

# Quantum liquids in Nanoporous Media and on Surfaces

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National Nanotechnology Initiative  
Workshop on X-rays and Neutrons  
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# Goals

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**Neutron scattering studies of structure and excitations of quantum liquids at nanoscales.**

**Impact of confinement on superfluidity, Bose-Einstein Condensation (BEC), phonon - roton modes and other modes.**

**Reveal the interdependence of Bose-Einstein Condensation (BEC), phonon-roton excitations and superfluidity.**

**Compare liquid  $^4\text{He}$  in bulk and at nanoscales.**

**Structure of  $^4\text{He}$  on and in nanotubes.**

# Science

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**Science drives tools.**

**High neutron flux**

**High resolution spectrometers**

**Variety of spectrometers**

**Analyze large data sets**

**Science drives materials.**

**Materials for nanoscale  
confinement.**

**Spectrum of pore sizes.**

**Uniform pore size**

**Large samples**

# Similar Science

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## Interplay of BEC and Superfluidity

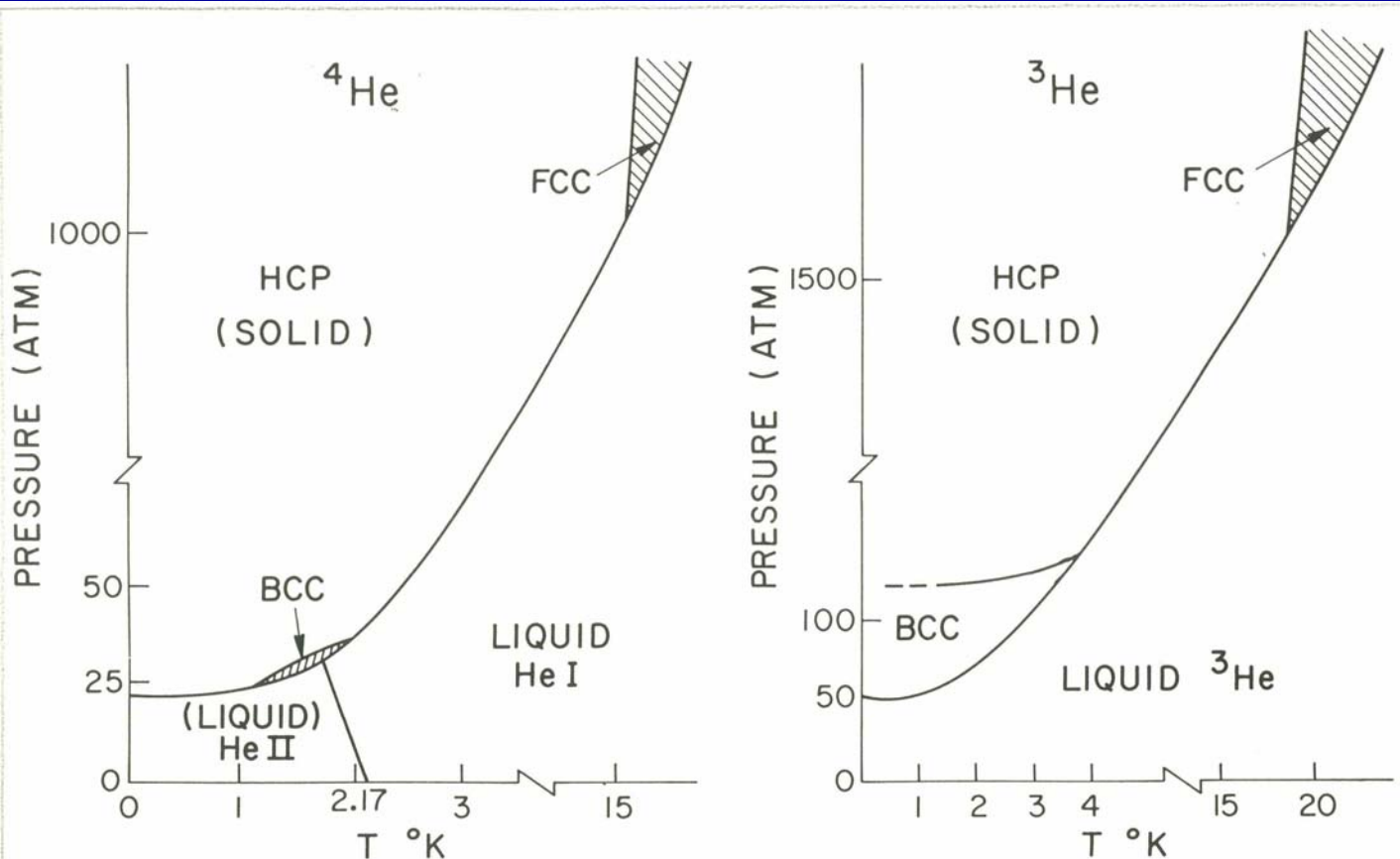
Josephson Junction Arrays.

Alkali atoms (bosons) in magnetic traps and optical lattices.

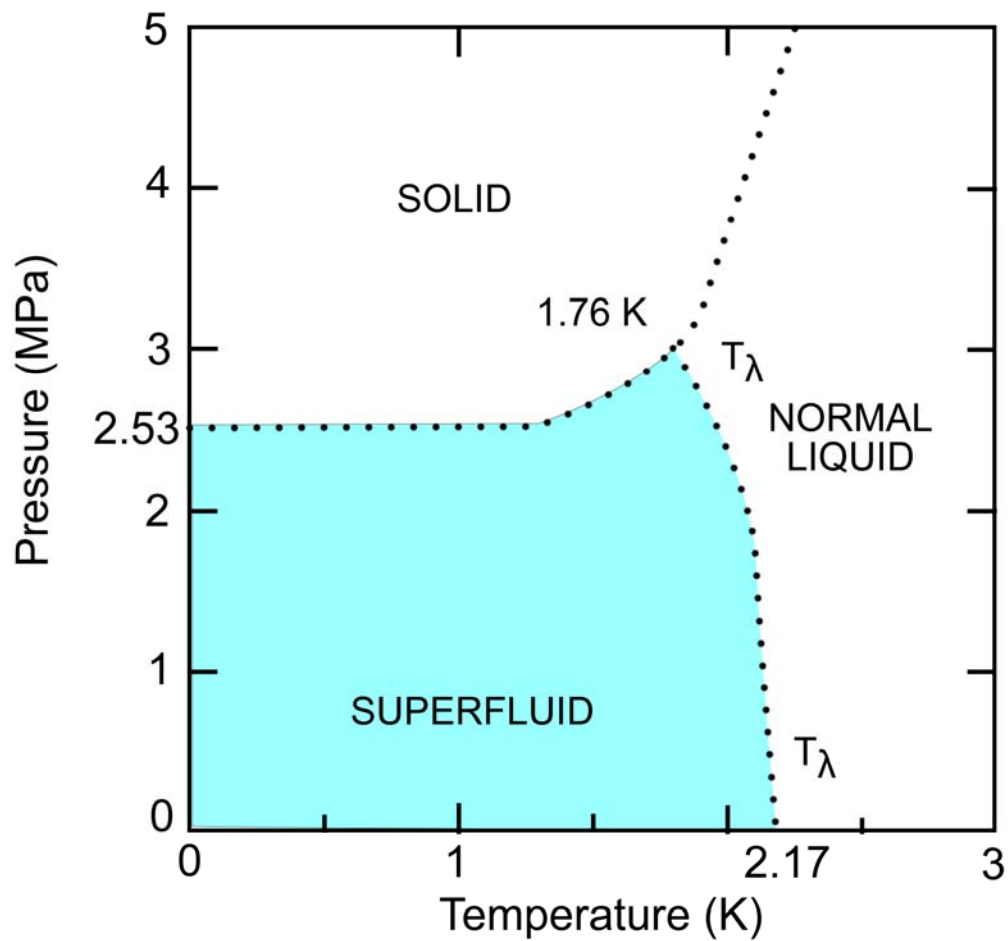
High Temperature superconductors.

Disordered thin films.

# Phase Diagram of Bulk Helium



# Phase Diagram of Bulk Helium



# Porous Media

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**AEROGEL\***                      95% porous  
    Open                        87% porous      A  
                                     87% porous      B  
- Some grown with deuterated materials

**VYCOR (Corning)**                      30% porous  
    70 Å pore Dia.                      -- grown with B<sup>11</sup> isotope

**GELSIL (Geltech, 4F)**                      50% porous  
    25 Å pores  
    44 Å pores  
    34 Å pores

**MCM-41**                                      30% porous  
    47 Å pores

**NANOTUBES (Nanotechnologies Inc.)**

Inter-tube spacing in bundles 1.4 nm  
2.7 gm sample

\* University of Delaware, University of Alberta

# Superfluid Properties at Nanoscales

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Confinement reduces  $T_c$  below  $T_\lambda = 2.17K$  .

Confinement modifies  $\rho_s(T)$  ( $T$  dependence).

Confinement reduces  $\rho_s(T)$  (magnitude).

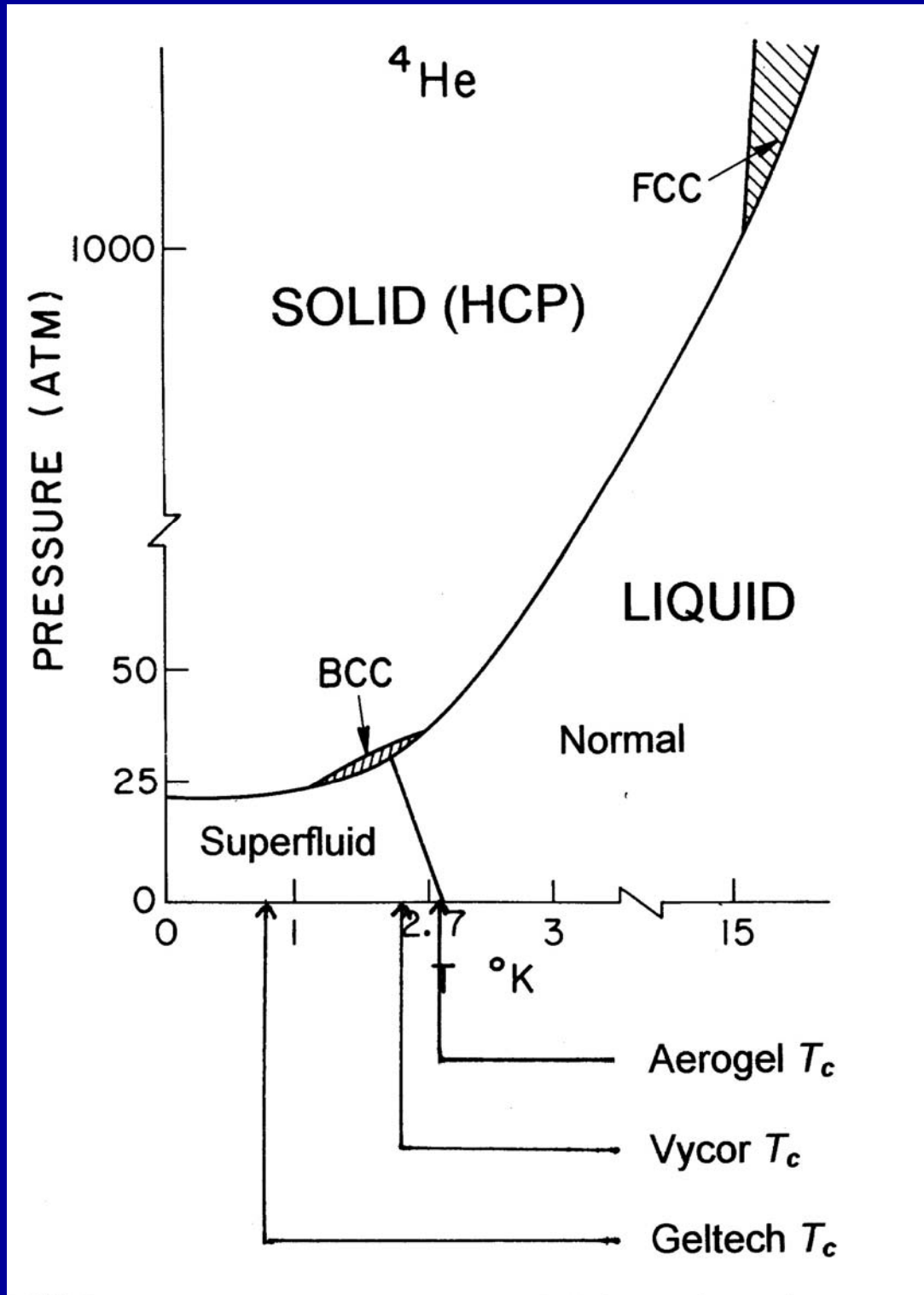
Porous media is a “laboratory” to investigate the relation between superfluidity, excitations, and BEC.

Measure corresponding excitations and condensate fraction,  $n_0(T)$ . (new, 1998)

**Localization of Bose-Einstein Condensation by Disorder**



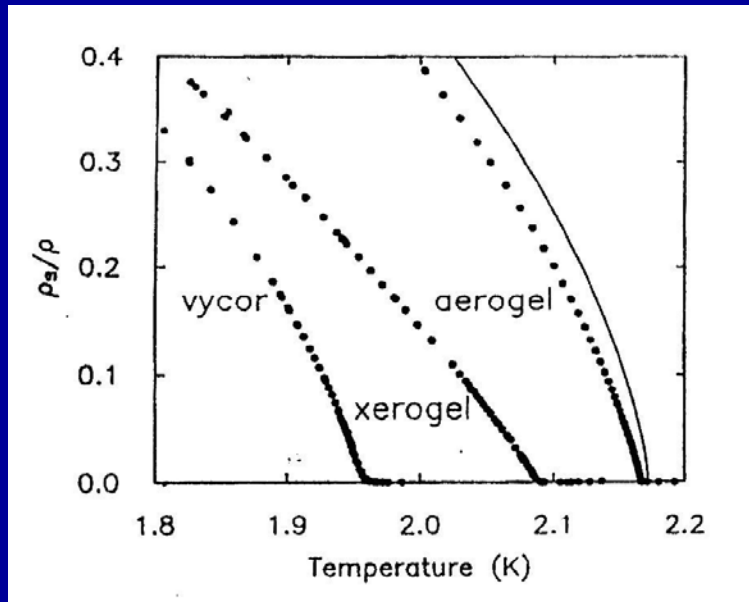
# $T_c$ in Porous Media



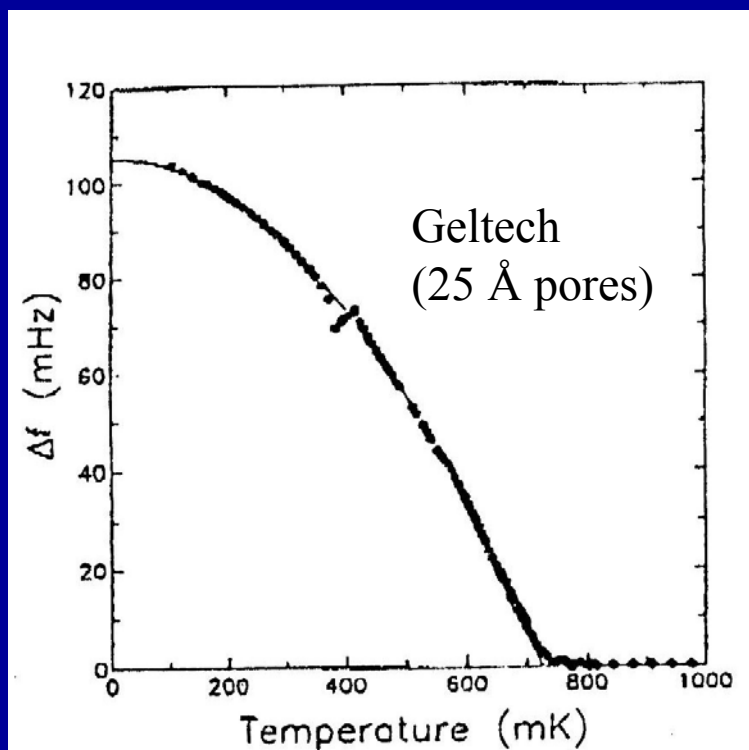
# Superfluid Density in Porous Media

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Chan *et al.* (1988)

