IXS Workshop APS, 2016

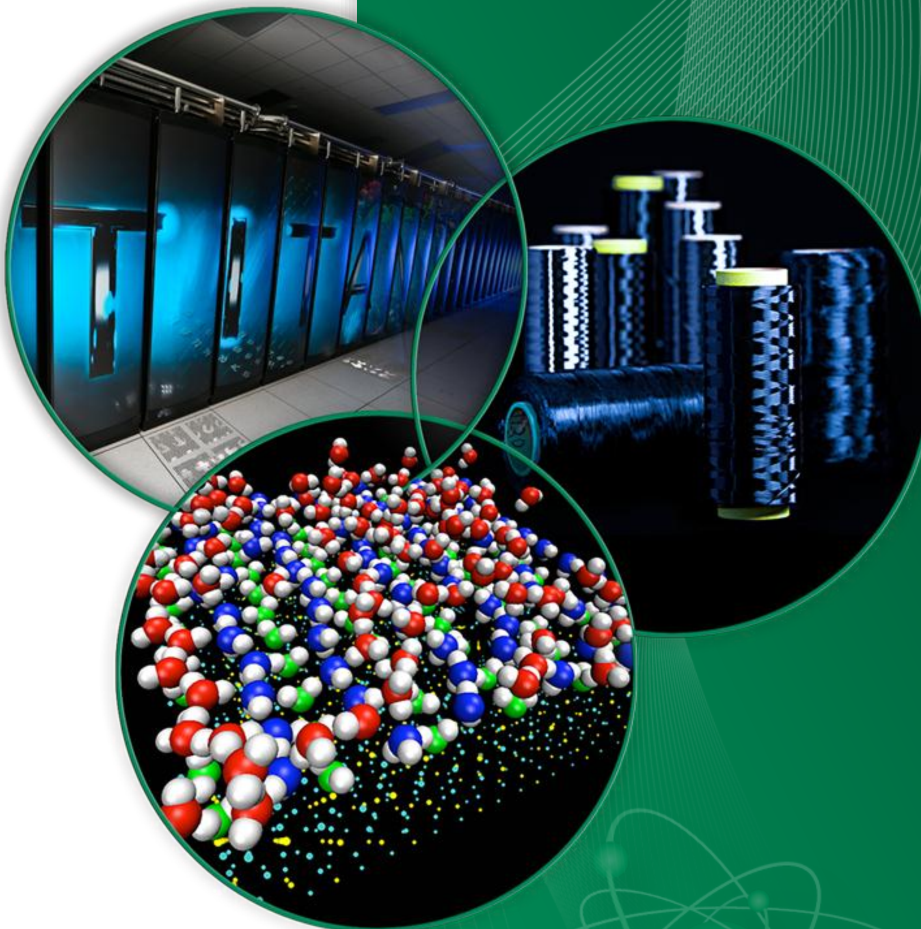
Real Space Analysis of Dynamics in Liquid and Glass

T. Egami, W. Dmowski and A. R.Q. Baron

Shull-Wollan Center - Joint Institute for Neutron Sciences, Department of Materials Science and Engineering, Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996 USA

and Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA

SPRING-8, Japan



Work supported by the Department of Energy, Office of Sciences, Office of Basic Energy Sciences, Materials Science and Engineering Division

JINS Joint Institute for Neutron Sciences

Oak Ridge National Laboratory
MANAGED BY UT-BATTELLE FOR THE U.S. DEPARTMENT OF ENERGY

PHYSICAL REVIEW VOLUME 95, NUMBER 1 JULY 1, 1954

Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles

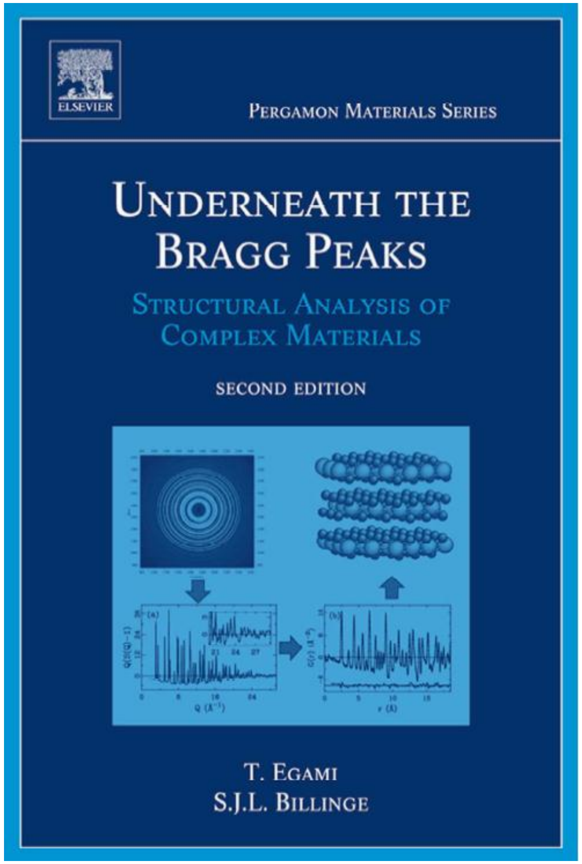
LÉON VAN HOVE
Institute for Advanced Study, Princeton, New Jersey
(Received March 16, 1954)

$$S(\boldsymbol{\kappa},\omega)=(2\pi)^{-1}N\int \exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)]\cdot G(\mathbf{r},t)d\mathbf{r}dt, \quad (6)$$

or

$$G(\mathbf{r},t)=(2\pi)^{-3}N^{-1}\int \exp[i(\omega t-\boldsymbol{\kappa}\cdot\mathbf{r})]\cdot S(\boldsymbol{\kappa},\omega)d\boldsymbol{\kappa}d\omega. \quad (7)$$

Nothing is static



- Powder Diffraction
  - Diffuse scattering underneath the Bragg peaks
  - Total scattering
  - **PDF**
- Inelastic Scattering
  - Diffuse scattering underneath the dispersion curves
  - Total inelastic scattering
  - **DPDF, Van Hove function**

Instantaneous PDF

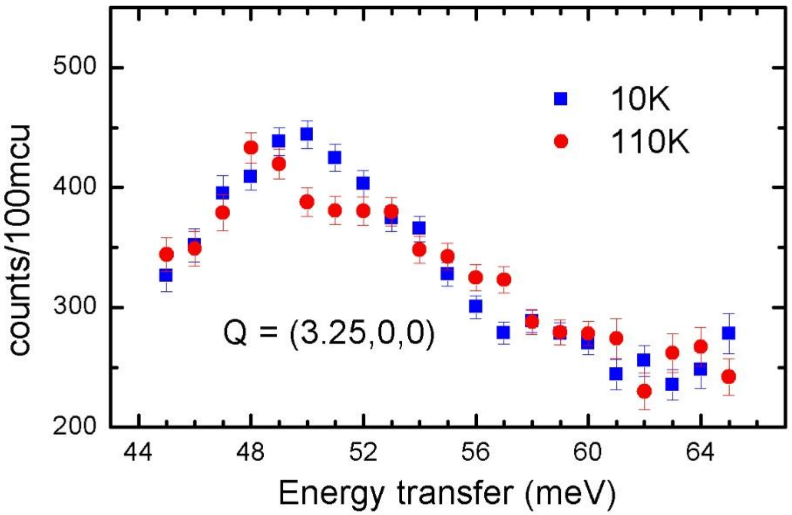
- Energy integrated structure factor describes the instantaneous (snap-shot) structure (same time correlations):

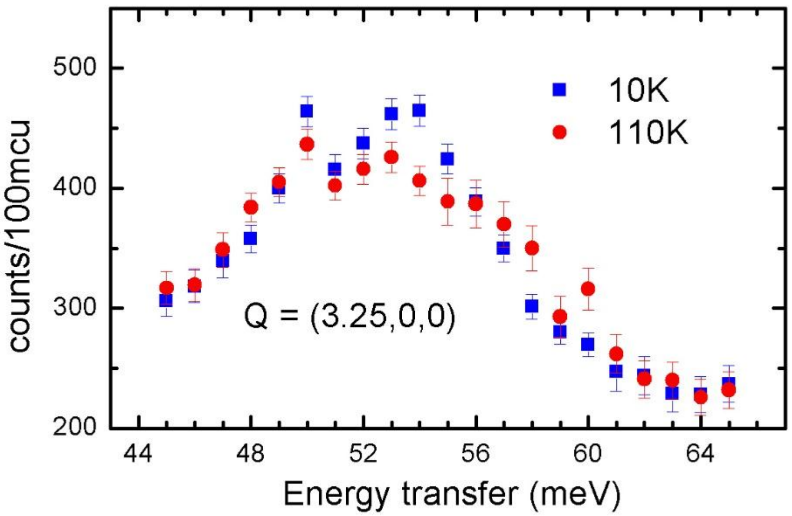
$$S_{total}(\mathbf{Q}) = \int_{-\infty}^{\infty} S(\mathbf{Q},\omega)\, d\omega$$

$$= \frac{1}{N\langle b\rangle^2} \sum_{\nu,\mu} b_\nu b_\mu \int\int \left\langle\left\langle e^{i\mathbf{Q}\cdot(\mathbf{R}_\nu(0)-\mathbf{R}_\mu(t))}\right\rangle\right\rangle e^{-i\omega t}\, dt\, d\omega$$

$$= \frac{1}{N\langle b\rangle^2} \sum_{\nu,\mu} b_\nu b_\mu \left\langle\left\langle e^{i\mathbf{Q}\cdot(\mathbf{R}_\nu(0)-\mathbf{R}_\mu(0))}\right\rangle\right\rangle$$

