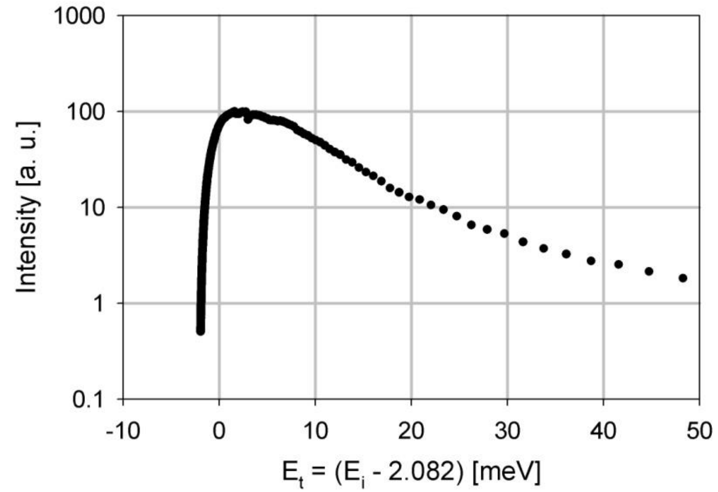


- Energy resolution (Q-averaged): 3.5 μeV (FWHM)
- Signal-to-background ratio (at the elastic line): better than 1000:1
- Dynamic range: variable (affects counting statistics, but <u>not</u> the energy resolution)