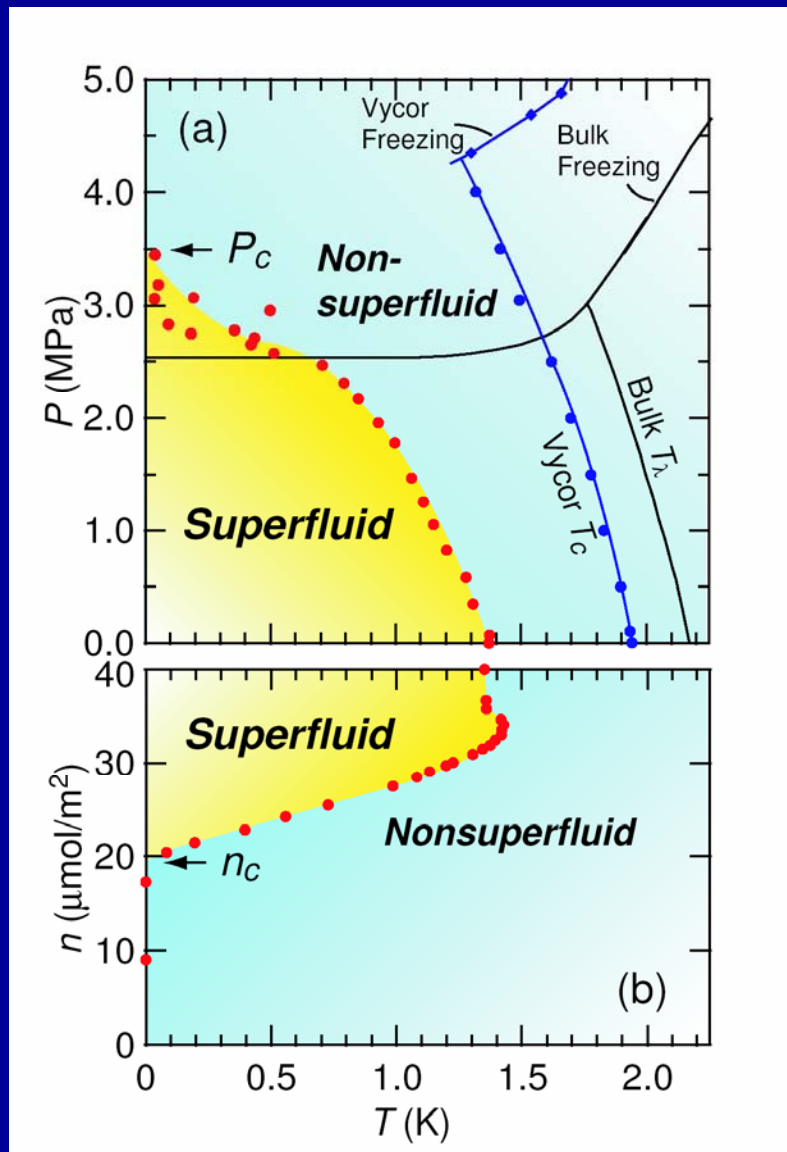


Miyamoto and Takeno (1996)

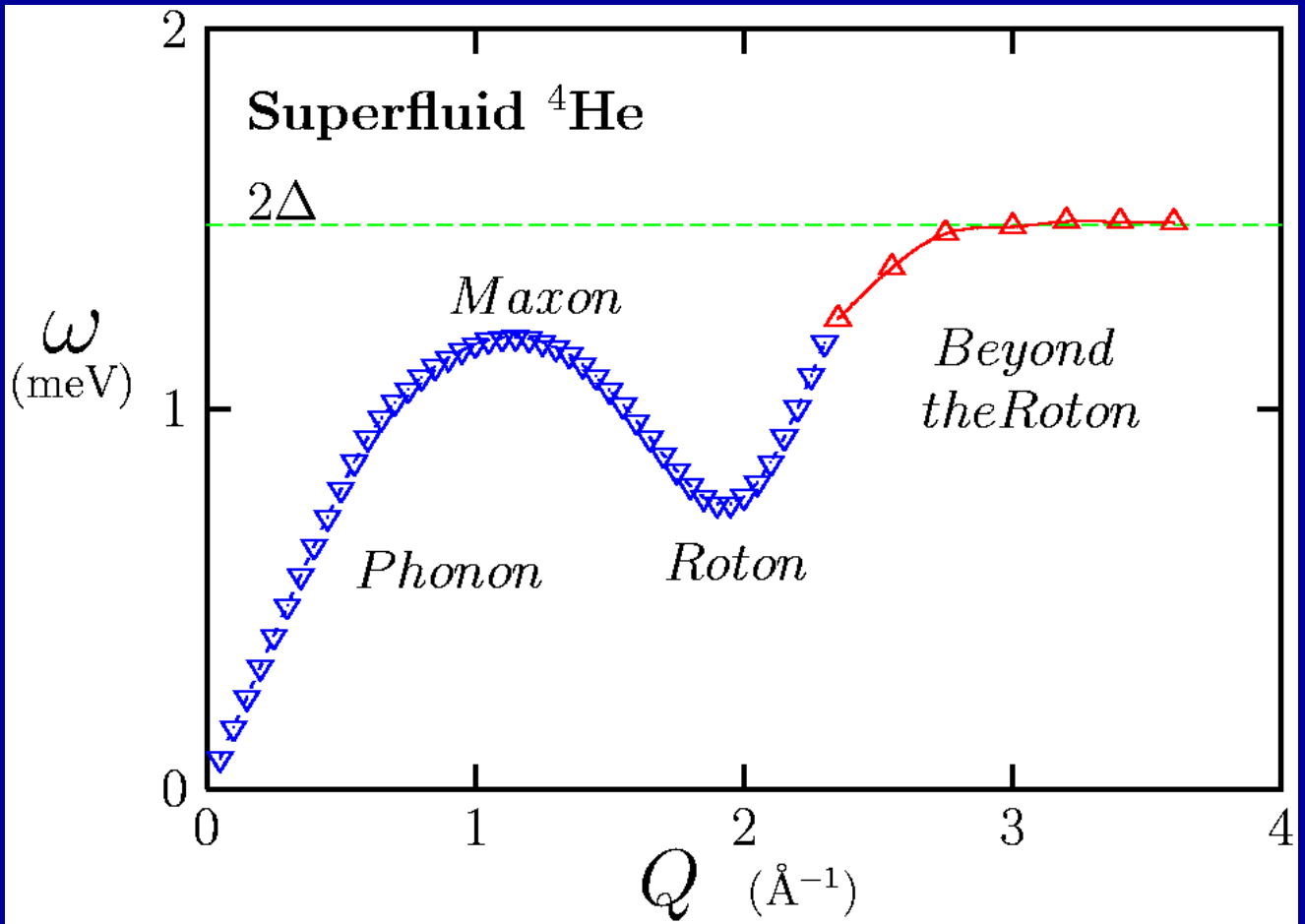


# Phase Diagram of gelsil: nominal 25 Å pore diameter

- Yamamoto et al,  
Phys. Rev. Lett. 93, 075302 (2004)

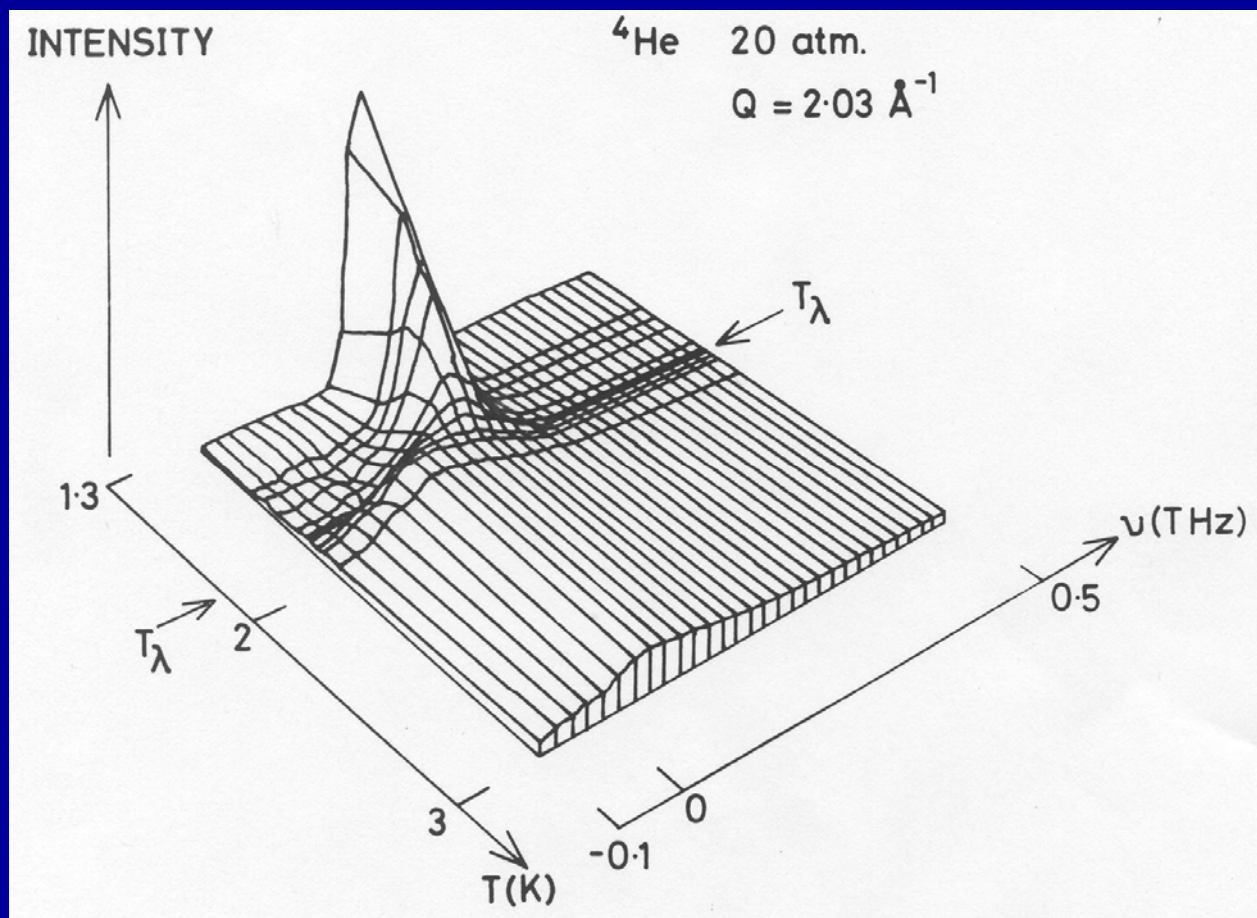


# Phonon-Roton Dispersion Curve



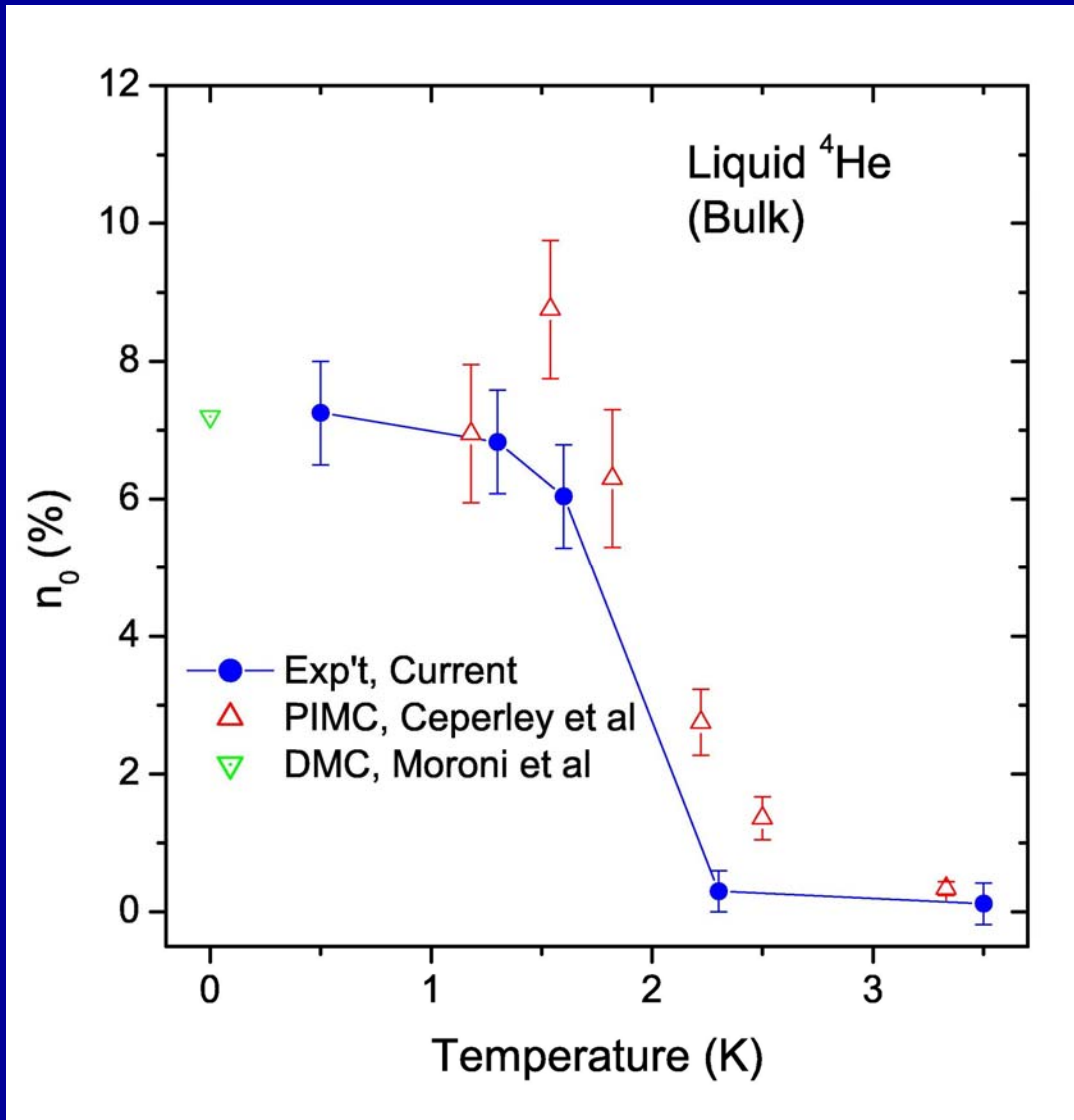
- $\nabla$  Donnelly *et al.*, *J. Low Temp. Phys.* (1981)
- $\triangle$  Glyde *et al.*, *Euro Phys. Lett.* (1998)