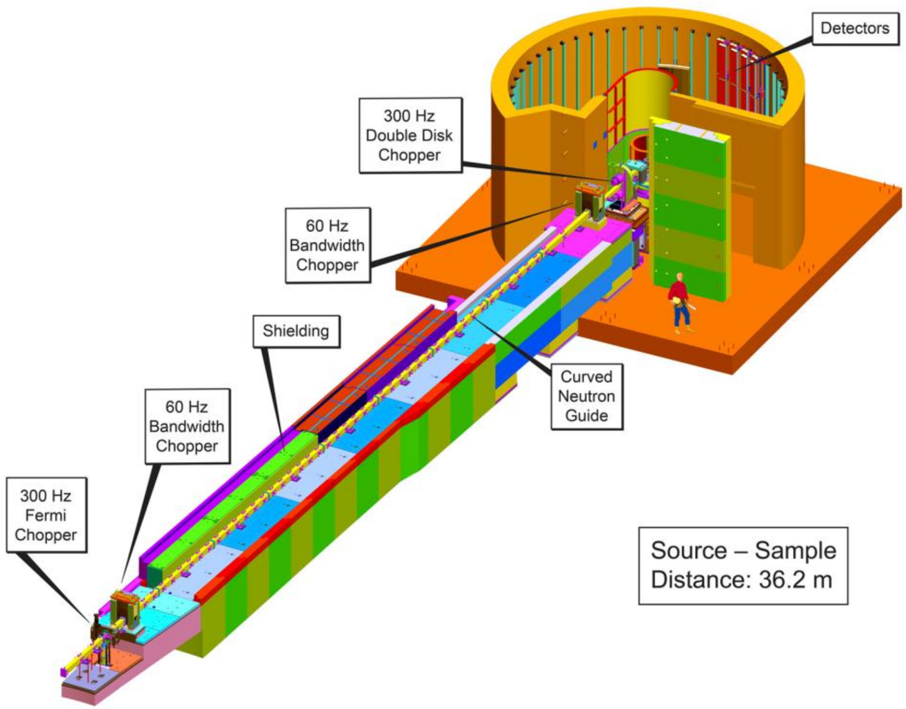
INS with TAS

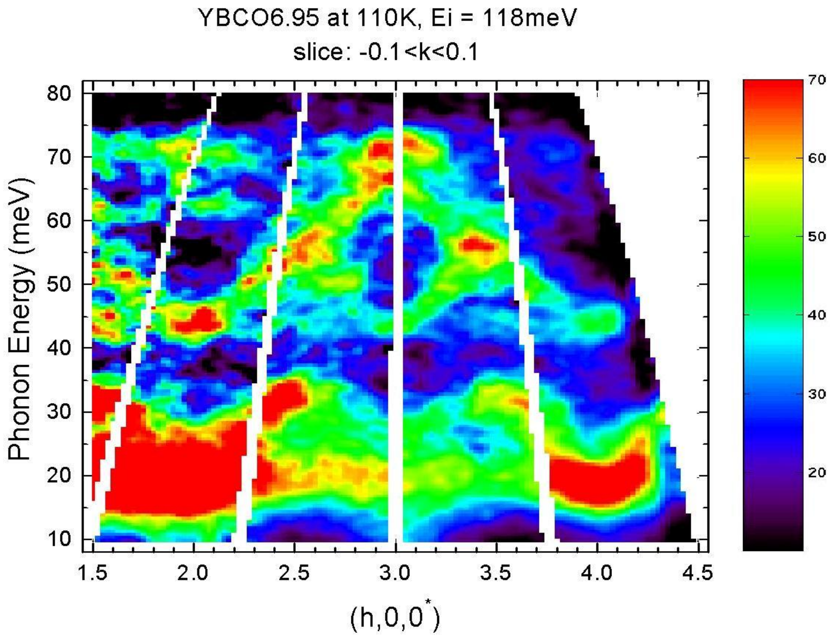




- *E* or ***Q*** scan with fixed ***Q*** or *E*.
- Hours per scan.

INS with PNS



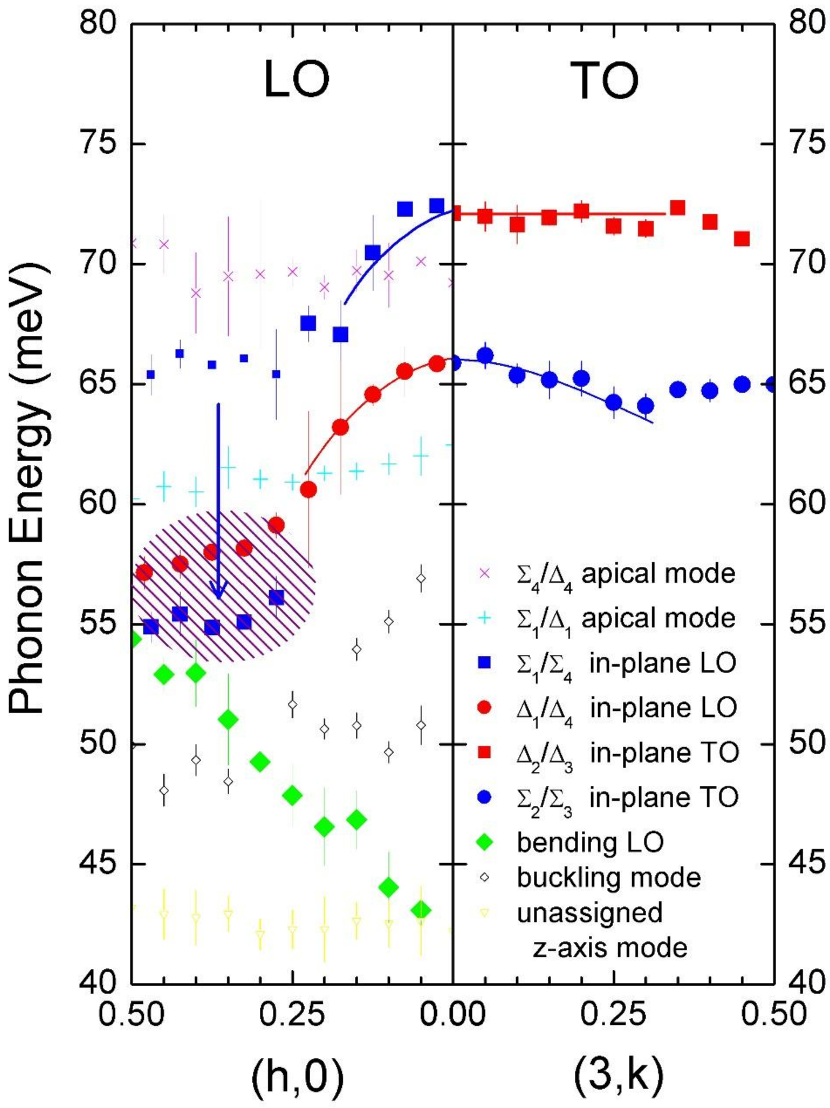


J.-H. Chung, *et al*., *PRB* **67**, 014517 (2003).

- Simultaneous 3D (4D) determination of $S(\mathbf{Q}, E)$
- Large amount of data (> 10^4) than TAS

Yet, the same analysis !

Only 1 % of the data used



New Information
We can get ONLY with PNS ?, IXS ?

- Wider *Q* and *E* space
  - More of the same

- Inelastic diffuse scattering
  - Usually thrown out as background
  - Provides information on local dynamics

$$F(\mathbf{Q},t)=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu} b_\nu b_\mu \left\langle\left\langle e^{i\mathbf{Q}\cdot\left(\boldsymbol{R}_\nu(0)-\boldsymbol{R}_\mu(t)\right)}\right\rangle\right\rangle$$

$$S(Q,E) \Rightarrow F(Q,t)$$

Intermediate Scattering Function

$$\Downarrow \qquad\qquad \Downarrow$$

$$g(r,E) \Rightarrow g(r,t)$$

Dynamic PDF **Van Hove function**

Not a Trivial Task

- **Powder diffraction and PDF**
  - **PD: *Q* in high resolution, intensity, *I*(*Q*), in low resolution**
  - **PDF: *Q* and *I* in the same resolution, *S*(*Q*) well normalized.**
- **Dispersion and DPDF/VHove**
  - **Disp: *Q* and *E* in high resolution, *I* in low resolution**
  - **DPDF: *Q*, *E*, *I*(*Q*, *E*) all in high resolution,**

    ***S*(*Q*, *E*) well normalized.**

Dynamic PDF

- Dynamic structure factor:

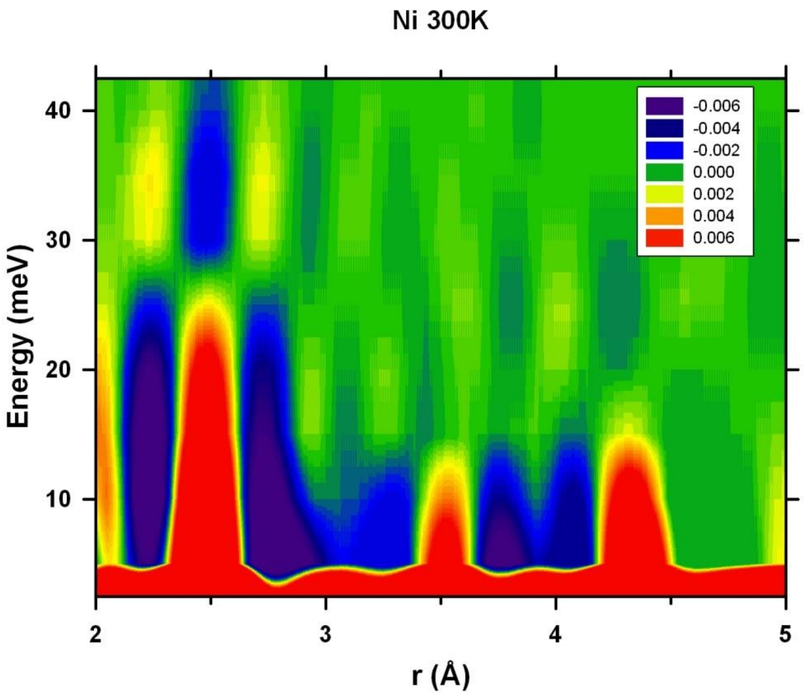
$$S(\mathbf{Q},\omega)=\frac{1}{N\langle b\rangle^{2}}\sum_{\nu,\mu}b_{\nu}b_{\mu}\int\left\langle\left\langle e^{i\mathbf{Q}\cdot\left(\mathbf{R}_{\nu}(0)-\mathbf{R}_{\mu}(t)\right)}\right\rangle\right\rangle e^{-i\omega t}dt$$

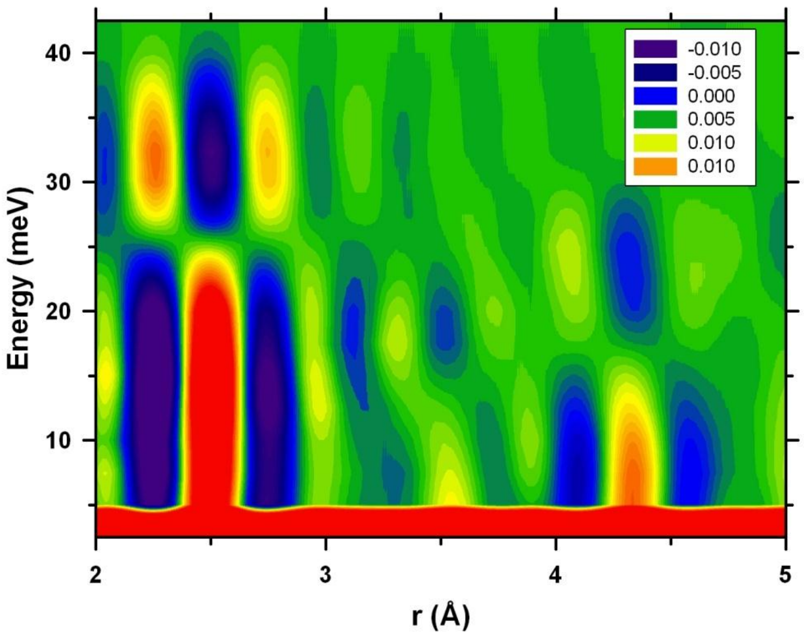
- Dynamic PDF

$$\rho(\mathbf{r},\omega)=\int S(\mathbf{Q},\omega)e^{i\mathbf{Q}.\mathbf{r}}d\mathbf{Q}$$

$$=\frac{1}{N\langle b\rangle^{2}}\sum_{\nu,\mu}b_{\nu}b_{\mu}\int\delta\left(r-\left[\mathbf{R}_{\nu}(0)-\mathbf{R}_{\mu}(t)\right]\right)e^{i\omega t}dt$$