Incident spectrum and (Q,ω) coverage

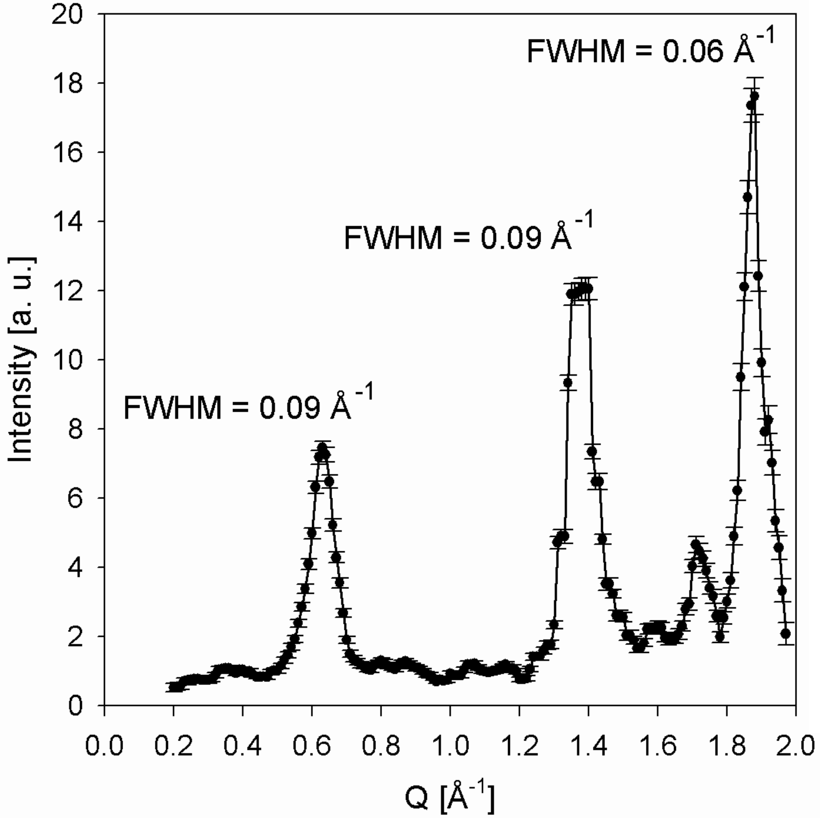


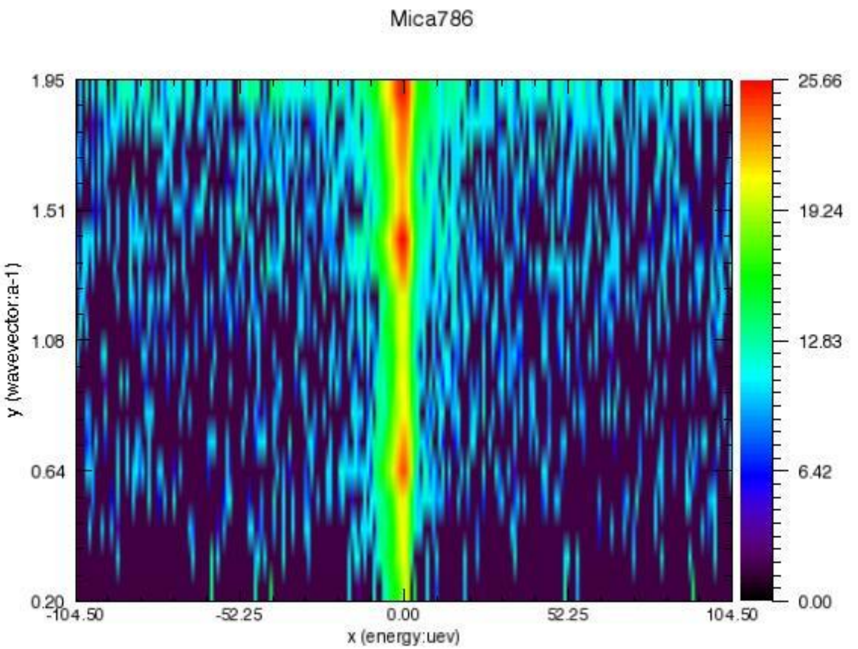




- **Incident band (full chopper opening): (60/ν)*[0.5 Å], where ν = 60, 30, 20, 15, 12, 10 Hz**
- **Inelastic resolution: δE ≈ 0.001*E_i at high energy transfers**
- 1 Hz signal (no frame overlap), 1/v efficiency corrections applied

Q-resolution at the elastic line





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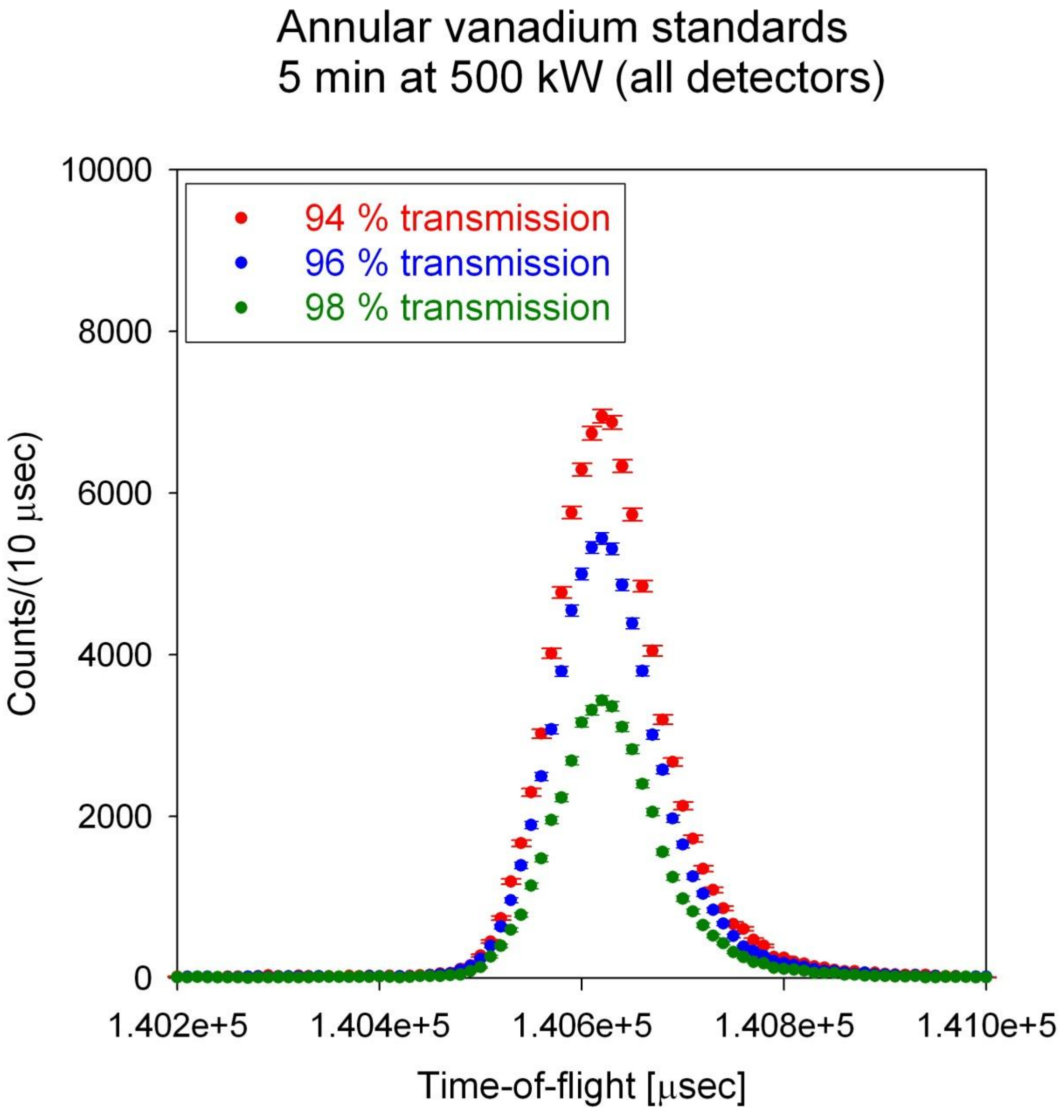
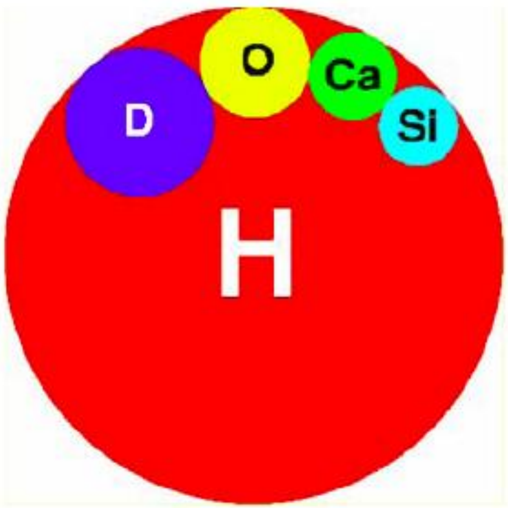
Data collection rates