# Roton in Bulk Liquid $^4\text{He}$



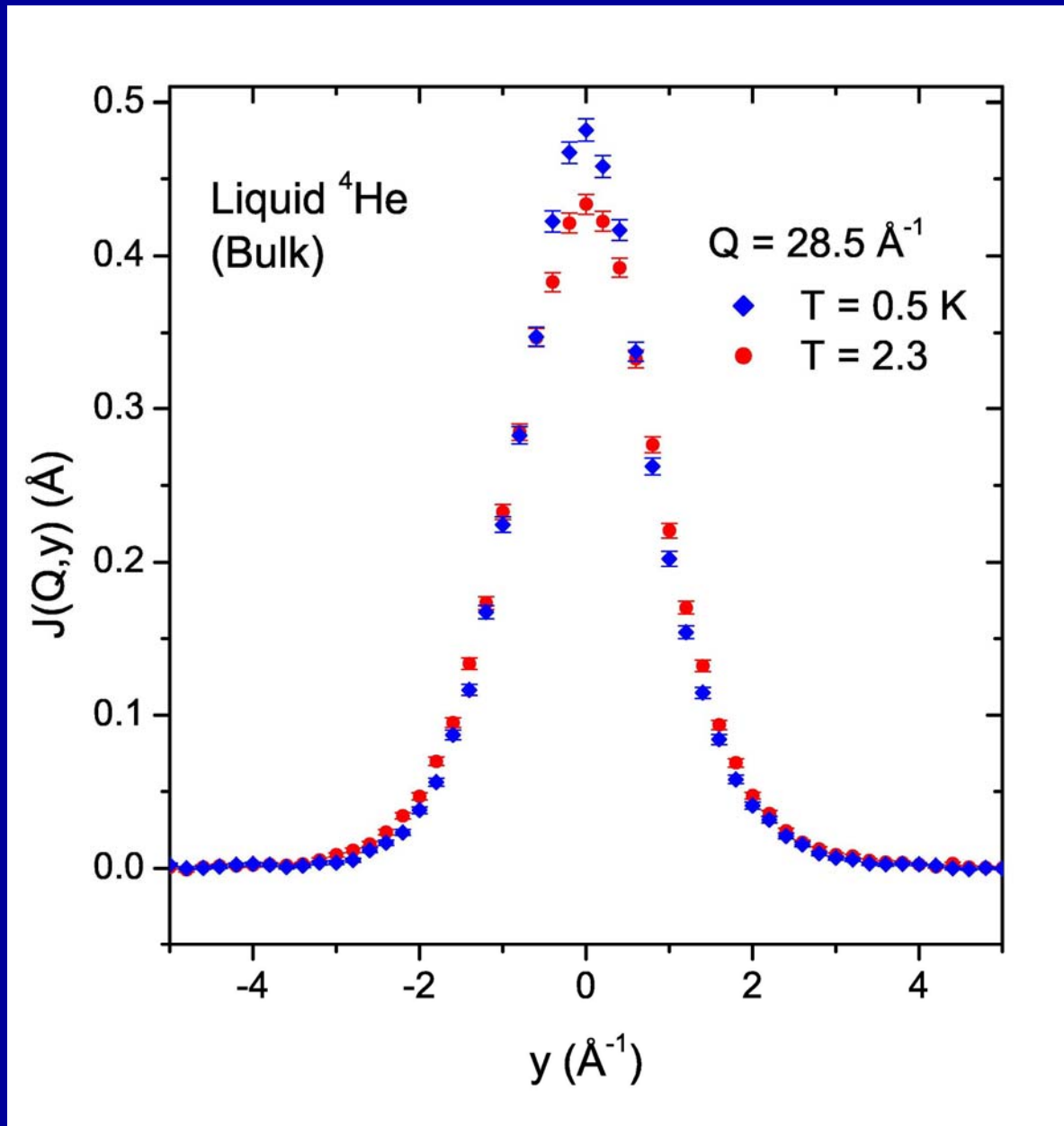
Talbot *et al.*, PRB, 38, 11229 (1988)

# Bose-Einstein Condensation



$$n_0(T) = n_0(0) \left[ 1 - \left( \frac{T}{T_\lambda} \right)^\gamma \right],$$

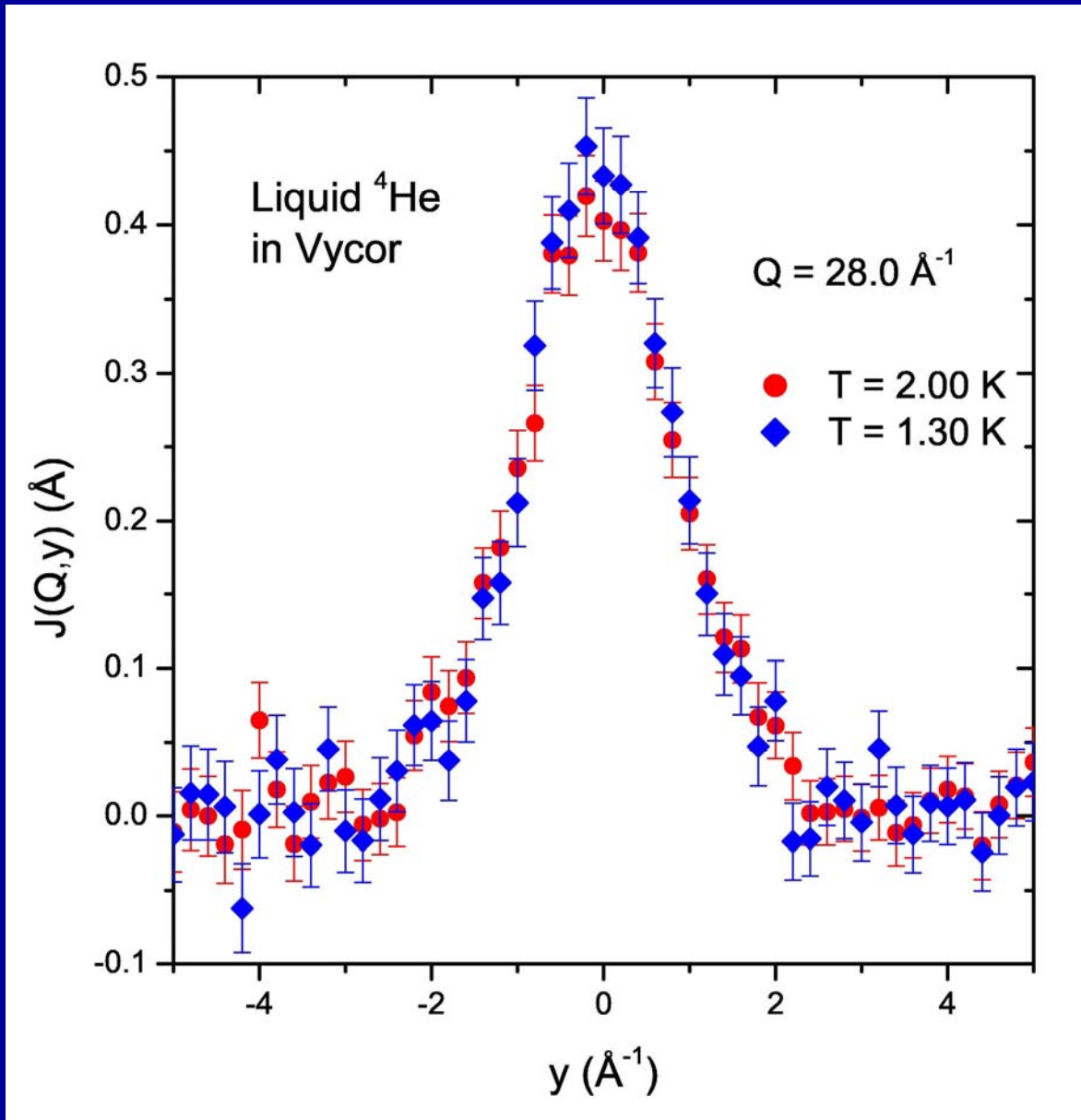
# Bose-Einstein Condensation



Glyde, Azuah, and Sterling  
*Phys. Rev.*, 62, 14337 (2001)

# Bose-Einstein Condensation Liquid $^4\text{He}$ in Vycor

$$T_c \text{ (Superfluidity)} = 1.95\text{-}2.05 \text{ K}$$

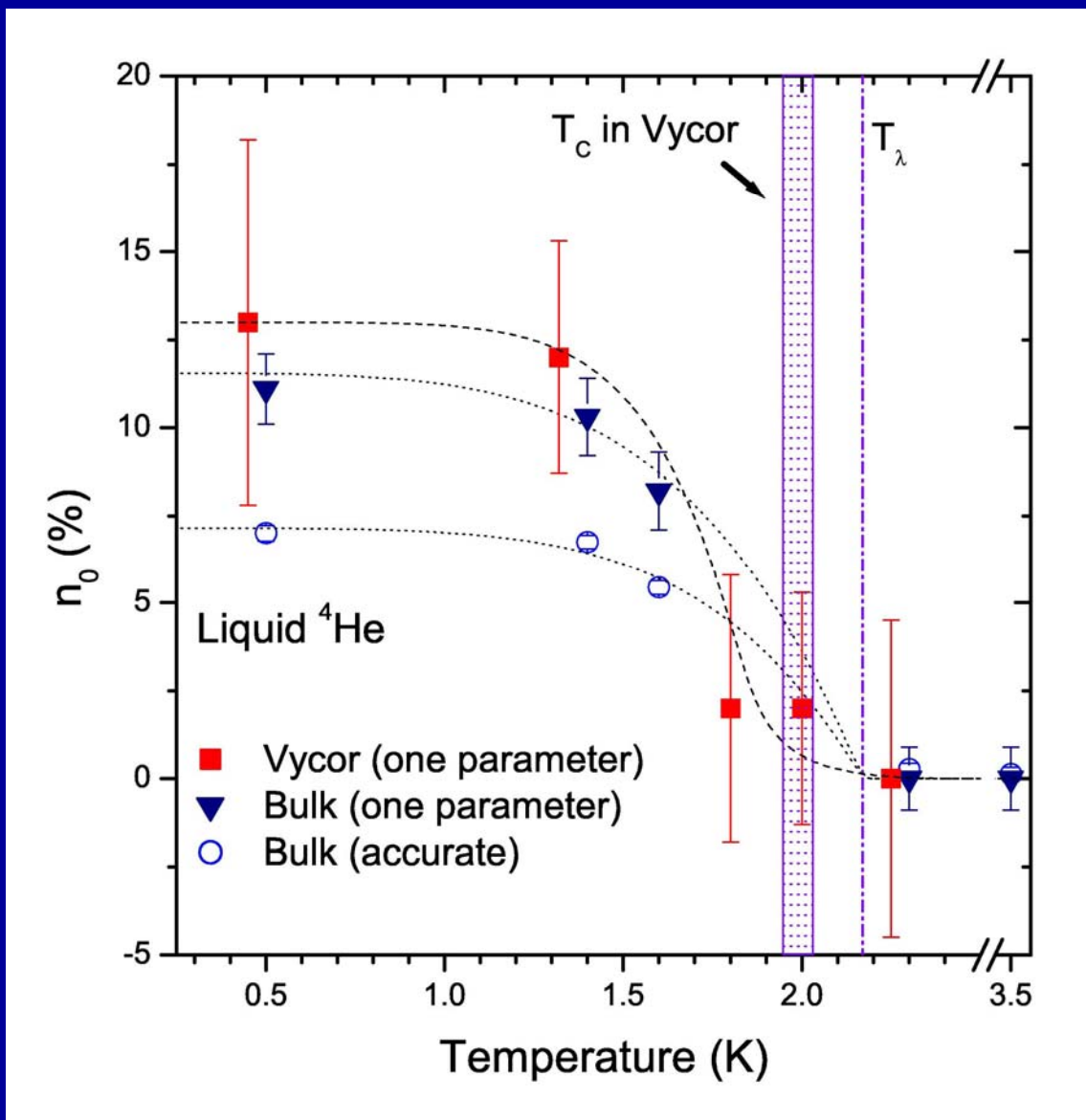


Azuah *et al.*, JLTP (2003)



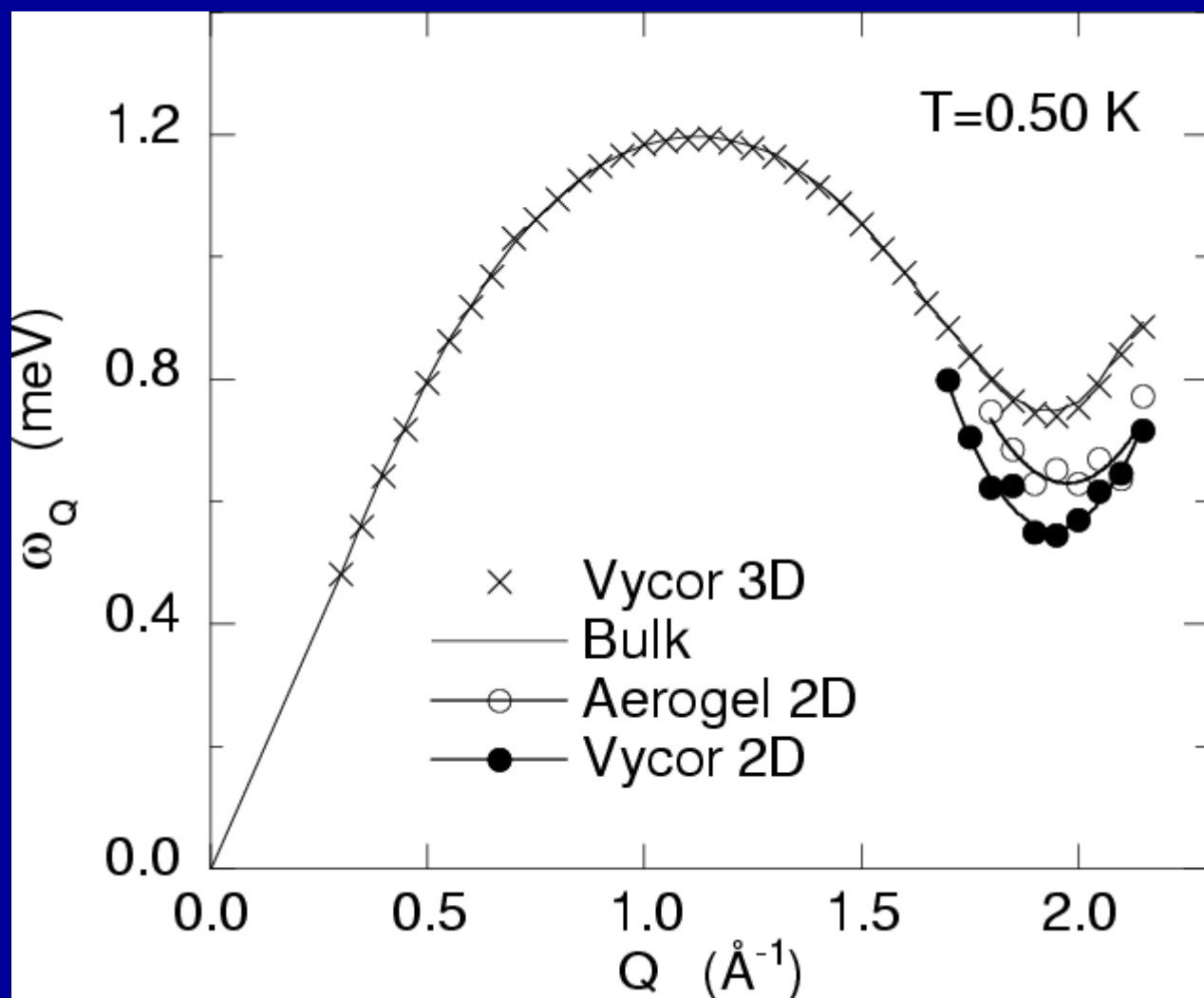
# Bose-Einstein Condensation Liquid $^4\text{He}$ in Vycor