Dynamic PDF of Ni at 300 K





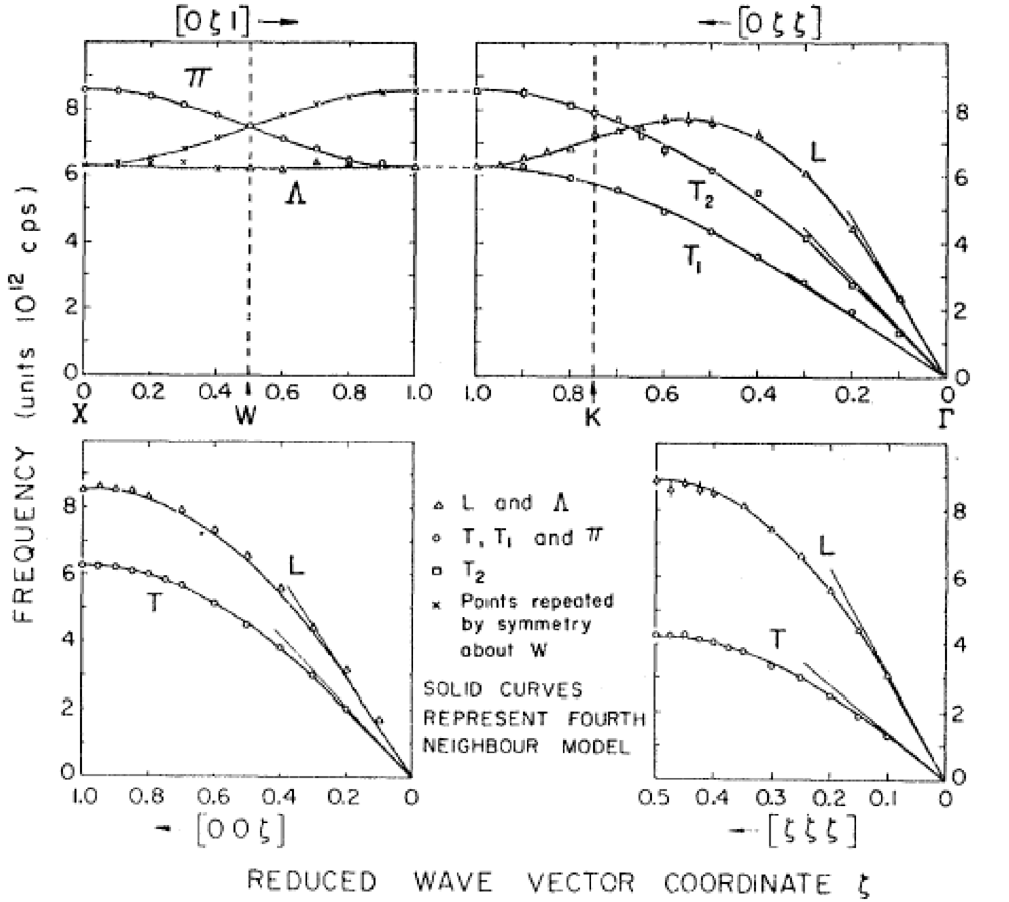
Measured DPDF **Simulation**

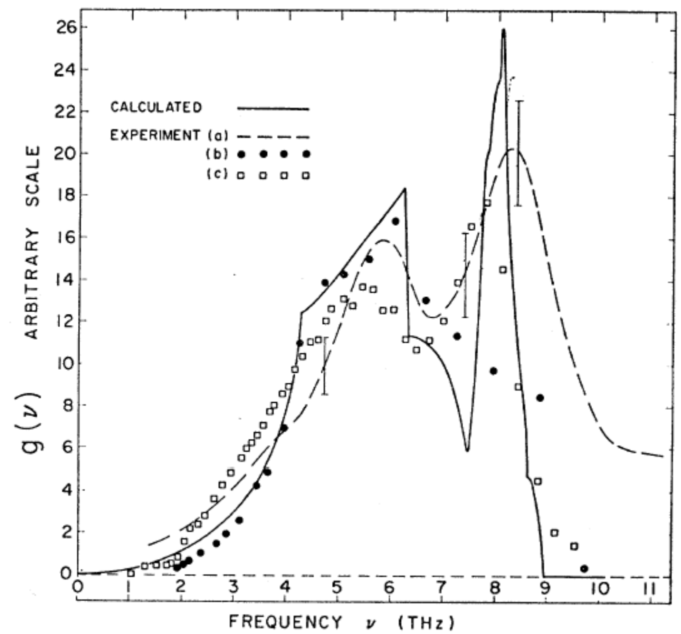
- Local phonons near the saddle points are well resolved.

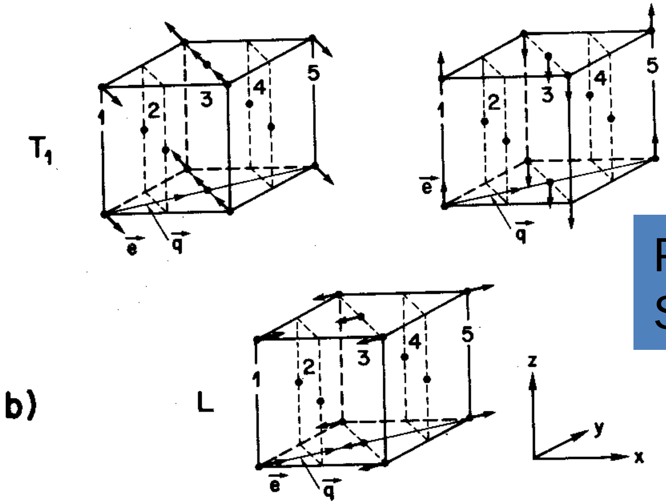
PHYSICAL REVIEW VOLUME 136, NUMBER 5A 30 NOVEMBER 1964

Normal Modes of Vibration in Nickel

R. J. BIRGENEAU,* J. CORDES,† G. DOLLING, AND A. D. B. WOODS
Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada
(Received 13 July 1964)







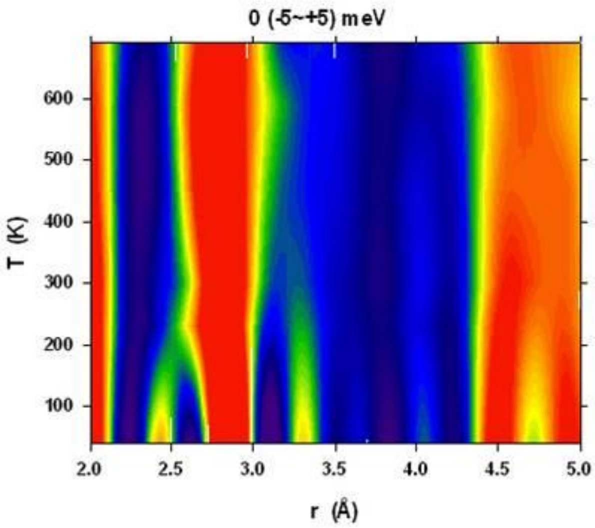
P. Brüesch, 'Phonons: Theory and Experiment, Springer-Verlag'

Fig.3.17. Pattern of atomic displacements in the fcc structure for a) $\vec{q}_{ZB} = (2\pi/a)(1,0,0)$; the entire plane of atoms move in phase and neighbouring planes move in the opposite directions; the wavelength is $\lambda = a$; b) $\vec{q} = (2\pi/a)(1,1,0)$; neighbouring odd-numbered planes move in opposite directions while even-numbered planes are at rest; the wavelength is $\lambda = \sqrt{2}a$

T. Egami, W. Dmowski, "Dynamic Pair-Density Function Method for Neutron and X-ray Inelastic Scattering", Zeitschrift für Kristallographie, 227, 233-237, 2012

"Elastic" PDF of PMN

Short Pb-O bond at 2.5 Å and long Pb-O bond at ~ 3.2 Å are seen up to the ~250K Therefore, static polarization due to Pb displacements is observed only below freezing temperature.

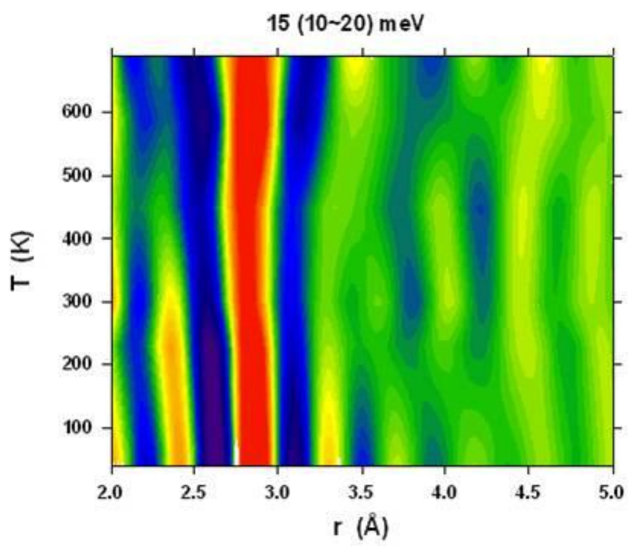


Short Pb-O bond at 2.5 Å and long Pb-O bond at ~ 3.2 Å are seen up to the ~600K.

Therefore, dynamic polarization due to Pb displacements is observed up to the Burns temperature.

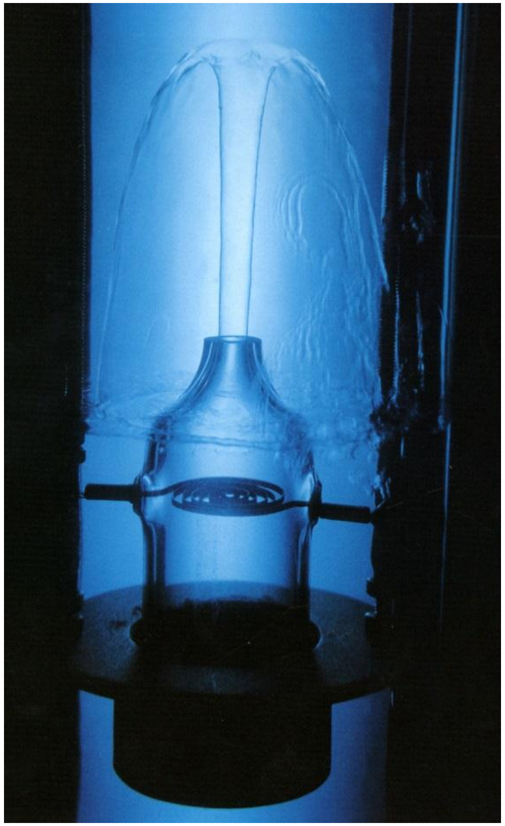
Interaction with soft phonons involving Pb-O displacements

Dynamic PDF of PMN

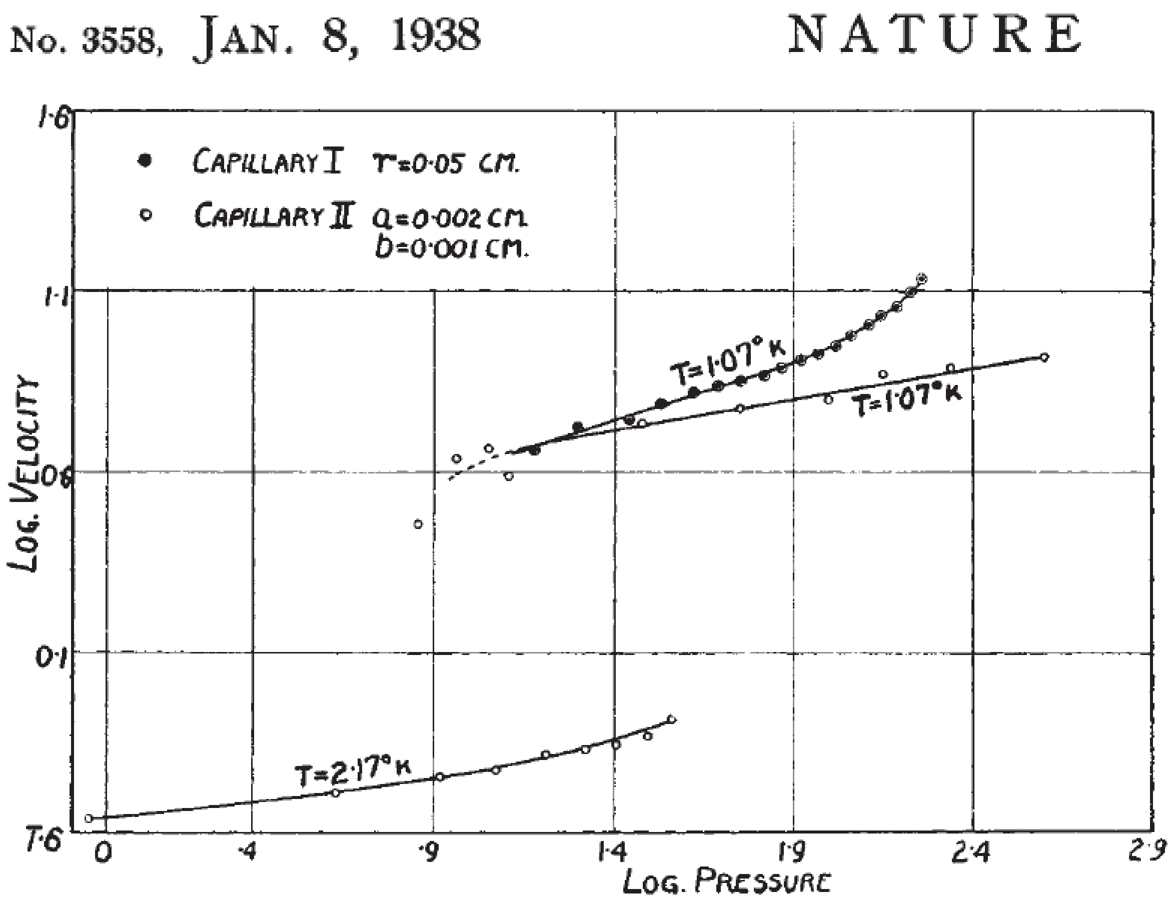


W. Dmowski, et al., "Local Lattice Dynamics and the Origin of the Relaxor Ferroelectric Behavior", Phys Rev. Letters, 100, 137602 (2008)

Superfluid ^{4}He



- Discovered in 1938 by P. Kapitza and by J. F. Allen and A. D. Misener.