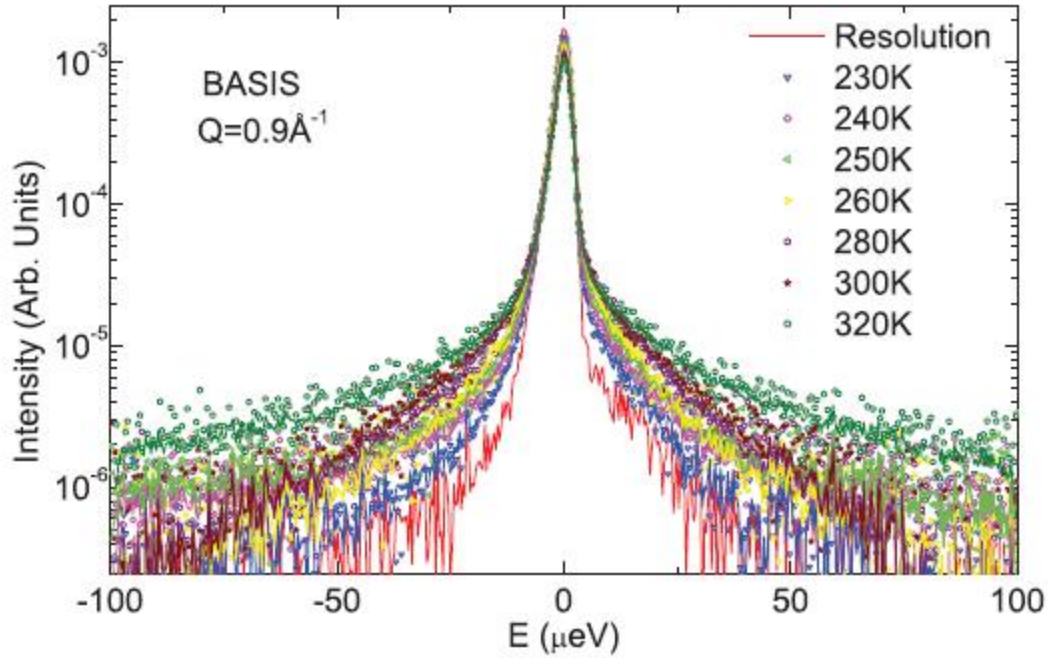


60 Hz, center of the chopper transmission band on the elastic line

Incident flux on the sample: about 1.3×10^7 n/cm^{2}s

We measure single-particle dynamics in H-bearing samples in 90 % of our experiments





PHYSICAL REVIEW E **84**, 031505 (2011)

Diffusion processes in water on oxide surfaces: Quasielastic neutron scattering study of hydration water in rutile nanopowder

Xiang-qiang Chu,[1] Georg Ehlers,[1] Eugene Mamontov,[1,*] Andrey Podlesnyak,[1] Wei Wang,[2] and David J. Wesolowski[3]

Total neutron scattering cross-section

Hydrogen dwarfs all the other elements due to its huge incoherent scattering cross-section:

σ_{coh} = 1.76 barn, σ_{inc} = 80.26 barn

Watch the following development in the near future

IN16B: commissioning of the two projects BATS and GaAs

https://www.ill.eu/news-press-events/news/scientific-news/in16b-commissioning-of-the-two-projects-bats-and-gaas/

MIRACLES Backscattering Spectrometer

MIRACLES will be the time-of-flight backscattering instrument of the European Spallation Source.

https://europeanspallationsource.se/instruments/miracles

Neutron backscattering technique, BASIS and beyond: Conclusion

- Backscattering spectrometers are built for high energy resolution; this is a must!

- The feature of BASIS most appreciated by users (besides the high count rate) is a combination of a high energy resolution and a broad accessible range of energy transfers; this is the only way to probe multiple dynamic processes at once

- Exciting developments are underway in Europe in elsewhere

Acknowledgement

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Question 1 (easy): Would a liquid sample give rise to any elastic scattering, irrespective of the temperature? How about supercooled liquids?

Question 2 (medium): The resolution function is measured best when the sample is cooled down to cryogenic temperatures. Why? Can you think of systems where this approach fails (even at helium temperatures)? Hint: can you think of systems where 100 K is not low enough for the resolution measurement – there are many of them?

Question 3 (difficult): A typical sample-analyzer-detector arrangement is usually perfectly cylindrical with respect to the vertical axis passing through the sample center. Yet the shape of the resolution functions is often Q-dependent (that is, dependent on the scattering angle in the horizontal plane). Why? When is this effect negligible, and when not? Hint: consider the incident beam propagation.