$$T_c \text{ (Superfluidity)} = 1.95\text{-}2.05 \text{ K}$$

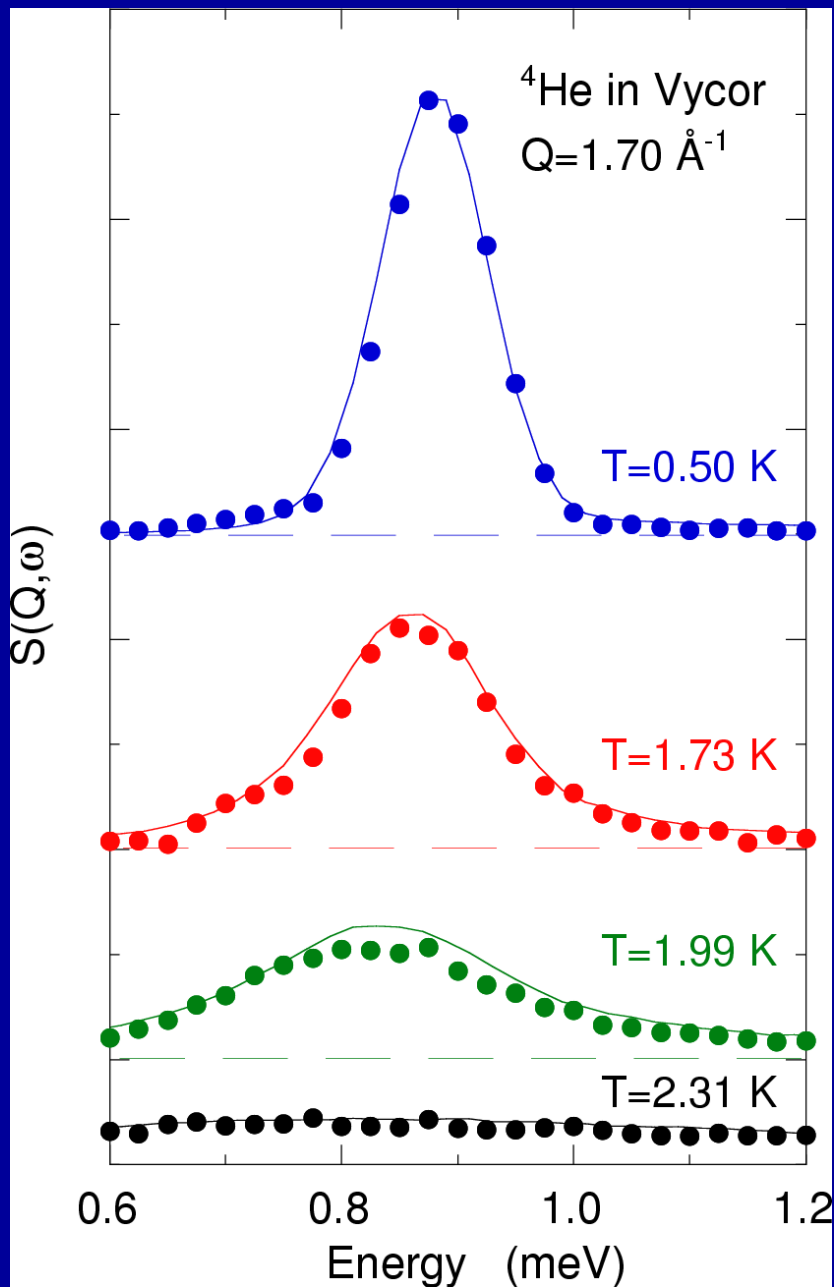


Azuah *et al.*, JLTP (2003)

# Phonons, Rotons, and Layer Modes in Vycor and Aerogel

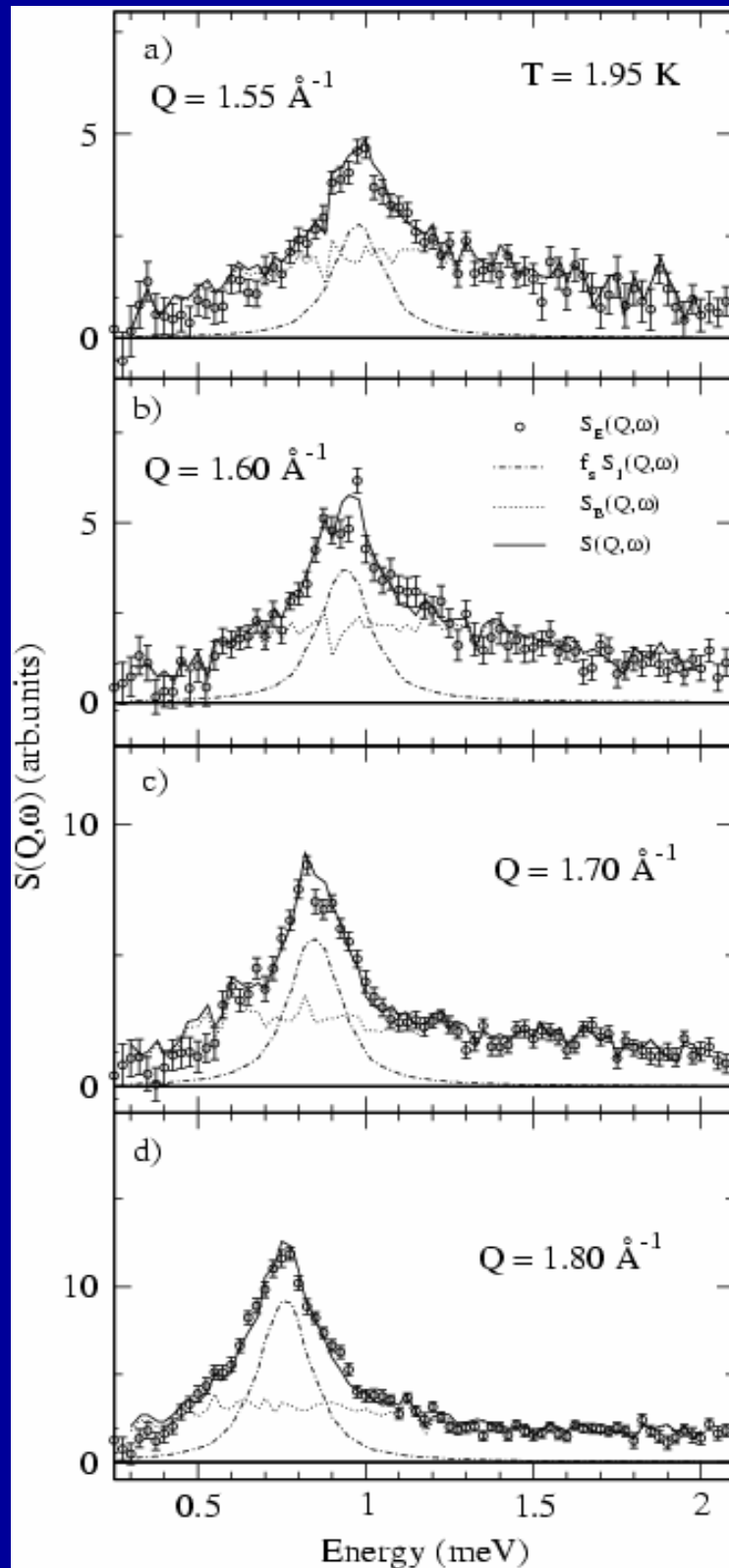


# Intensity in Single Excitation vs. $T$

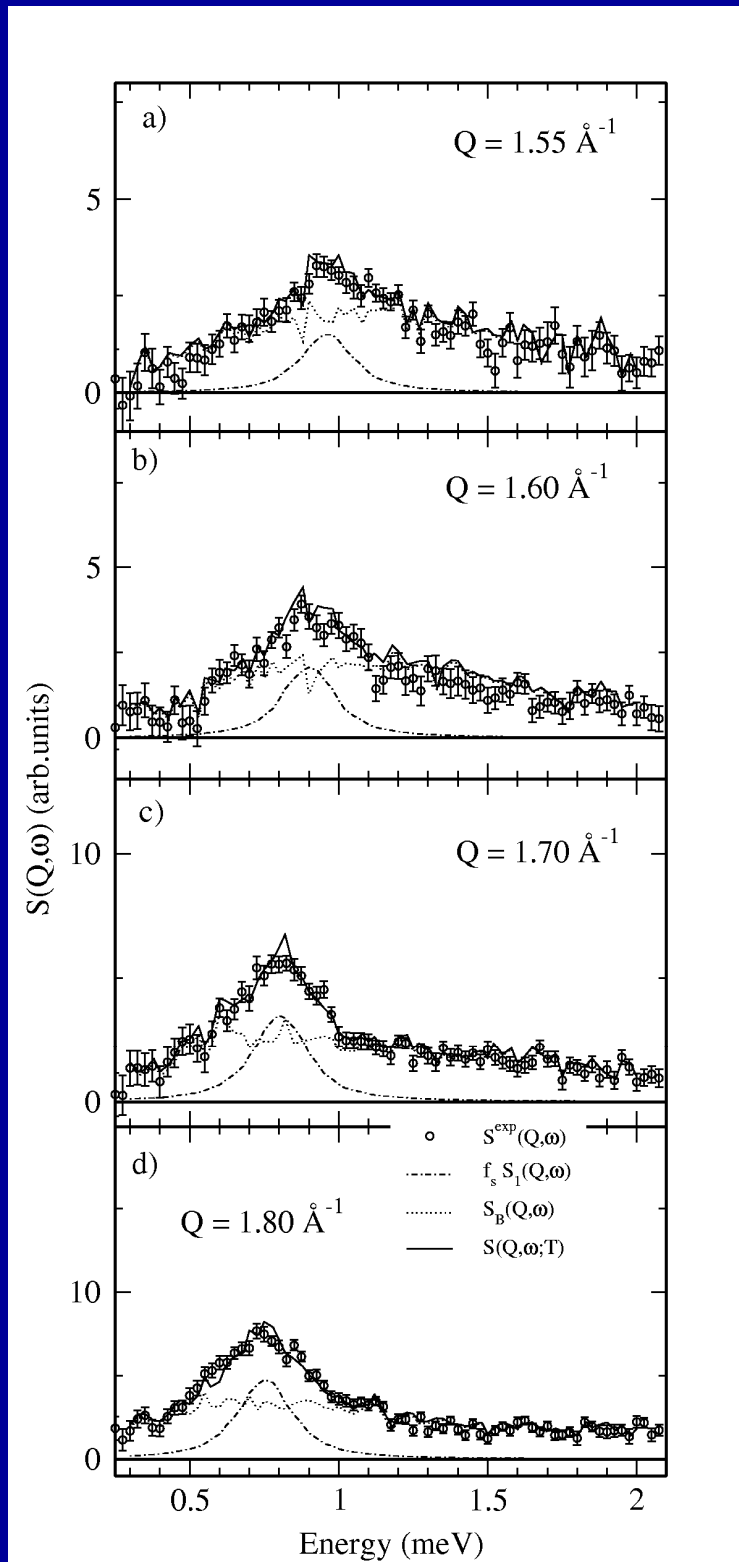


Glyde *et al.*, PRL, 84 (2000)

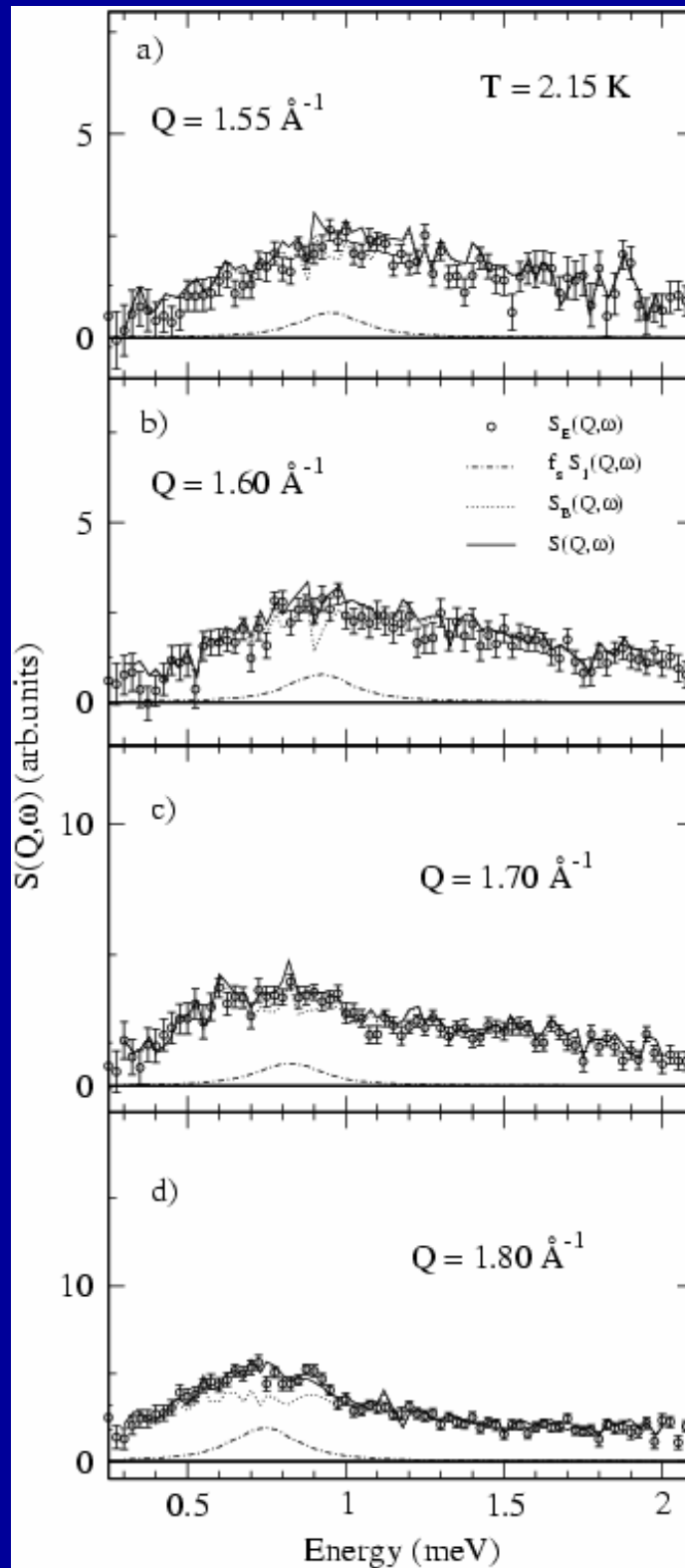
# Phonon-Roton Mode in Vycor: $T = 1.95 \text{ K}$