Bose-Einstein Condensation

NATURE APRIL 9, 1938, VOL. 141

The λ-Phenomenon of Liquid Helium and the Bose-Einstein Degeneracy

F. LONDON.

Institut Henri Poincaré,
Paris.
March 5.

1938 PHYSICAL REVIEW

On the Bose-Einstein Condensation

F. LONDON
*Institut Henri Poincaré, University of Paris, France**
(Received October 12, 1938)

$$f_{BE}\left(E,T\right)=\frac{1}{e^{(E-\mu)/kT}-1}$$

$$\mu=0,\quad T\le T_C$$

- Macroscopic quantum condensation to the ***k*** = 0 ground state.
- Defined for ideal gas.
- Helium is a strongly interacting liquid.

Landau Theory of Superfluidity

Т. 11 Журнал экспериментальной и теоретической физики Вып. 6

1941

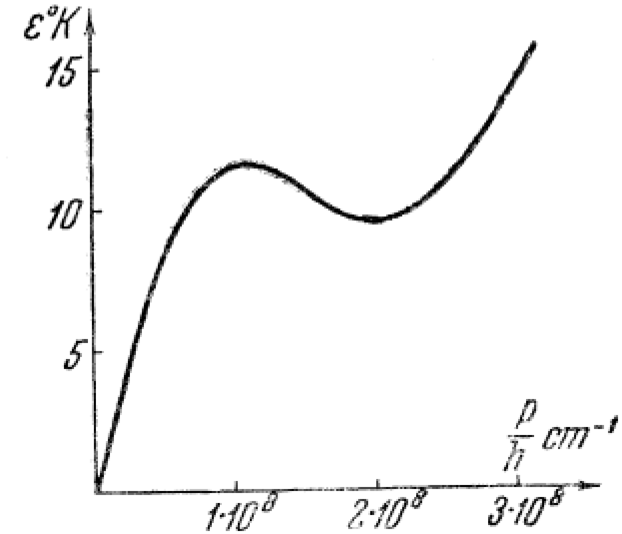
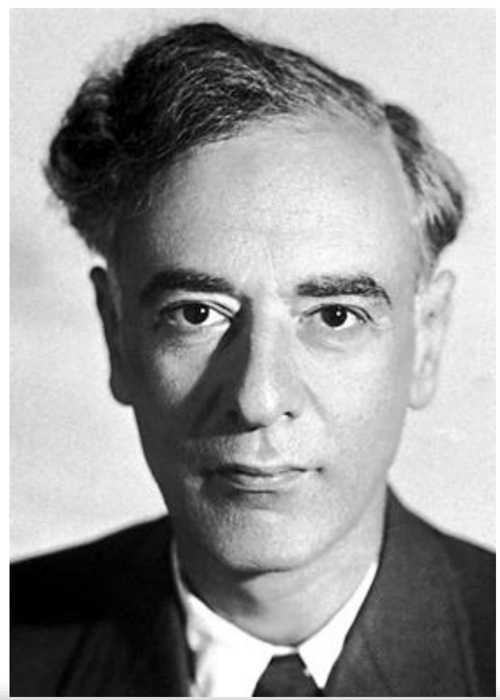


Fig. 1

ТЕОРИЯ СВЕРХТЕКУЧЕСТИ ГЕЛИЯ-II

Л. Ландау

- **Based upon "roton" excitation.**
- **No mention to BEC.**



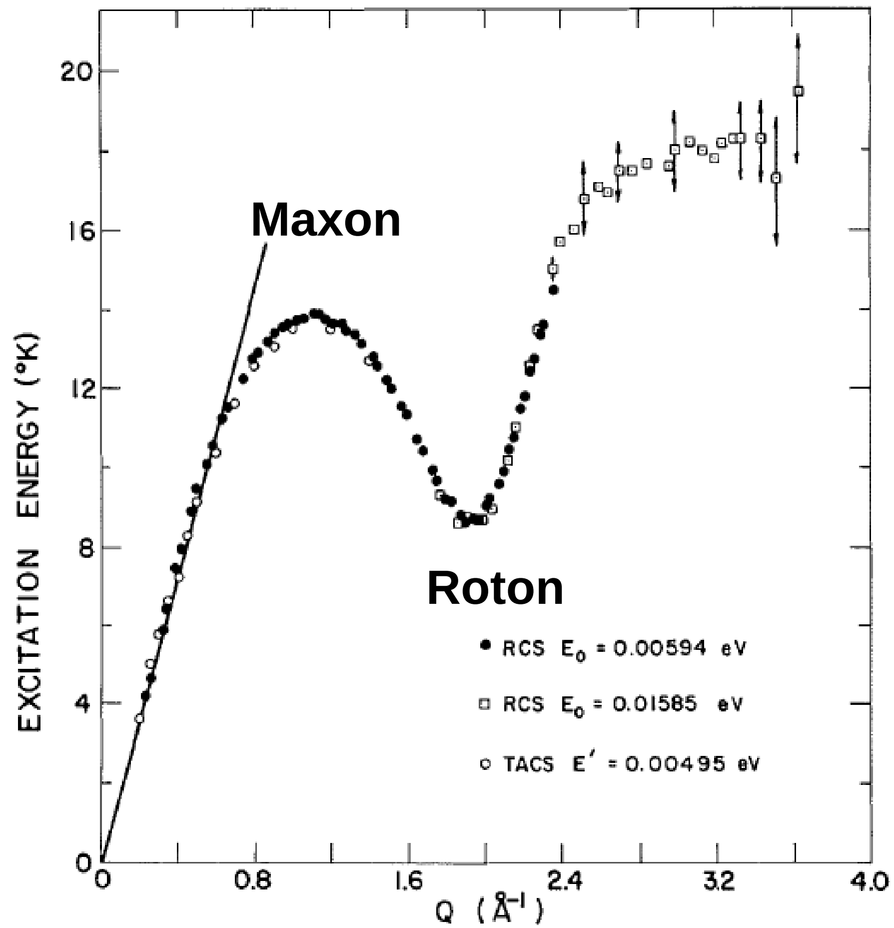
Lev D. Landau
Nobel Prize 1962

Roton

Inelastic Scattering of Thermal Neutrons from Liquid Helium

R. A. Cowley[1] and A. D. B. Woods
Atomic Energy of Canada Limited, Chalk River, Ontario
Received August 31, 1970

- **A strong minimum at the peak of *S*(*Q*).**
- **“Roton” is more related to the “boson” peak.**

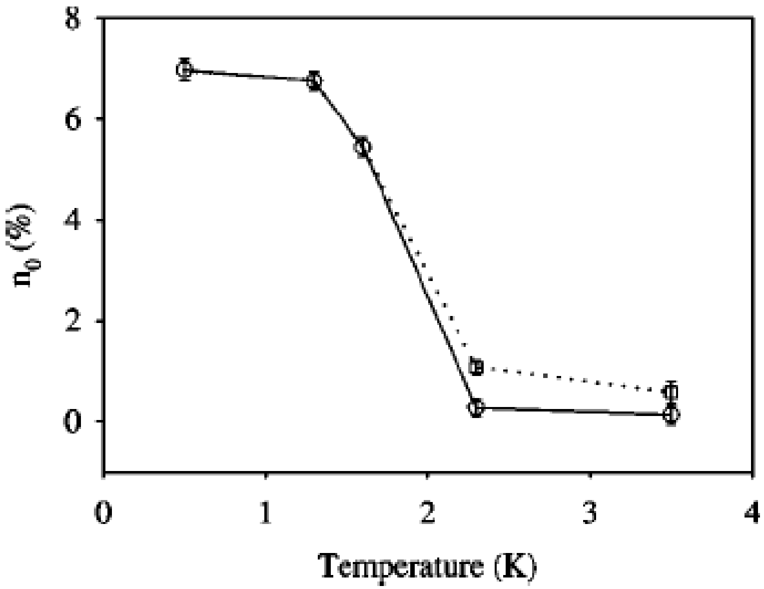


PHYSICAL REVIEW B VOLUME 62, NUMBER 21 1 DECEMBER 2000-I

Condensate, momentum distribution, and final-state effects in liquid ^{4}He

H. R. Glyde
Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716

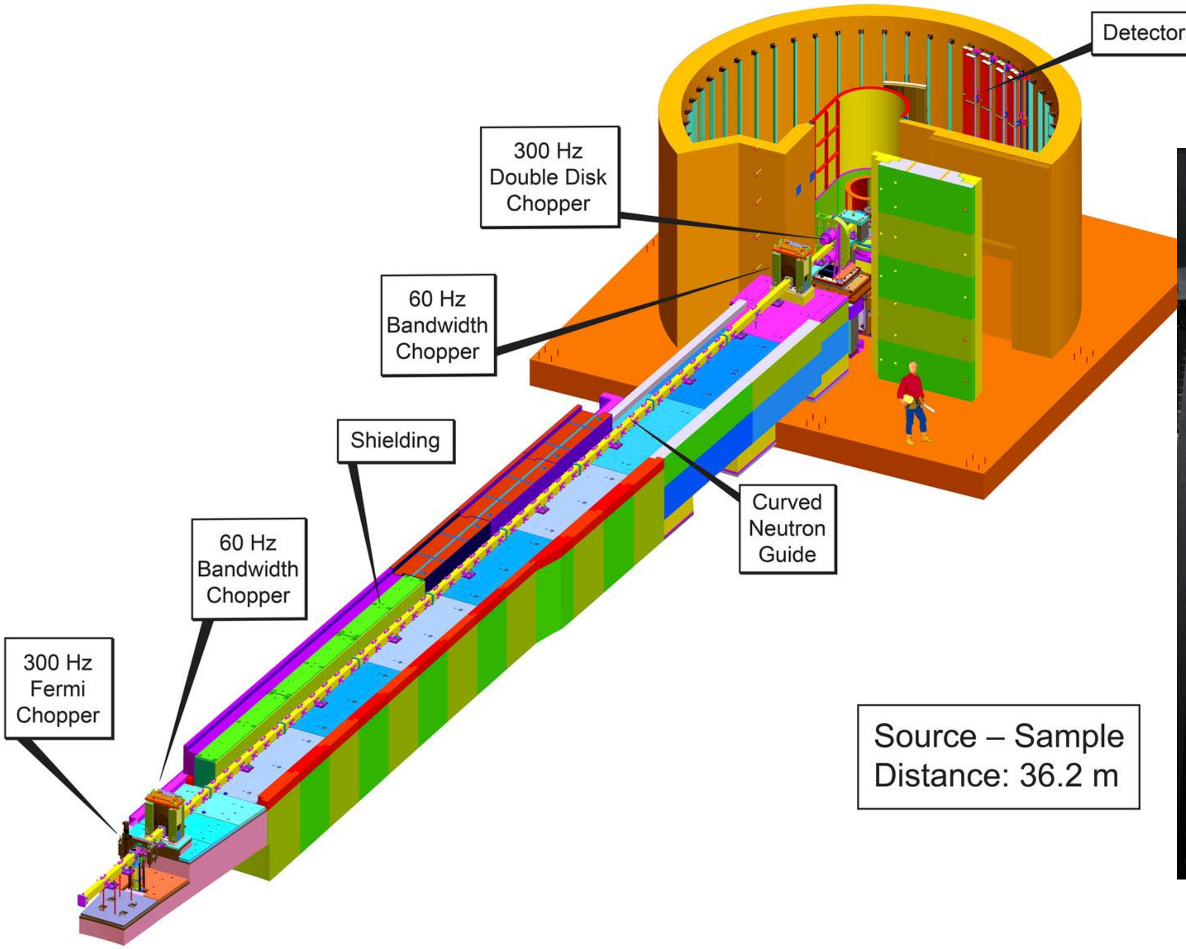
R. T. Azuah and W. G. Stirling
Department of Physics, Oliver Lodge Laboratory, University of Liverpool, Liverpool L69 3BX, United Kingdom
(Received 15 February 2000)

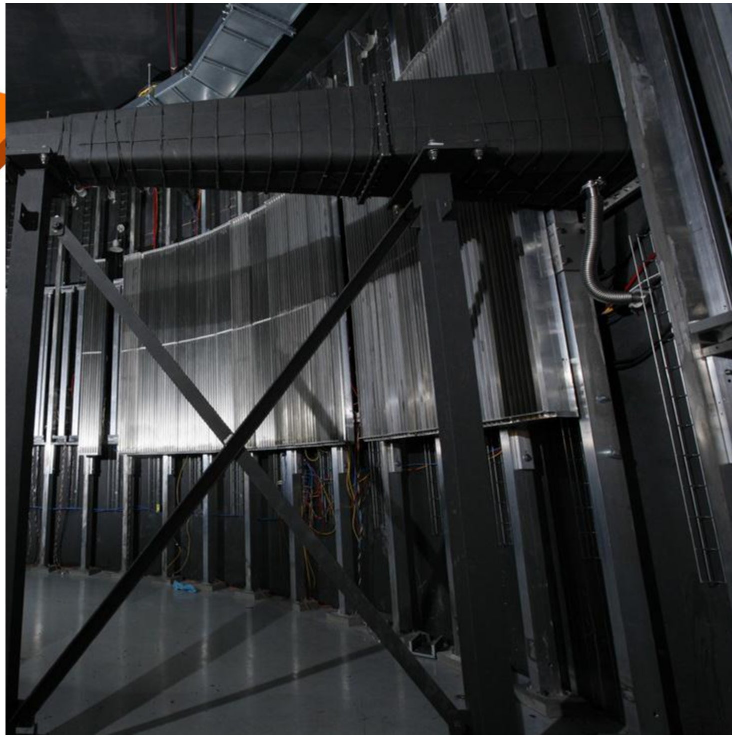


$$n_0(T) = n_0(0)[1-(T/T_\lambda)^\gamma]$$

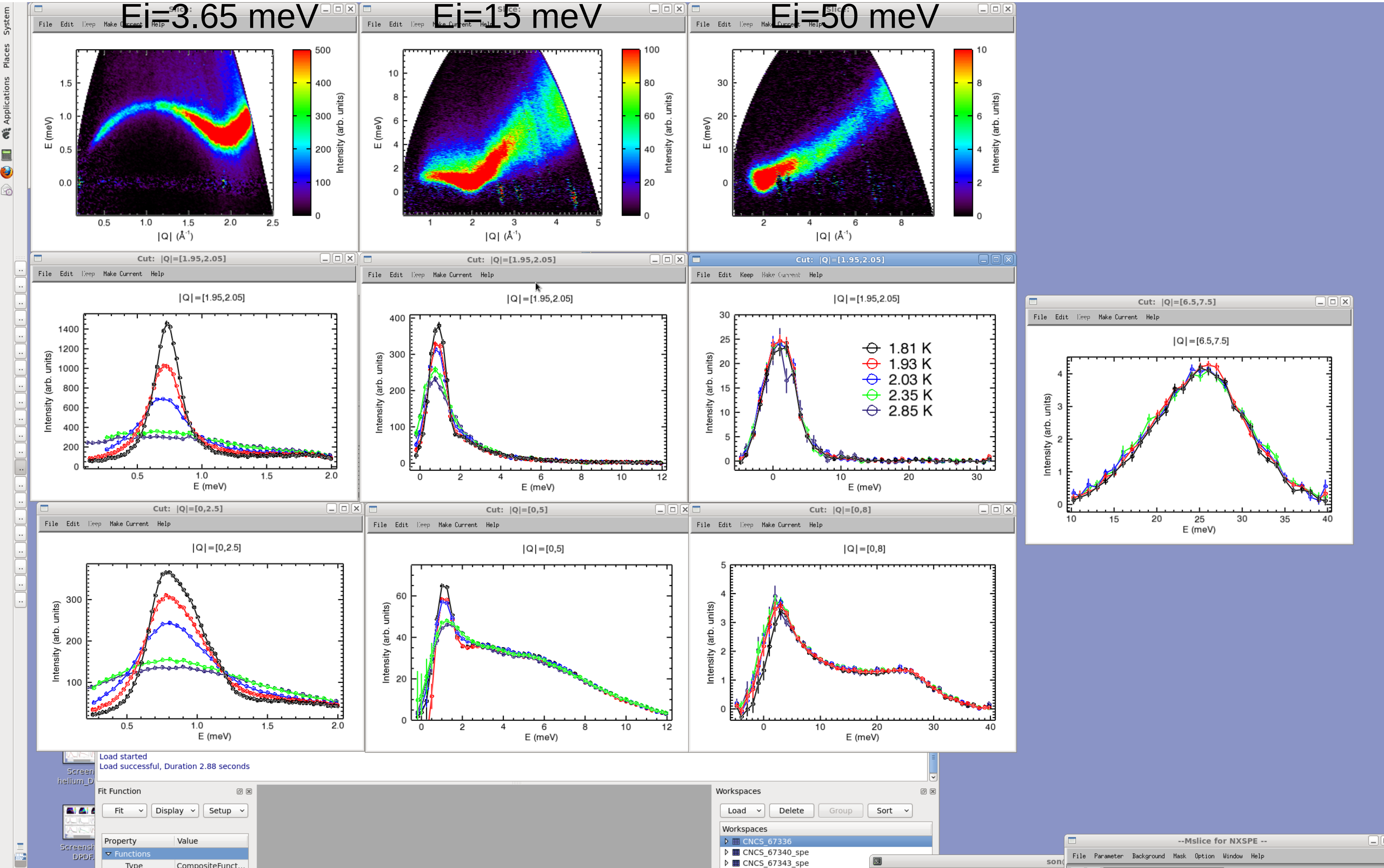
with $n_0(0) = (7.25 \pm 0.75)\%$ and $\gamma = 5.5 \pm 1.0$.

Cold Neutron Chopper Spectrometer (CNCS) of SNS to see Local Dynamics

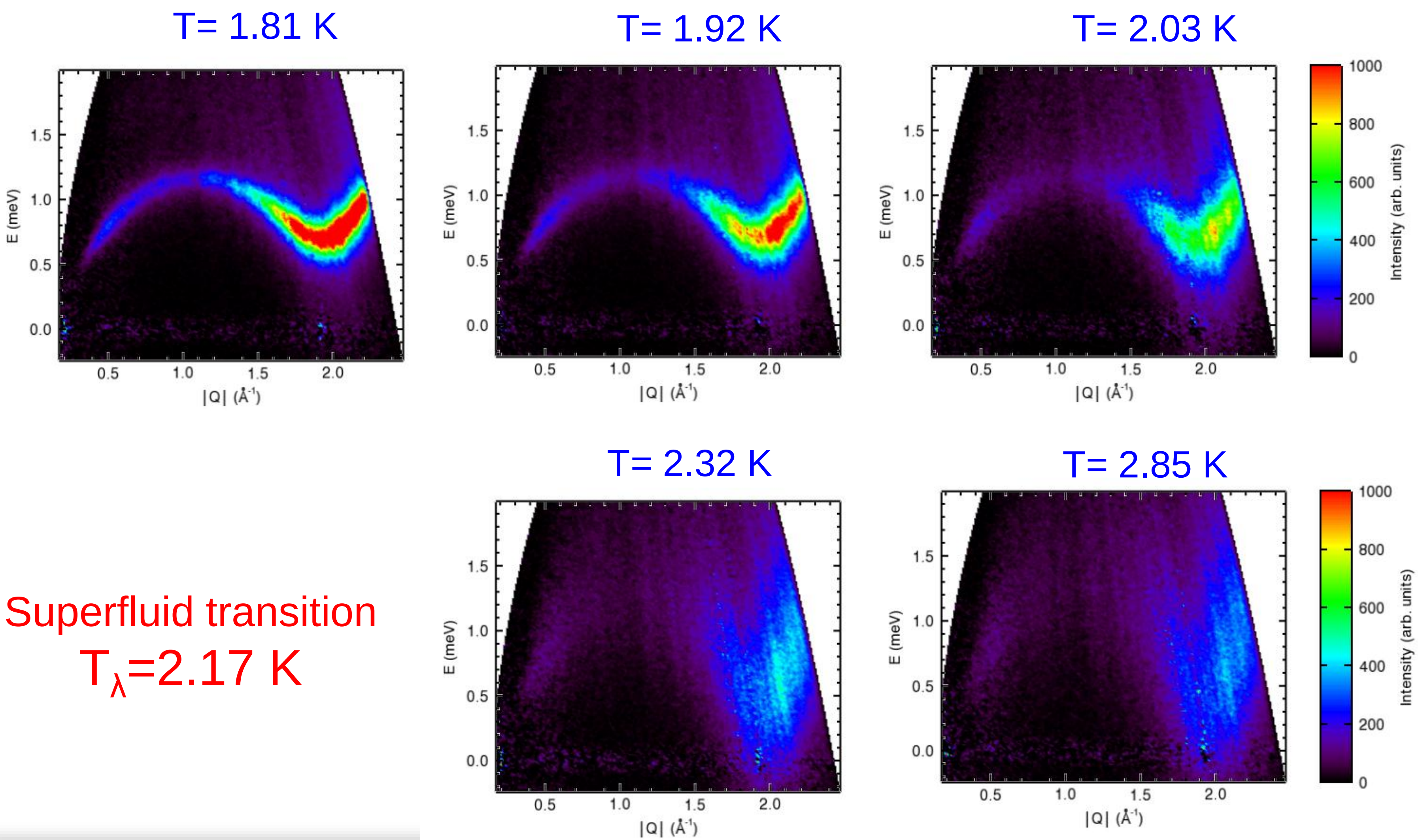




Raw Data


Ei=3.65 meV
Ei=15 meV
Ei=50 meV
E (meV)
|Q| (Å^{-1})
Intensity (arb. units)
|Q|=[1.95,2.05]
|Q|=[6.5,7.5]
|Q|=[0,2.5]
|Q|=[0,5]
|Q|=[0,8]
1.81 K
1.93 K
2.03 K
2.35 K
2.85 K
Load started
Load successful, Duration 2.88 seconds
Fit Function
Workspaces
CNCS_67336
CNCS_67340_spe
CNCS_67343_spe
--Mslice for NXSPE --