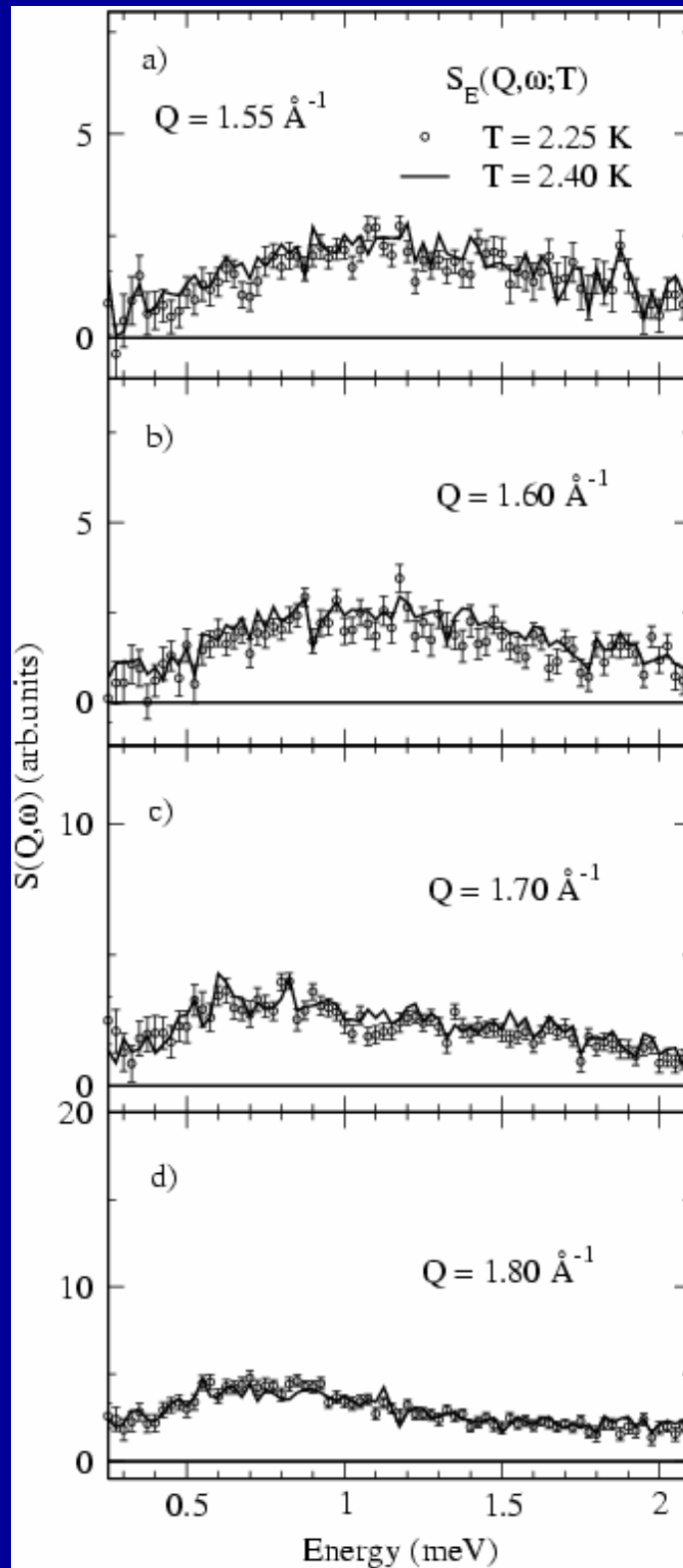
# Phonon-Roton Mode in Vycor: $T = 2.05 \text{ K}$



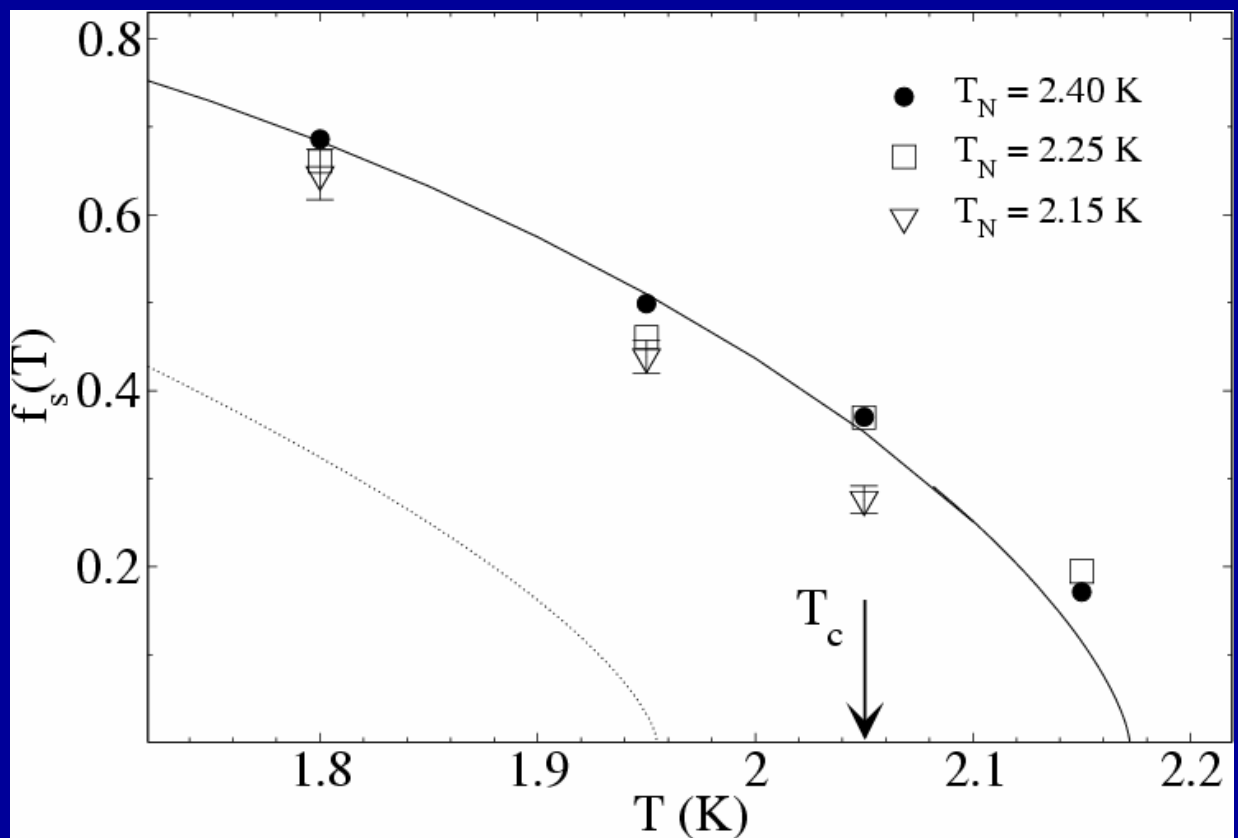
# Phonon-Roton Mode in Vycor: $T = 2.15 \text{ K}$



# Phonon-Roton Mode in Vycor: $T = 2.25 \text{ K}$



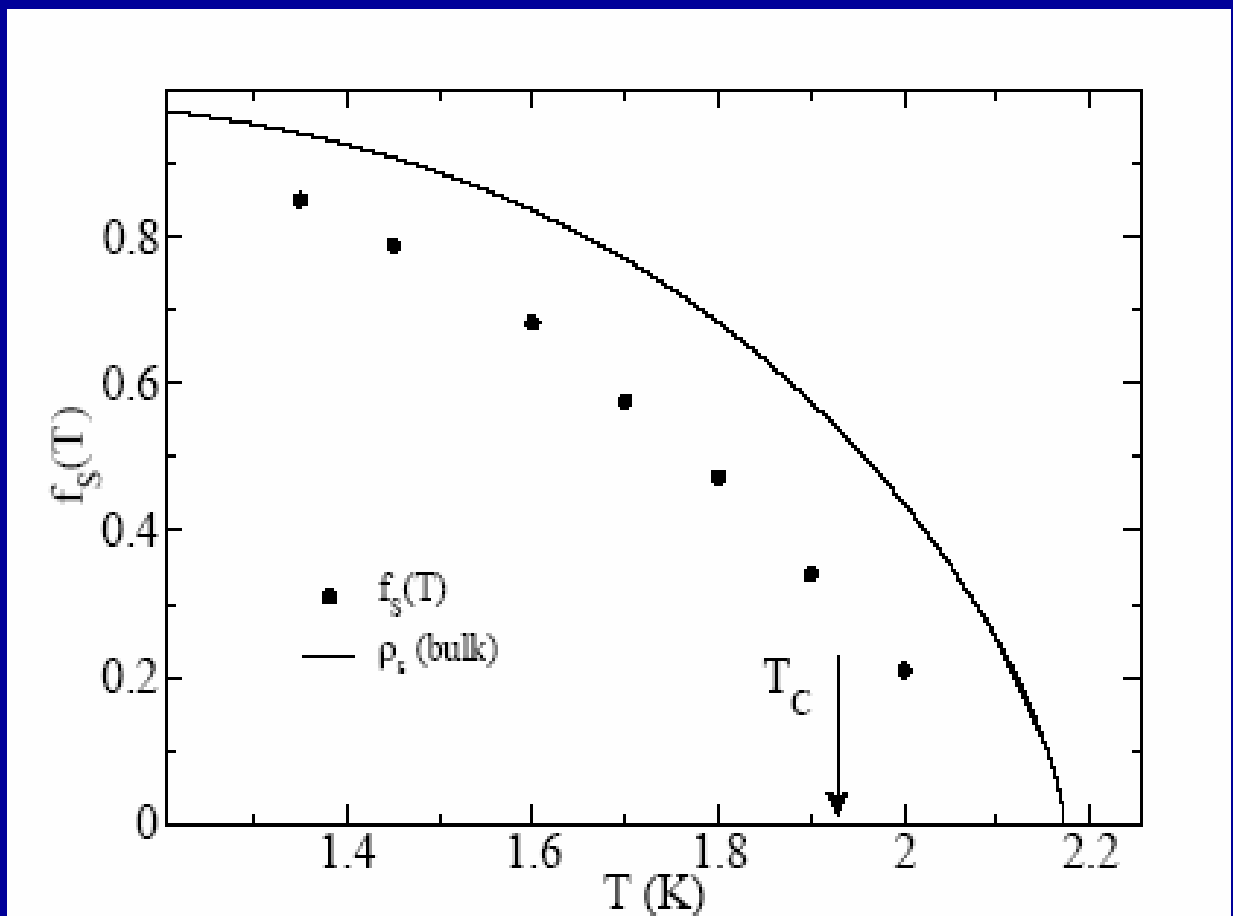
# Fraction, $f_s(T)$ , of Total Scattering Intensity in Phonon-Roton Mode - Vycor 70 A pores





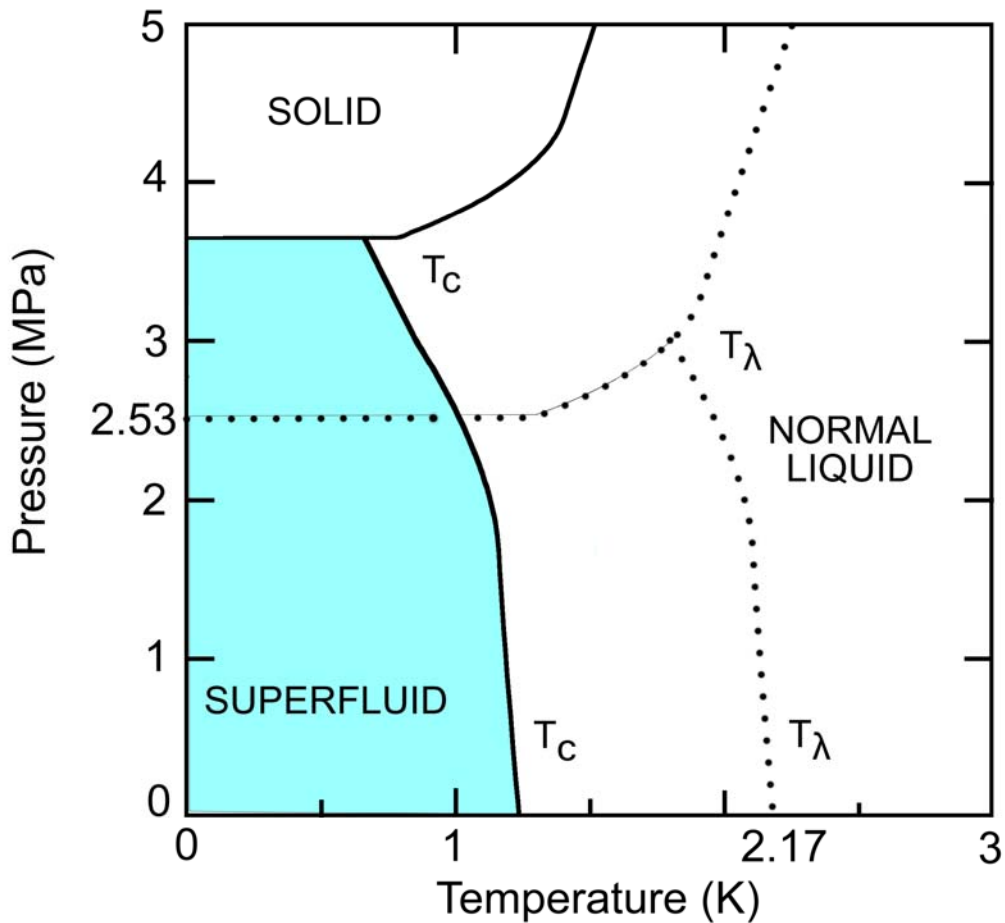
# Fraction, $f_s(T)$ , of total scattering intensity in Phonon-Roton Mode - gelsil 44 A pore diameter

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# Schematic Phase Diagram of Helium Confined to Nanoscales