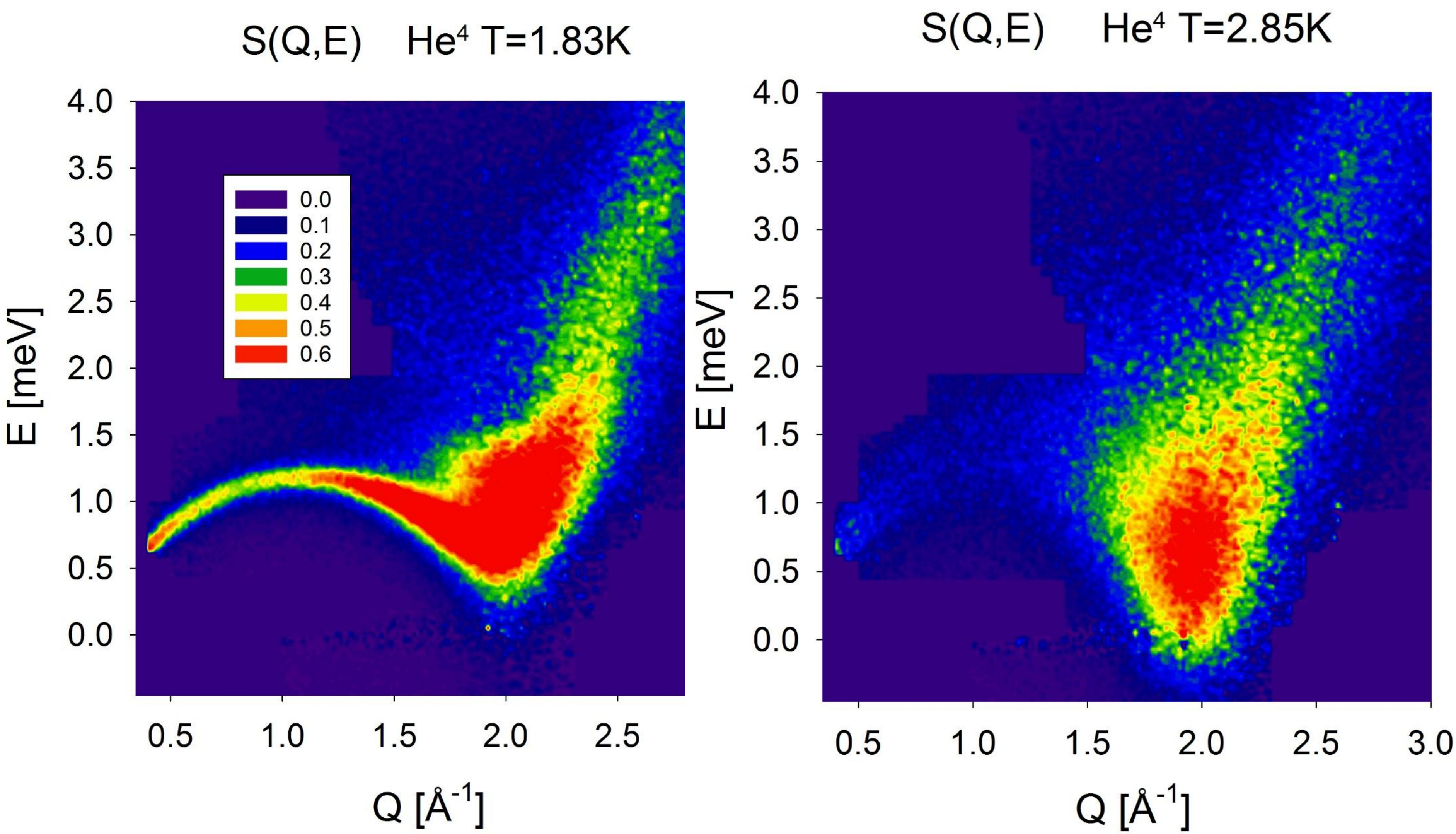
2D Map vs. T -- E_i=3.65 meV



Superfluid transition

T_λ=2.17 K

CNCS Data

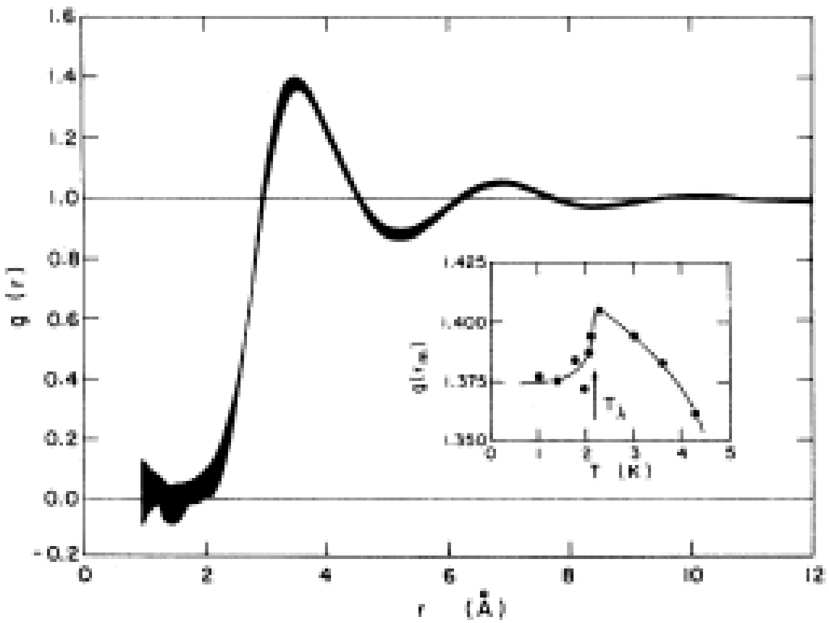

S(Q,E) He4 T=1.83K
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
E [meV]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.5
1.0
1.5
2.0
2.5
Q [Å-1]
S(Q,E) He4 T=2.85K
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
E [meV]
0.5
1.0
1.5
2.0
2.5
3.0
Q [Å-1]

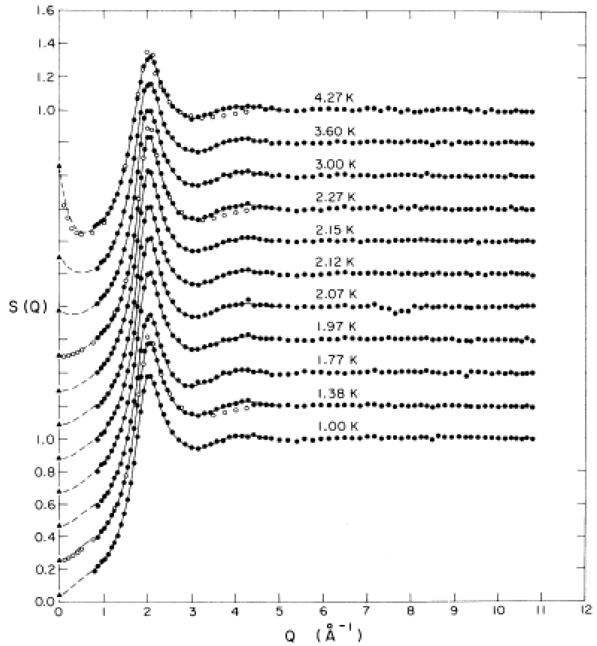
Previous Measurements

PHYSICAL REVIEW B VOLUME 21, NUMBER 8 15 APRIL 1980

Neutron-diffraction study of the static structure factor and pair correlations in liquid ^{4}He

E. C. Svensson, V. F. Sears, A. D. B. Woods,* and P. Martel
Atomic Energy of Canada Limited Research Company, Chalk River, Ontario, Canada KOJ 1JO
(Received 3 December 1979)





- Little change in static correlation with temperature.
- These are same time correlation functions! and integration is done at fixed angle

Dynamic PDF to see Local Dynamics

- Dynamic structure factor:

$$S(\mathbf{Q},E)=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\int\left\langle\left\langle e^{i\mathbf{Q}\cdot(\mathbf{R}_\nu(0)-\mathbf{R}_\mu(t))}\right\rangle\right\rangle e^{-iEt/\hbar}dt$$

- Dynamic PDF

$$\rho(\mathbf{r},E)=\int S(\mathbf{Q},E)e^{i\mathbf{Q}.\mathbf{r}}d\mathbf{Q}$$

$$=\frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu}b_\nu b_\mu\int\delta\left(r-\left[\mathbf{R}_\nu(0)-\mathbf{R}_\mu(t)\right]\right)e^{iEt/\hbar}dt$$

Van Hove Function

$$F(\mathbf{Q},t) = \frac{1}{N\langle b\rangle^2}\sum_{\nu,\mu} b_\nu b_\mu \left\langle\left\langle e^{i\mathbf{Q}\cdot\left(\boldsymbol{R}_\nu(0)-\boldsymbol{R}_\mu(t)\right)}\right\rangle\right\rangle$$

$$S(Q,E) \quad \Rightarrow \quad F(Q,t)$$

Intermediate Scattering Function

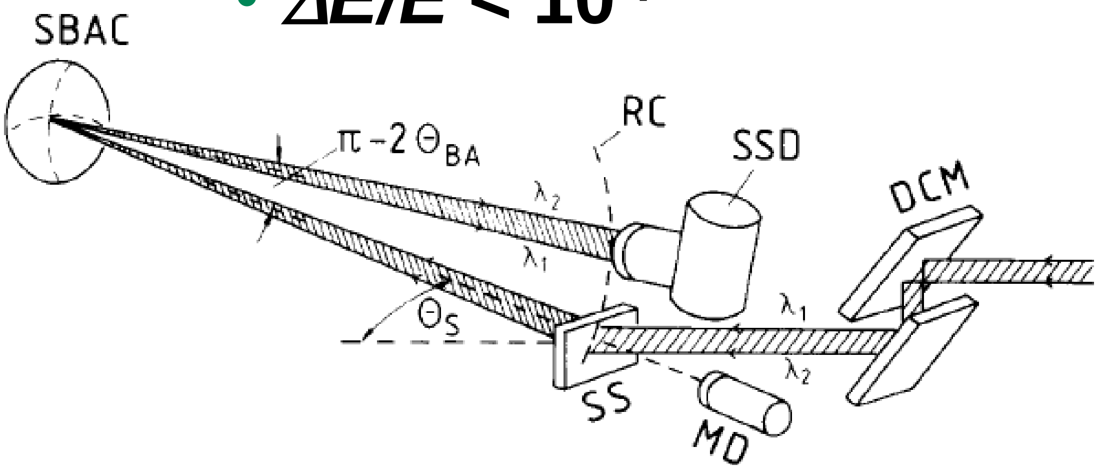
$$\Downarrow \qquad\qquad \Downarrow$$

$$g(r,E) \quad \Rightarrow \quad g(r,t)$$

Dynamic PDF **Van Hove function**

Inelastic X-ray Scattering (IXS) of Water at Spring-8

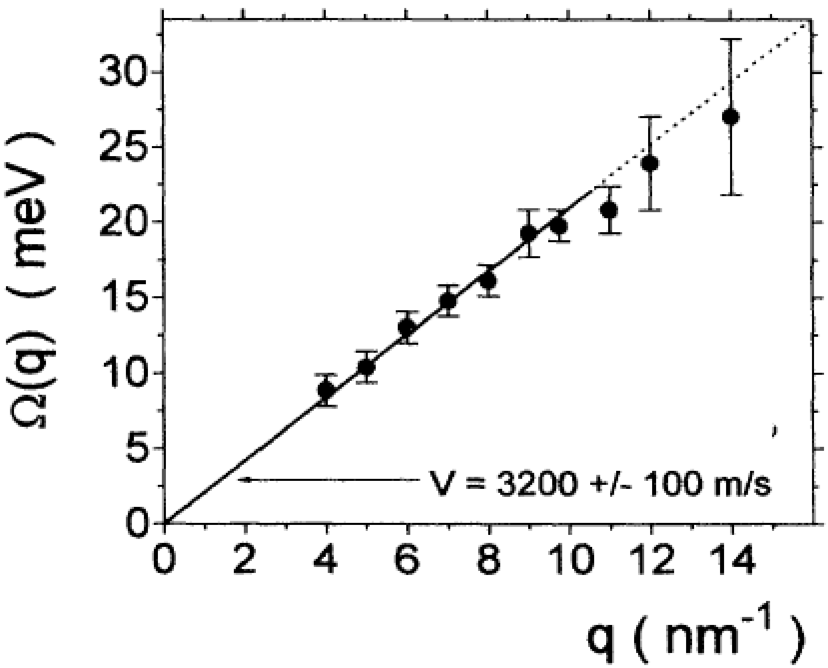
- **Incident energy *E* ~ 23 keV**
- **Energy resolution *ΔE* ~ 1 meV**
- **$\Delta E/E < 10^{-7}$**