e.g. 2 - 3 nm



# Excitations of superfluid $^4\text{He}$ at pressures up to 40 bars

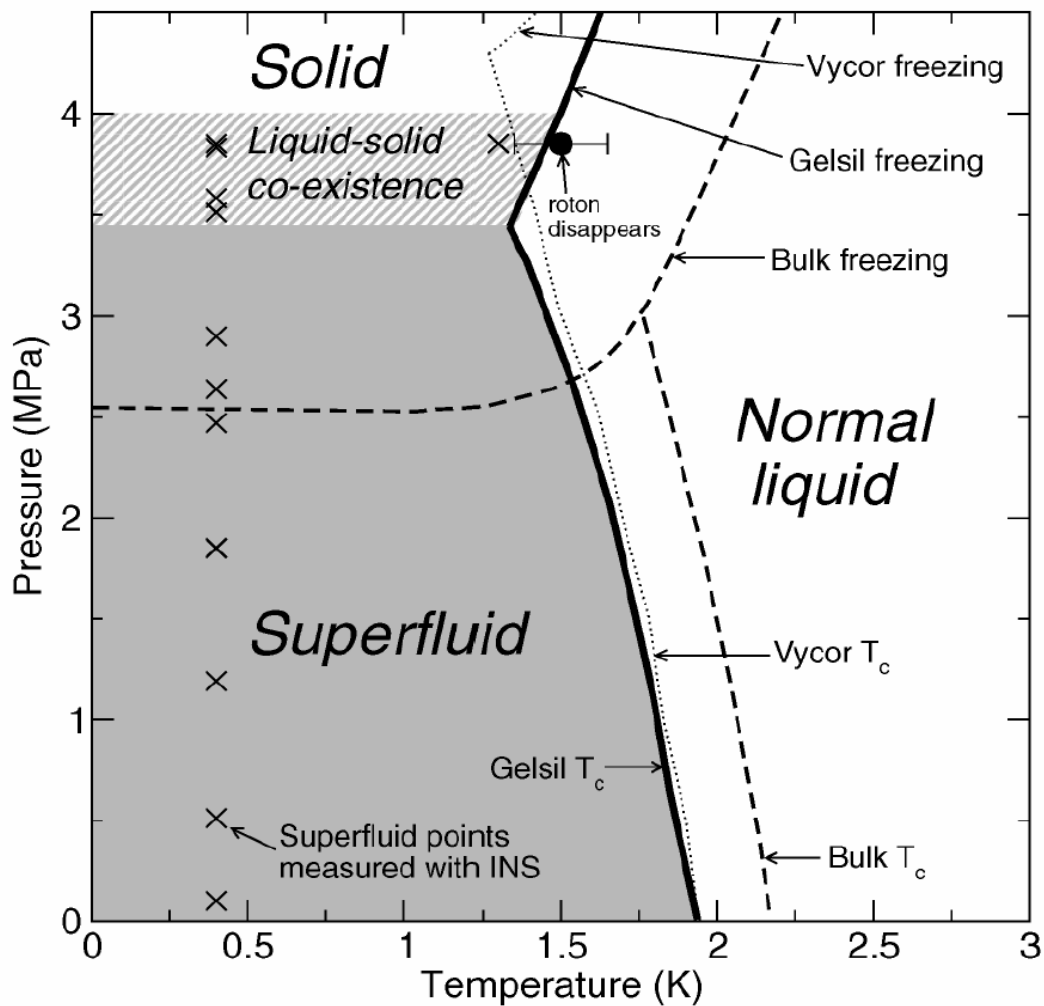
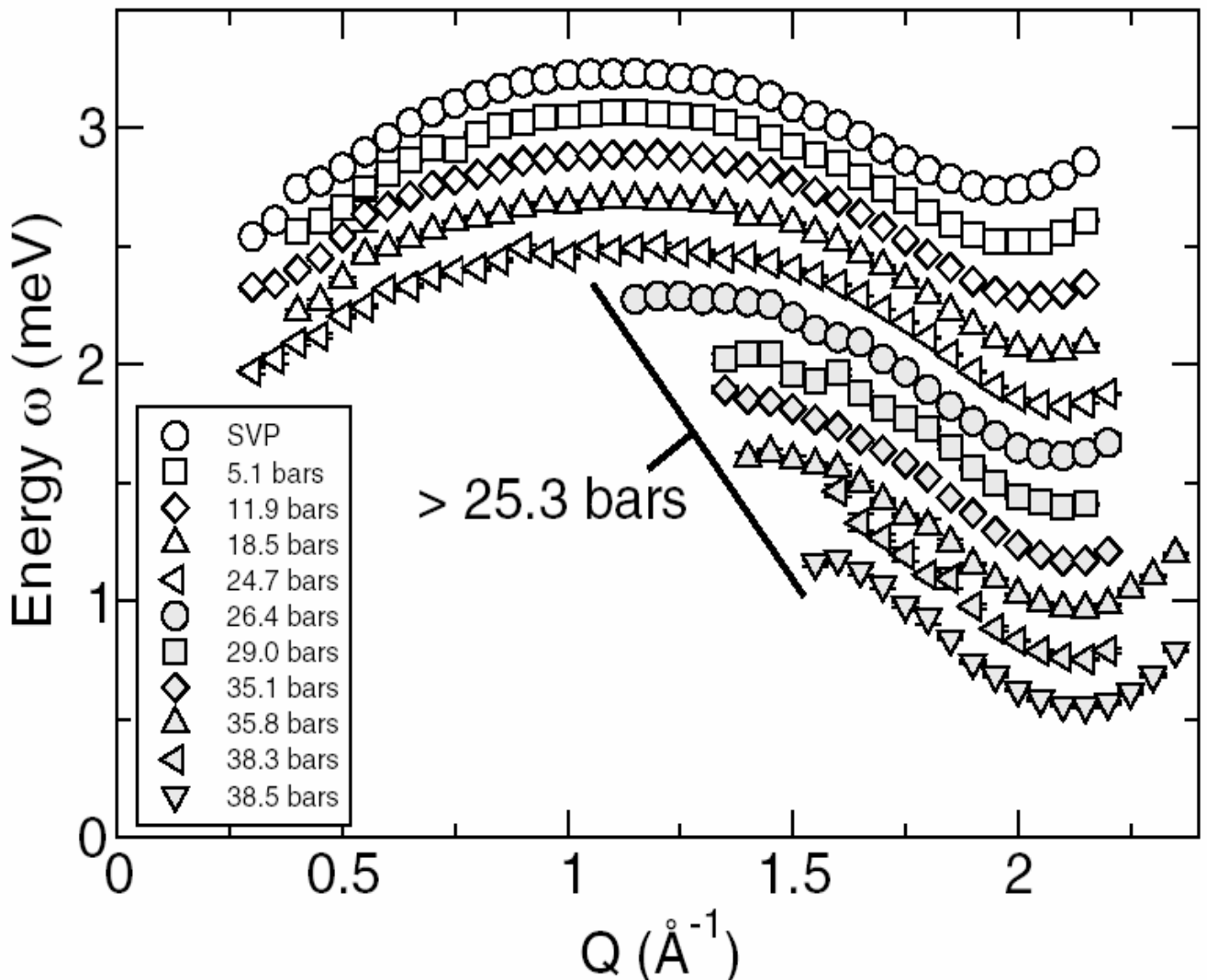


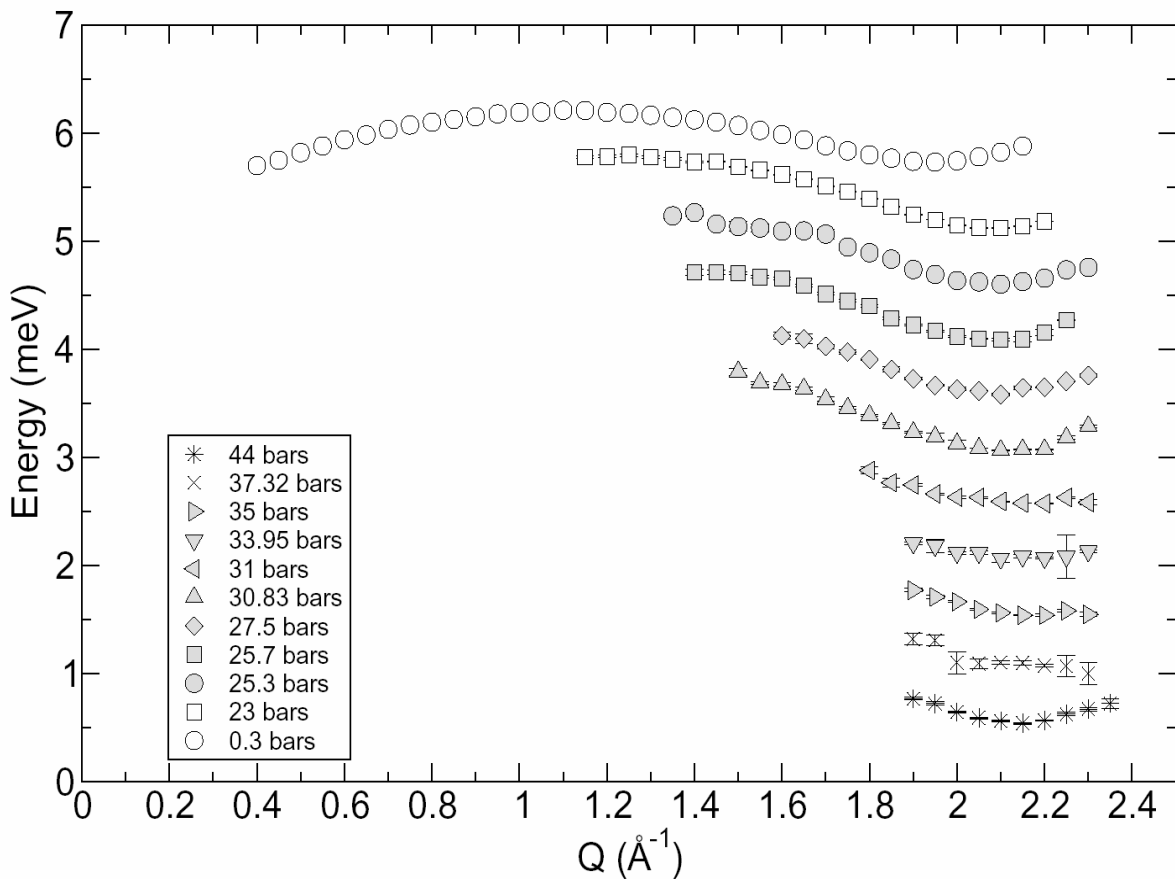
FIG. 1. Phase diagram of  $^4\text{He}$  confined in 44 Å porous gelsil.

# Excitations of superfluid $^4\text{He}$ at pressures up to 40 bars



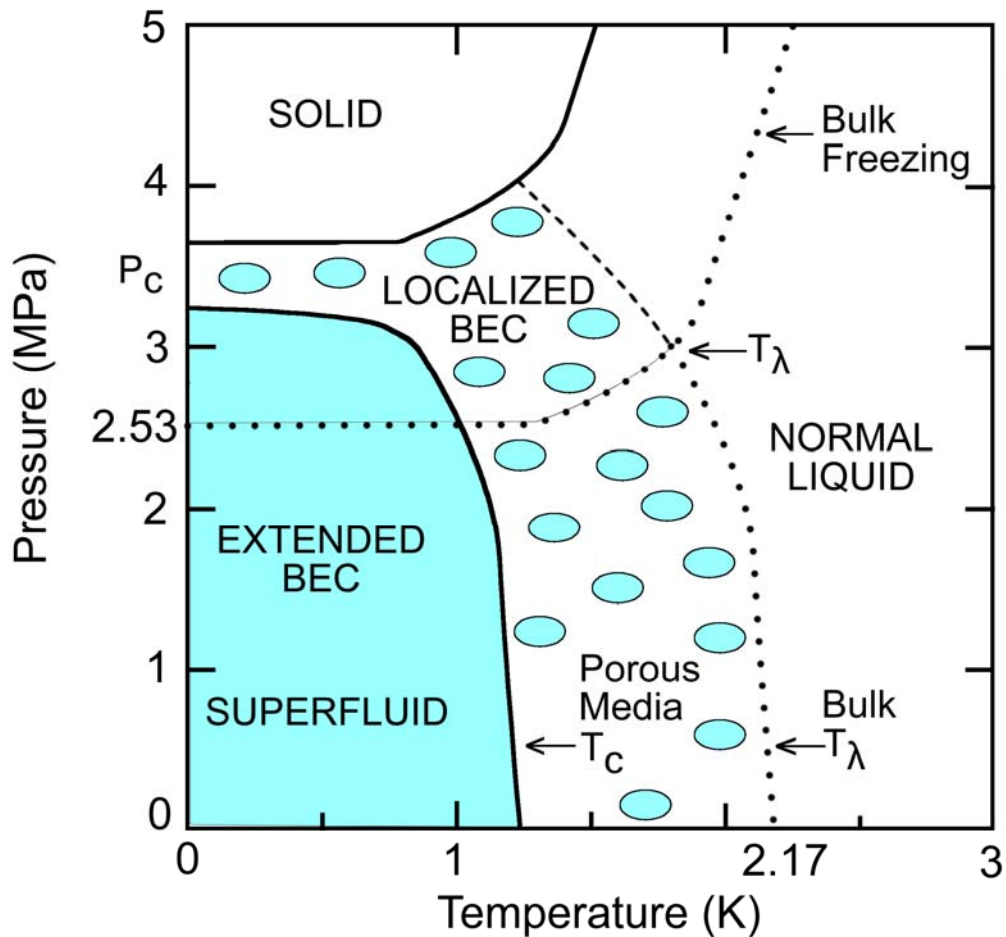
# Excitations of superfluid $^4\text{He}$ at pressures up to 44 bars

## 3.3 nm pore diameter gelsil



# Schematic Phase Diagram in Ideal Nanoscale media

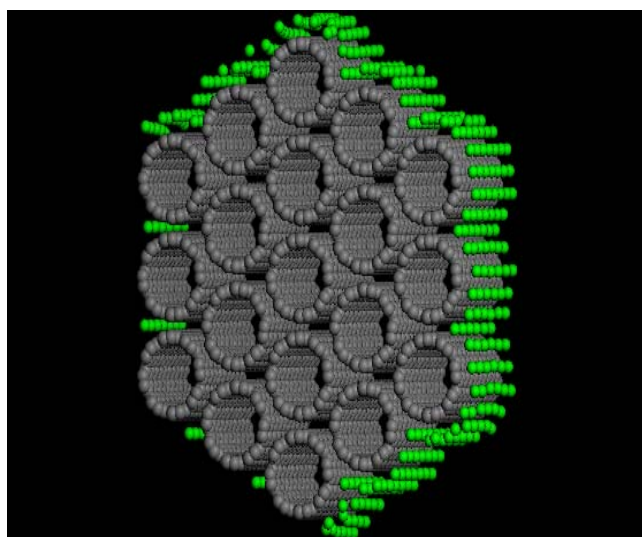
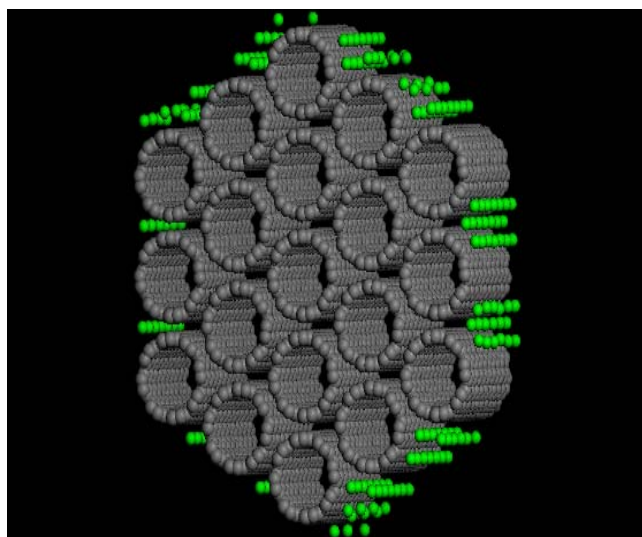
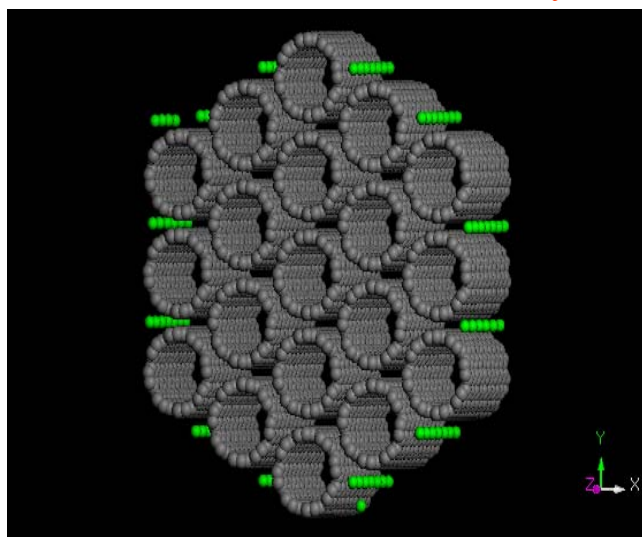
e.g. 2 - 3 nm



# Structure of $^4\text{He}$ adsorbed on carbon nanotubes

*J.V. Pearce, M.A. Adams, O.E. Vilches, M. Johnson, and H.R. Glyde*

*Figure: Helium on closed end nanotube bundles; green spheres are  $^4\text{He}$  atoms, grey spheres are carbon atoms. The configurations, generated using molecular dynamics simulations, reproduce neutron measurements. Top: 1D lines of  $^4\text{He}$  atoms, middle: “3-line phase”, bottom: 1 monolayer coverage (2D system).*



Carbon nanotubes are sheets of carbon atoms rolled into seamless cylinders of 1-2 nanometers diameter and thousands of nanometers long. They combine into long bundles or ropes containing many tubes, as shown opposite. Nanotubes are of great interest for their unique, nearly one dimensional (1D) character and many applications.

We report the first measurements of the structure of helium absorbed on nanotubes using neutron scattering. The aim is to test many remarkable predictions especially for 1D system. Results show that a genuine 1D system can be created and that there is a 1D to 2D crossover as filling increases. Higher fillings with open-ended nanotubes remain to be explored.





# Momentum distribution solid $^4\text{He}$

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## Quantum momentum distribution and kinetic energy in solid $^4\text{He}$

S. O. Diallo,<sup>1</sup> J. V. Pearce,<sup>2</sup> R. T. Azuah,<sup>3,4</sup> and H. R. Glyde<sup>1</sup>

<sup>1</sup>*Department of Physics and astronomy, University of Delaware, Newark, DE 19716-2570*

<sup>2</sup>*Institut Laue-Langevin, BP 156, 38042, Grenoble, France*

*Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115*

<sup>4</sup>*NIST Center for Neutron Research, Gaithersburg, MD 20899-8562*

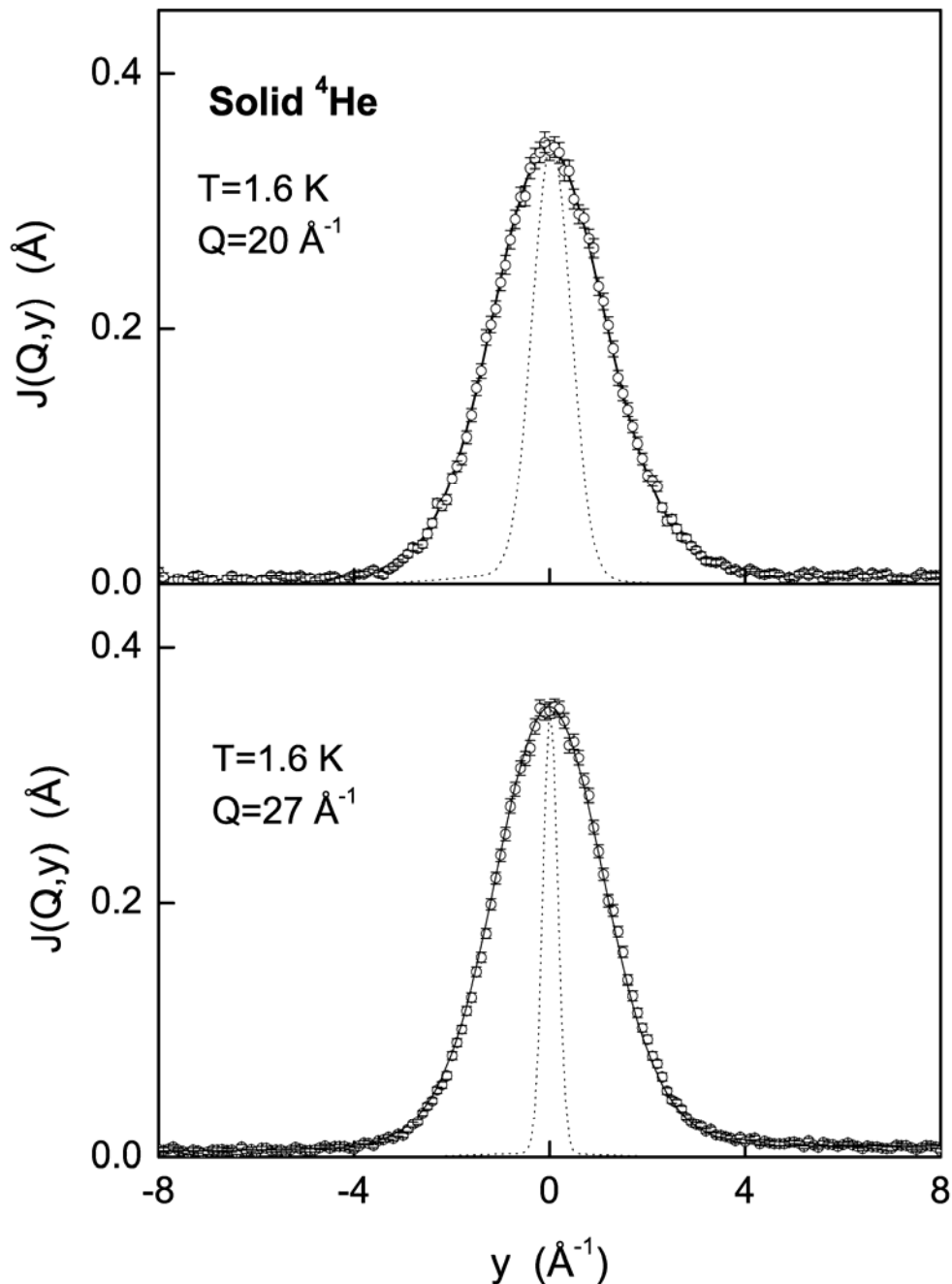
(Dated: May 28, 2004)

We present measurements of neutron scattering from solid  $^4\text{He}$  at high momentum transfer. The solid is held close to the melting line at molar volume  $20.87 \text{ cm}^3/\text{mol}$  and temperature  $T=1.6 \text{ K}$ . From the data, we determine the shape of the momentum distribution,  $n(\mathbf{k})$ , of atoms in the solid and the leading Final State contribution to the scattering. We show that  $n(\mathbf{k})$  in this highly anharmonic, quantum solid differs significantly from a Gaussian. The  $n(\mathbf{k})$  is more sharply peaked with larger occupation of low momentum states than in a Maxwell-Boltzmann distribution, as found in liquid  $^4\text{He}$  and predicted qualitatively by Path Integral Monte Carlo calculations. The atomic kinetic energy is  $\langle K \rangle = (24.25 \pm 0.2) \text{ K}$ . If  $n(\mathbf{k})$  is assumed to be Gaussian, as is usually the practice, a  $\langle K \rangle$  10% smaller is obtained.

PACS numbers: 67.80.-s 61.12.Ex 67.40.-w

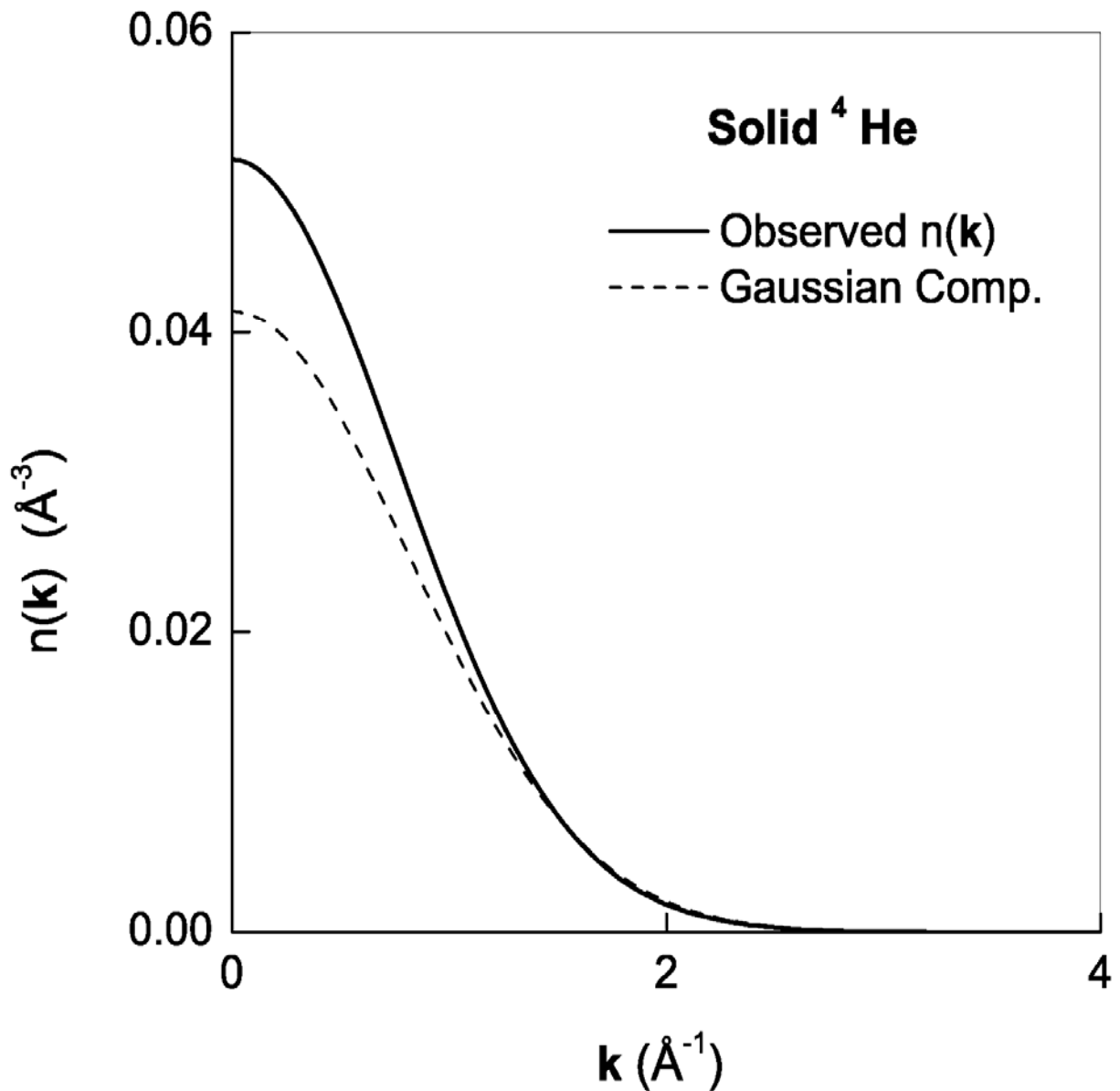


# Momentum distribution solid $^4\text{He}$

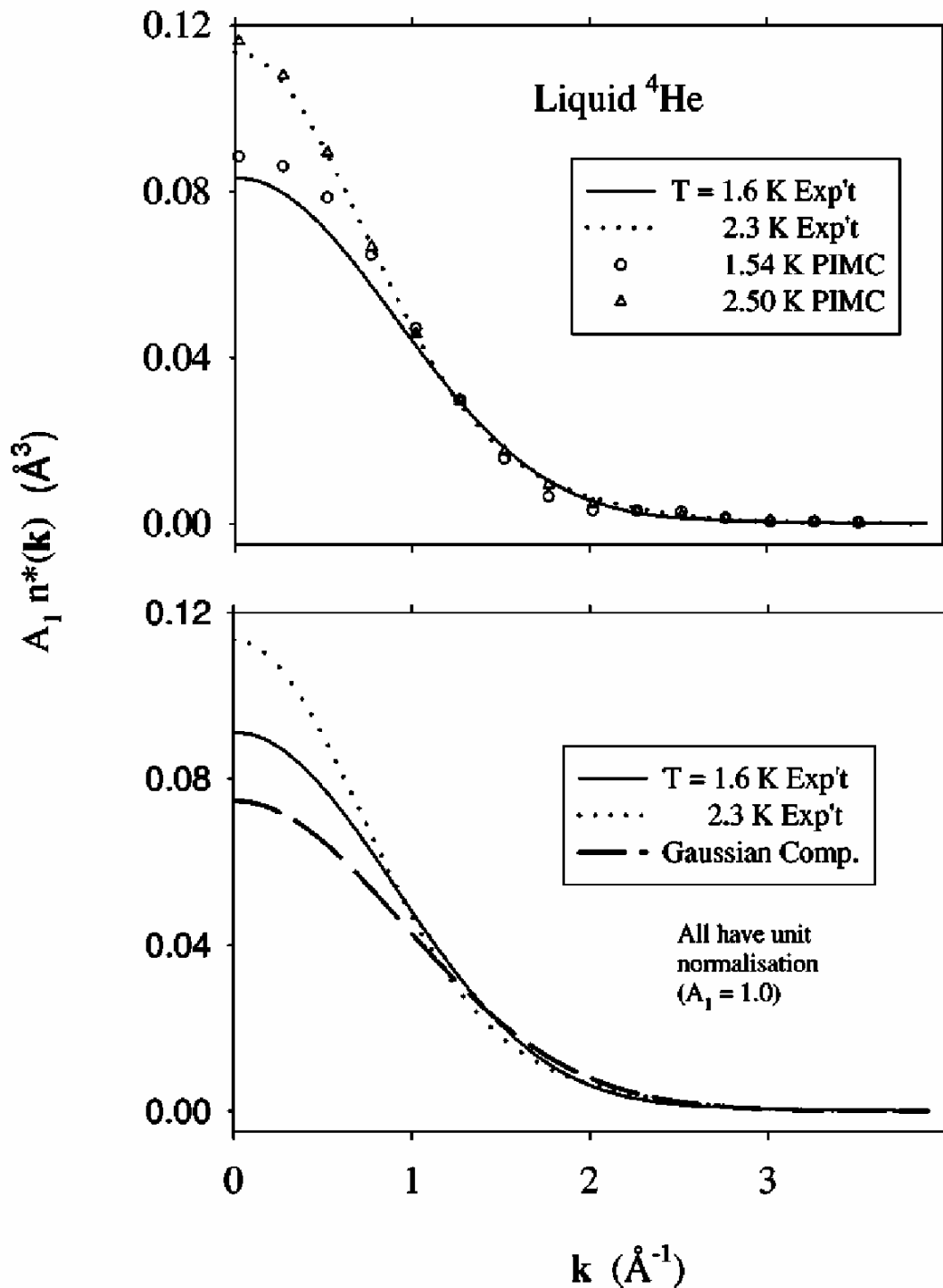


# Momentum distribution solid $^4\text{He}$

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# Momentum distribution: $^4\text{He}$



# Liquid $^4\text{He}$ at Negative Pressure

PHYSICAL REVIEW LETTERS

## Phonon-Roton Excitations in Liquid $^4\text{He}$ at Negative Pressures

Francesco Albergamo,<sup>1</sup> Jacques Bossy,<sup>2</sup> Pierre Averbuch,<sup>3</sup> Helmut Schober,<sup>1</sup> and Henry R. Glyde<sup>4</sup>

<sup>1</sup>*Institut Laue-Langevin, Boîte Postale 156, 38042 Grenoble, France*

<sup>2</sup>*Centre de Recherche sur les Très Basses Températures, CNRS, Boîte Postale 166, 38042 Grenoble Cedex 9, France*

<sup>3</sup>*Laboratoire des Champs Magnétiques Intenses, CNRS, Boîte Postale 166, 38042 Grenoble Cedex 9, France*

<sup>4</sup>*Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716, USA*

(Received 15 January 2004)

We present neutron scattering measurements of the phonon-roton excitations of superfluid  $^4\text{He}$  held at negative pressures from zero to  $-5$  bar. The liquid was stretched to negative pressures by immersing it in the porous medium MCM-41. In the wave vector range  $0.35 \leq Q \leq 1.55 \text{ \AA}^{-1}$  and temperature  $T = 0.4$  K investigated, the phonon and maxon energies decrease systematically below bulk values as the negative pressure is increased. The energies are consistent with extrapolation of positive pressure values from which the negative internal pressure can be estimated. The maximum negative pressure realized is consistent with surface tension arguments and the MCM-41 pore diameter of  $47 \text{ \AA}$ .