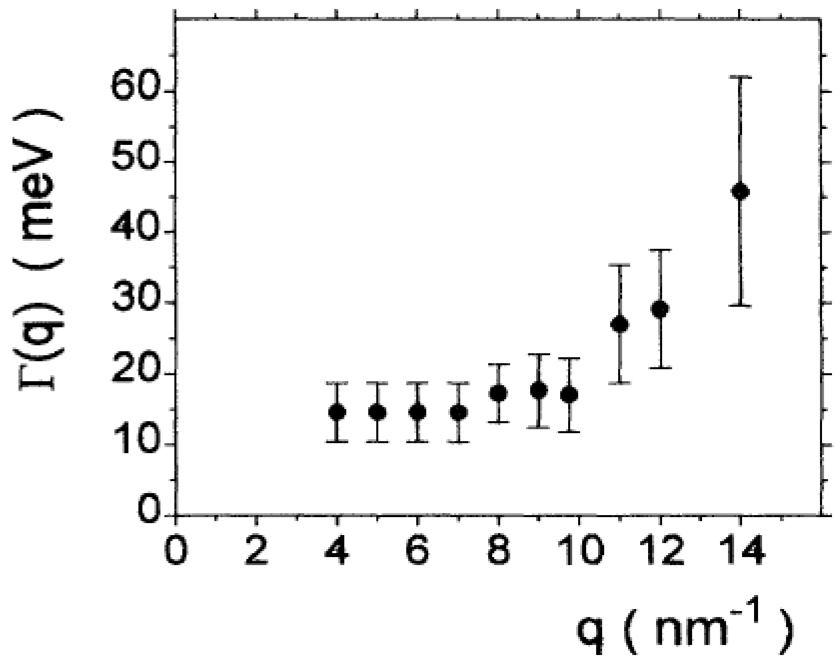


$$S(\mathbf{Q},\omega)=\frac{1}{N}\sum_{j,j'}\int\left\langle e^{i\mathbf{Q}\cdot\left[\mathbf{R}_j(0)-\mathbf{R}_{j'}(t)\right]}\right\rangle e^{i\omega t}dt,\quad E=\hbar\omega$$

Collective Dynamics in Water by High Energy Resolution Inelastic X-Ray Scattering

F. Sette,[1] G. Ruocco,[2] M. Krisch,[1] U. Bergmann,[1] C. Masciovecchio,[1,2] V. Mazzacurati,[2] G. Signorelli,[2] and R. Verbeni[1]



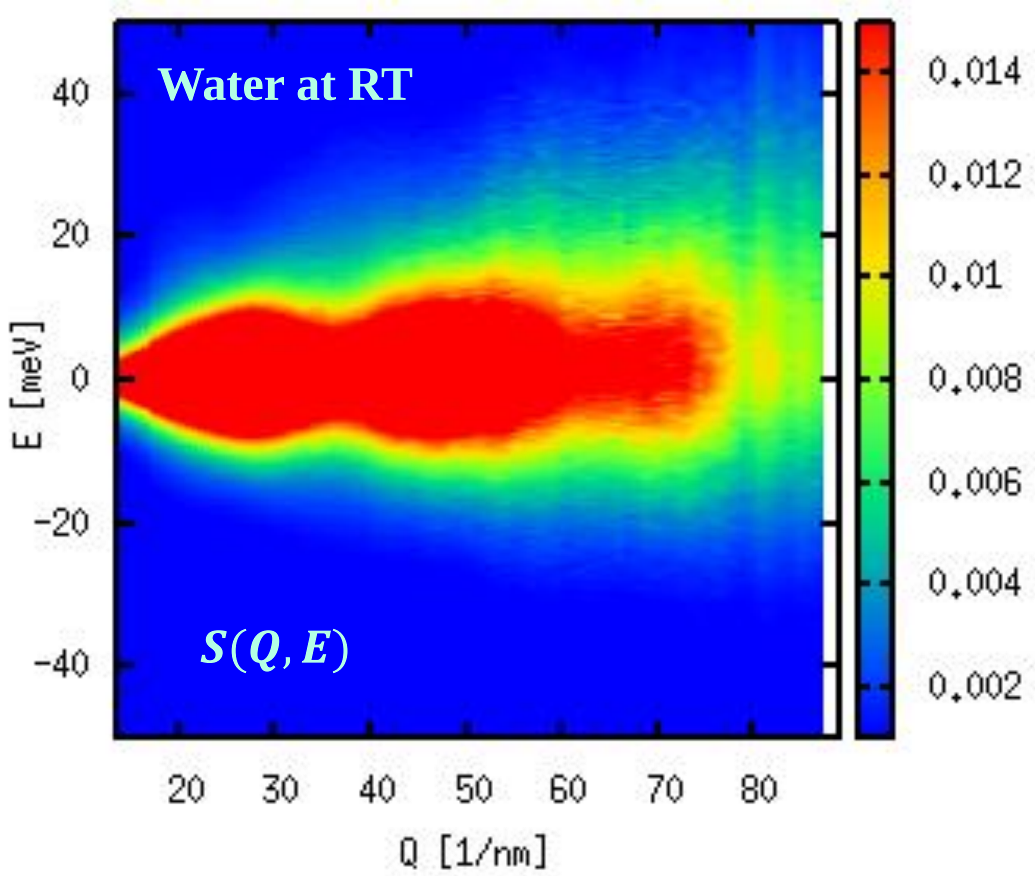


- $\Gamma > \Omega$. Phonons are overdamped.
- Anankeons are the elementary excitations.

IXS measurement of water at Spring 8

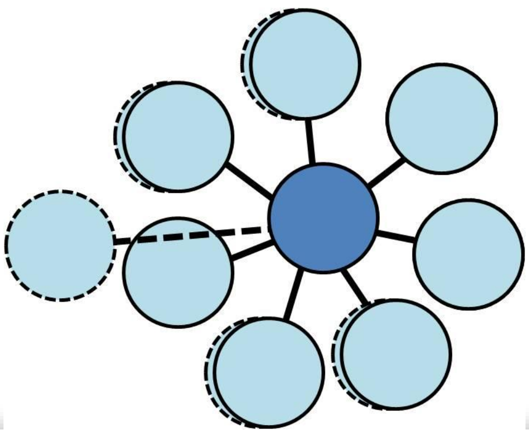
Dynamic structure function

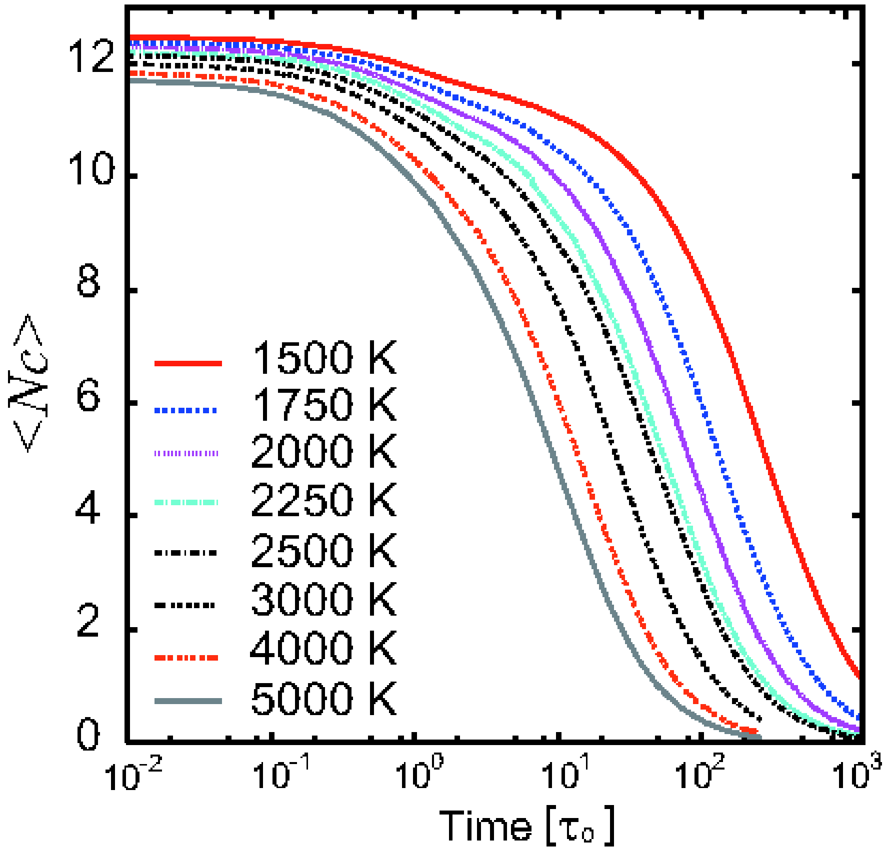
$$S(Q,E) \sim I_{scale}(Q,E)/\langle F(Q)\rangle^2$$



Local Atomic Connectivity and Coordination number

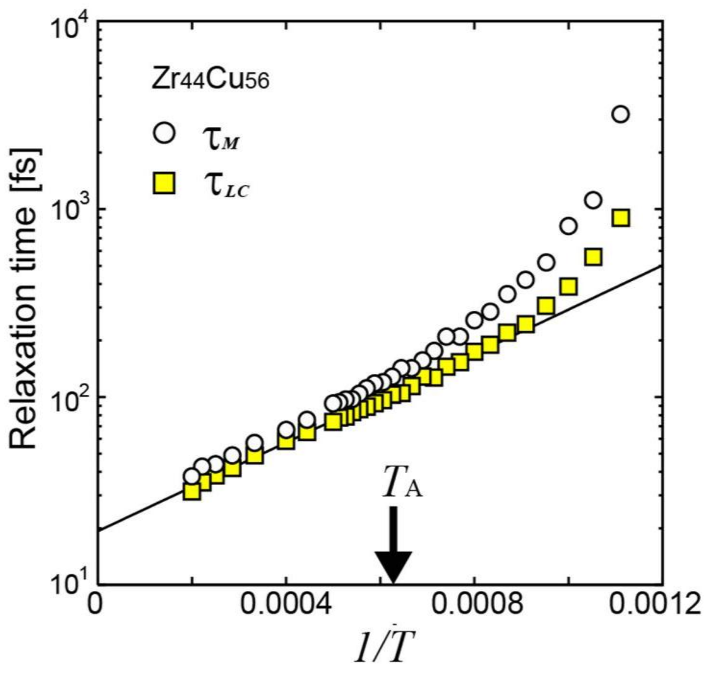
- **Local atomic connectivity is changed by gaining or losing a nearest neighbor (topological excitation).**
- **τ_{LC} is defined as the time to lose (or gain) ONE neighbor.**