DOI:

PACS numbers: 67.40.Db, 61.12.Ex, 62.10.+s, 68.03.Cd



# Phase Diagram of Liquid $^4\text{He}$ at Negative pressures

Bauer et al. 2000

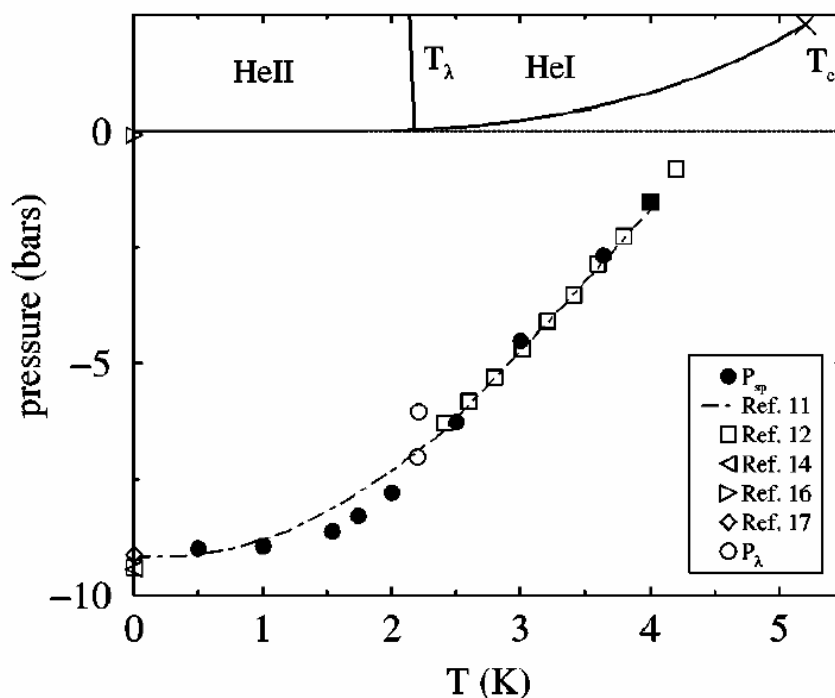


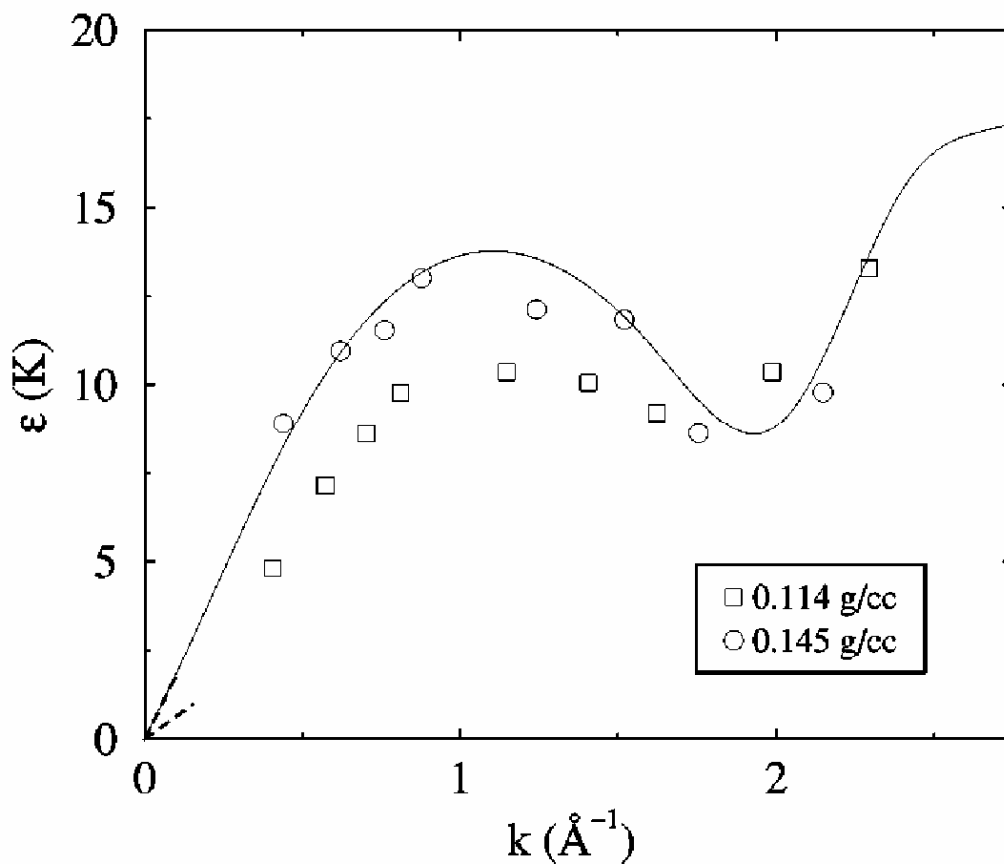
FIG. 4. Temperature dependence of the spinodal pressures and the superfluid transition at negative pressures are shown. At low temperatures the spinodal pressure is insensitive to temperature while at higher temperatures the behavior is linear. The upper solid lines form usual phase diagram.

# Phonon-Roton energies at

$p = 0$  and  $p \sim -9$  bar

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Bauer et al. 2000





# Liquid $^4\text{He}$ at Negative Pressure in Porous Media

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Liquid is attracted to pore walls

MCM-41,  $d = 47 \text{ \AA}$

Layers form on walls first

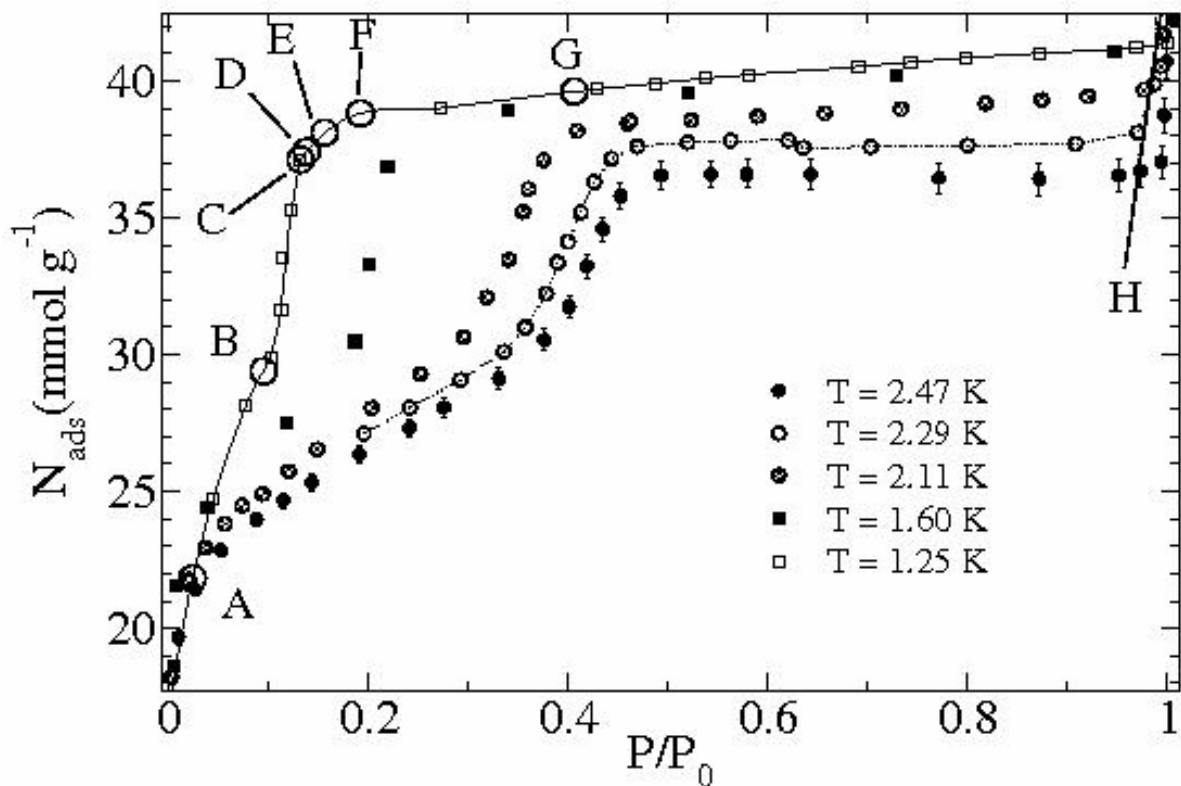
Then pores fill completely at a density less than bulk density.

Liquid is “stretched” between walls at lower than normal density (pressure is negative).

# Liquid $^4\text{He}$ at Negative Pressure MCM-41

## Adsorption isotherm

Pores are full with  $^4\text{He}$  at negative pressure at fillings C to H. C = -5.5 bar.

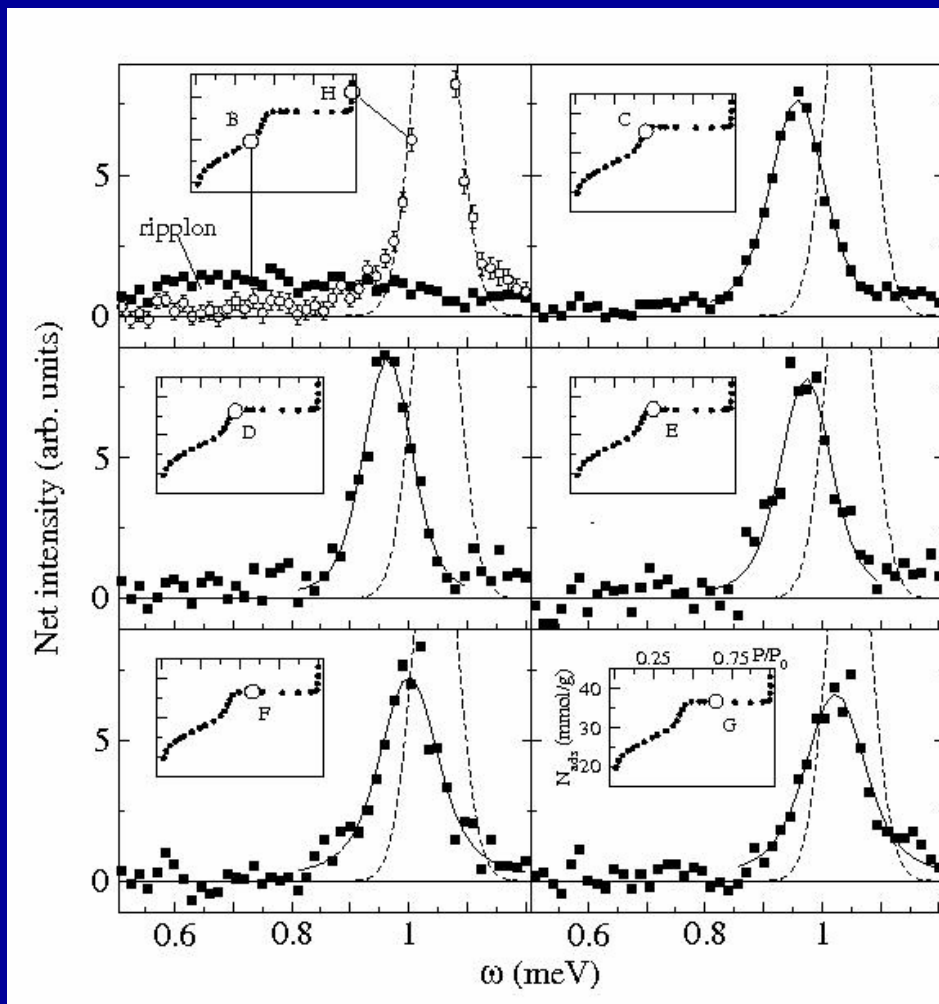


# Liquid $^4\text{He}$ at Negative Pressure

$S(Q, \omega)$  at  $Q = 1.5 \text{ \AA}^{-1}$  as a function of filling.

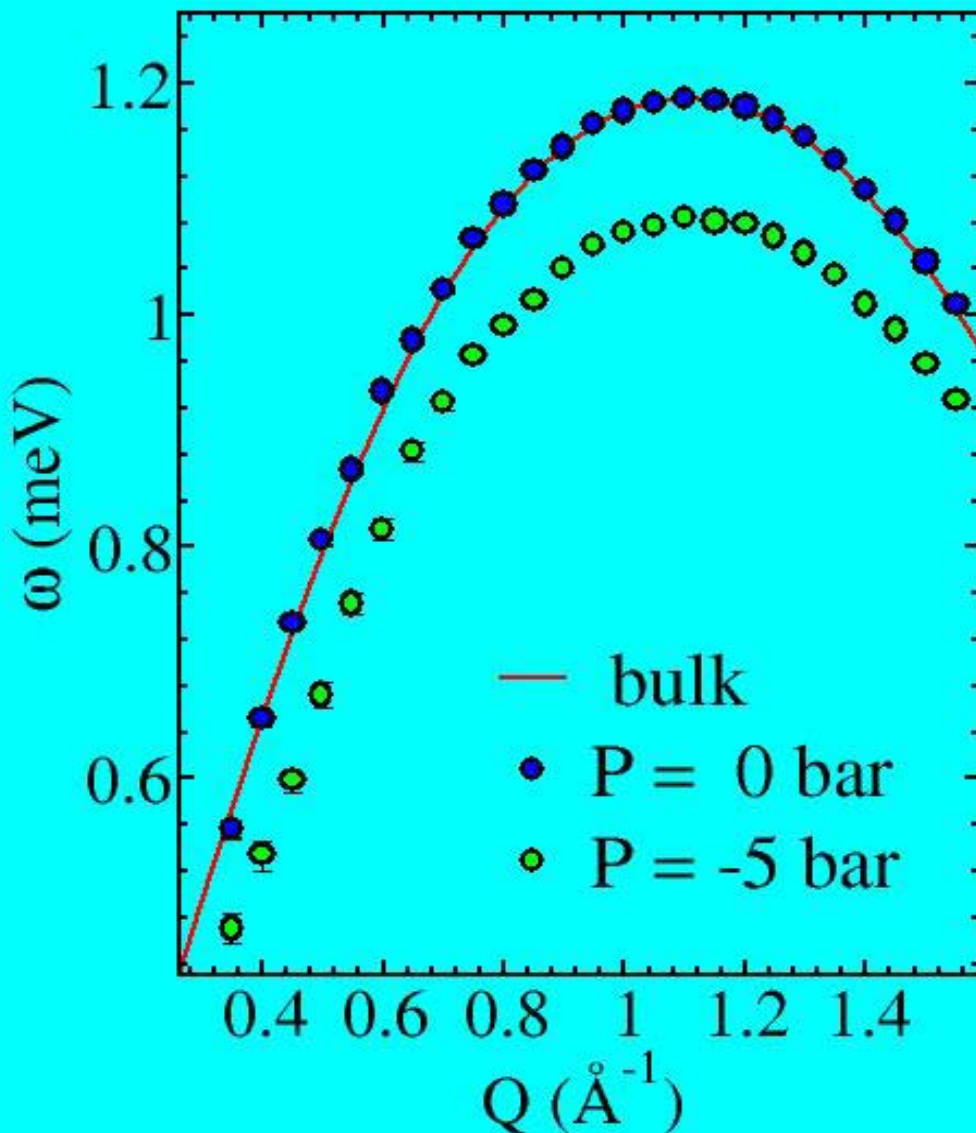
H – full filling,  $p = 0$ .

C – negative pressure,  $p = -5.5 \text{ bar}$



# Liquid $^4\text{He}$ at Negative Pressure

Dispersion curve at SVP and - 5 bar



# Liquid $^4\text{He}$ at Negative Pressure

Maxon energy at  $Q = 1.1 \text{ \AA}^{-1}$  as a function of pressure.