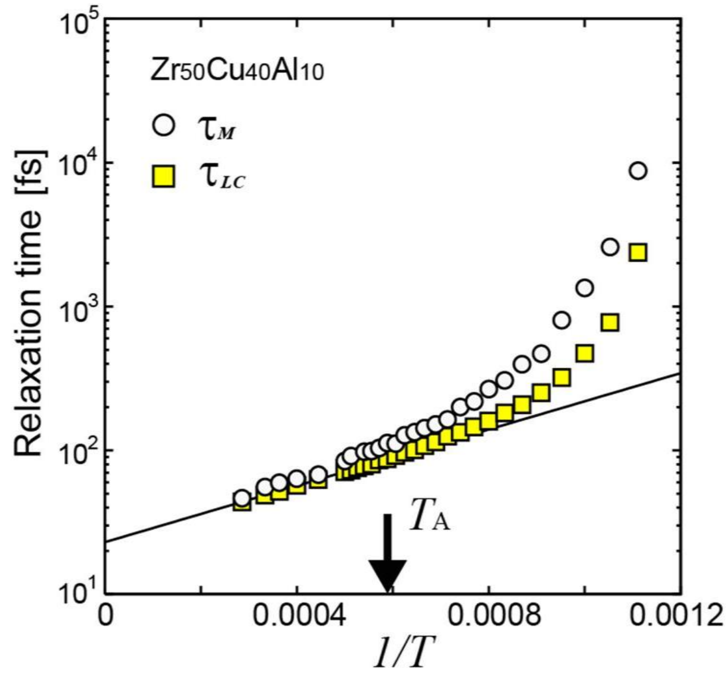




Elementary Excitations and Crossover Phenomenon in Liquids

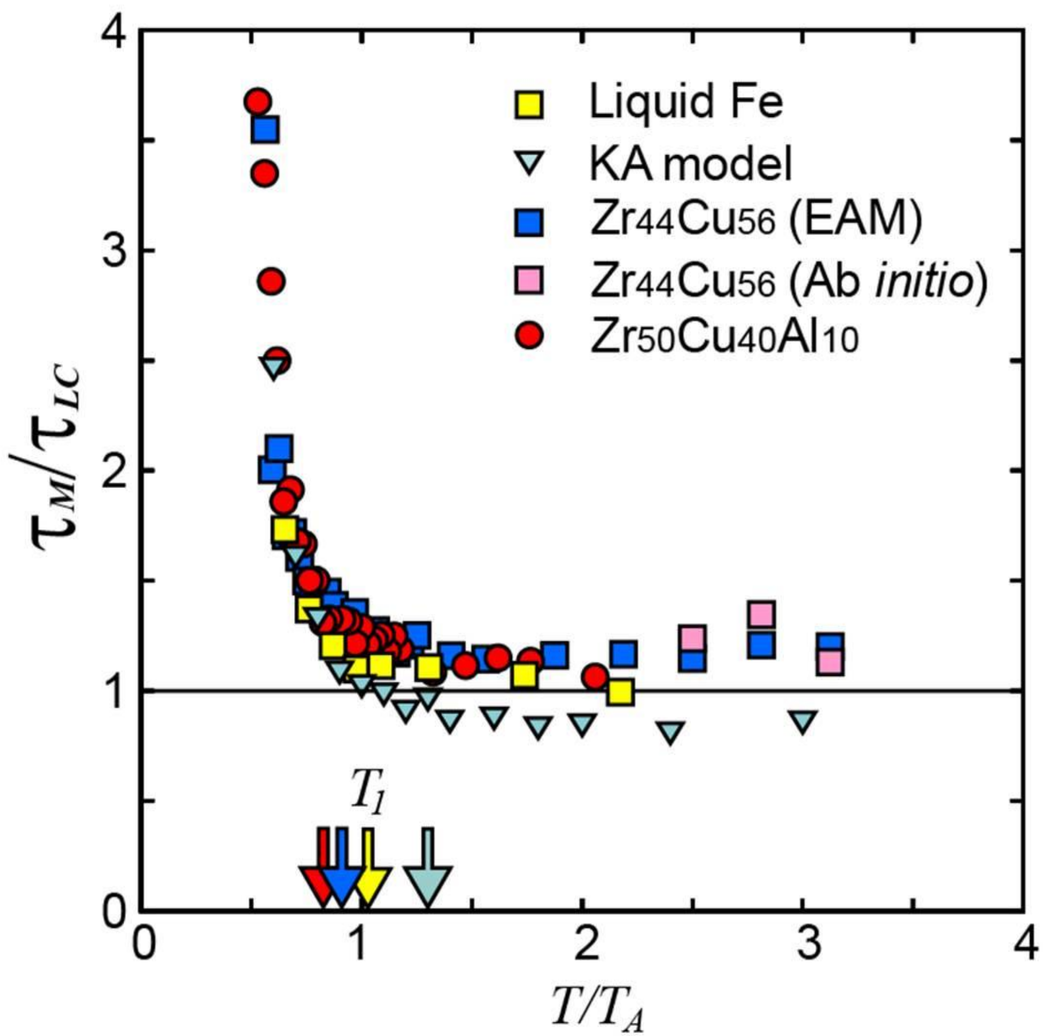
T. Iwashita,[1] D. M. Nicholson,[2] and T. Egami[1,2,3]
[1]Department of Physics and Astronomy, Joint Institute for Neutron Sciences, University of Tennessee, Knoxville, Tennessee 37996, USA
[2]Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
[3]Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA
(Received 23 January 2013; published 16 May 2013)





$$\tau_M = \frac{\eta}{G_\infty}$$

Universal Relationship

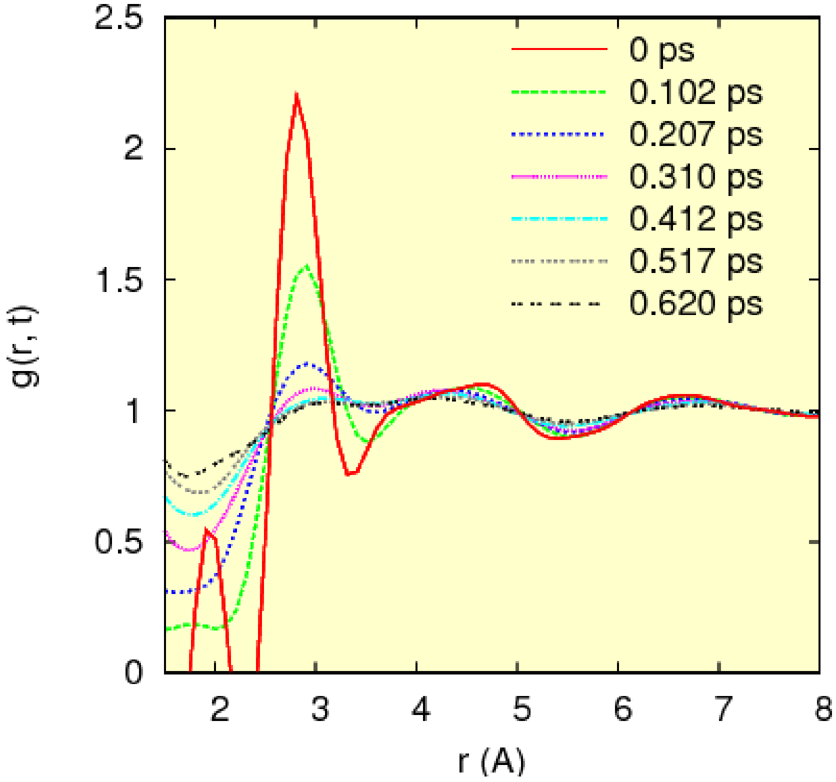


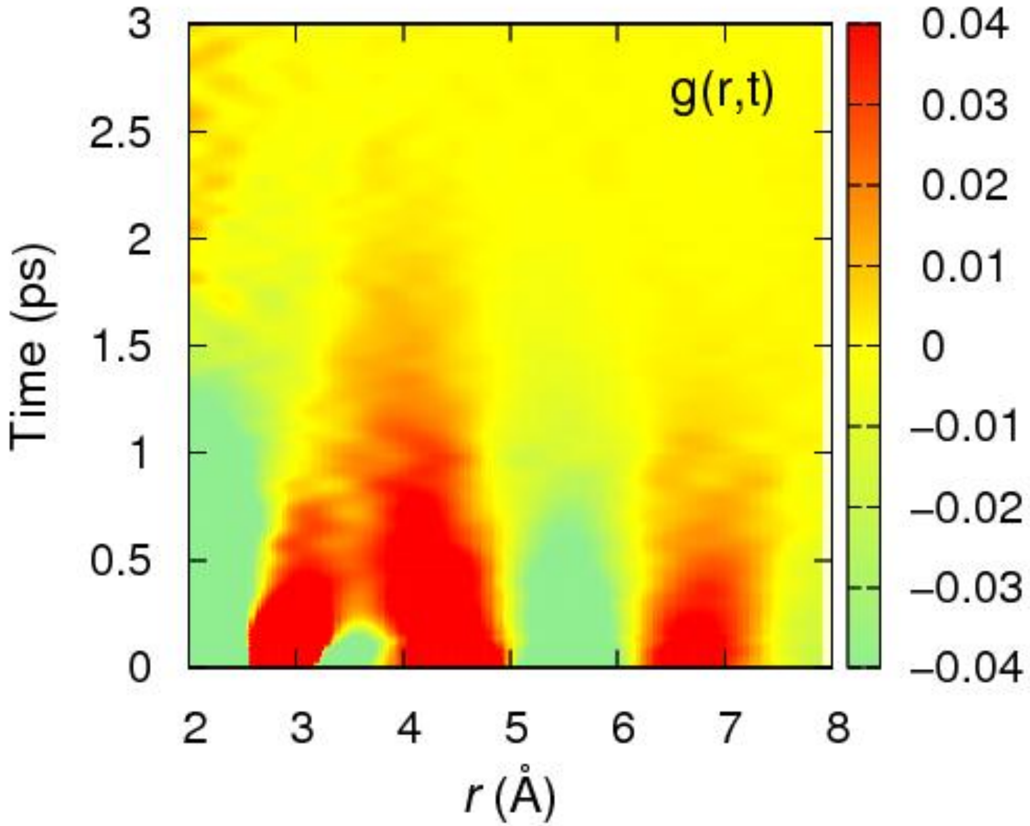
$$\tau_M = \tau_{LC}$$

- **Fe: Johnson potential**
- **KA: Kob-Andersen potential ($Ni_{80}P_{20}$)**
- **$Cu_{56}Zr_{44}$: EAM**
- **$Zr_{50}Cu_{40}Al_{10}$: EAM**
- **$Cu_{56}Zr_{44}$: DFT-MD**

T. Iwashita, D. M. Nicholson and T. Egami, *Phys. Rev. Lett.*, **110,** 205504 (2013)

Van Hove Function by IXS





$$\rho_X^{at}(r,t)$$

Conclusions

- **Plenty of new information hidden in inelastic diffuse scattering.**
- **Total inelastic scattering: The future.**
- **Dynamic PDF and Van Hove function to interpret the data.**
- **Measurement of S(Q,ω) limited by flux, E resolution and Q range**
- **Development of high flux IXS highly anticipated**