High pressure research at the University of Salford

Current and future synergies between electron imaging and high pressure research

University of Salford MANCHESTER

Dr. John Proctor

My career to date

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2004 – 2007: Ph.D. at Manchester University
Thesis title: High-pressure Raman spectroscopy of single-walled carbon nanotubes

2007 – 2011: Worked as a researcher at the Centre for Science at Extreme Conditions (CSEC) at Edinburgh University

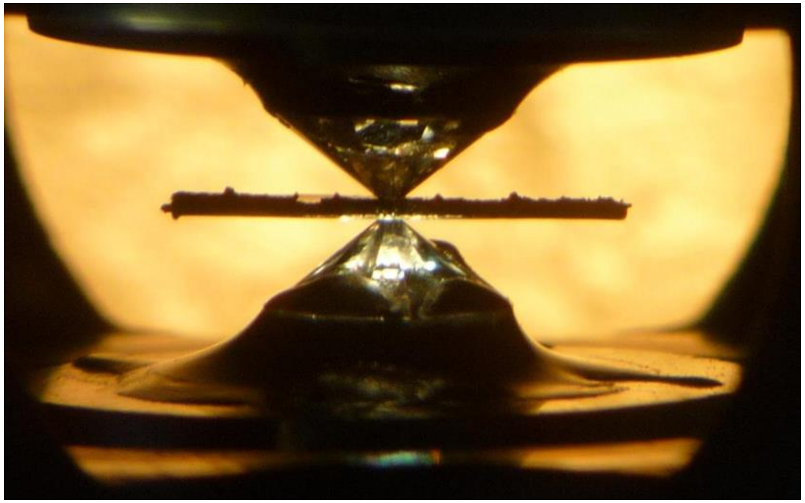
- Worked on synthesis of novel hydrides at high pressure
- Studied the equation of state of some transition metals, potassium and magnesium
- Produced the first study of graphene at high pressure

2011 – 2013: Worked as a lecturer at the University of Hull

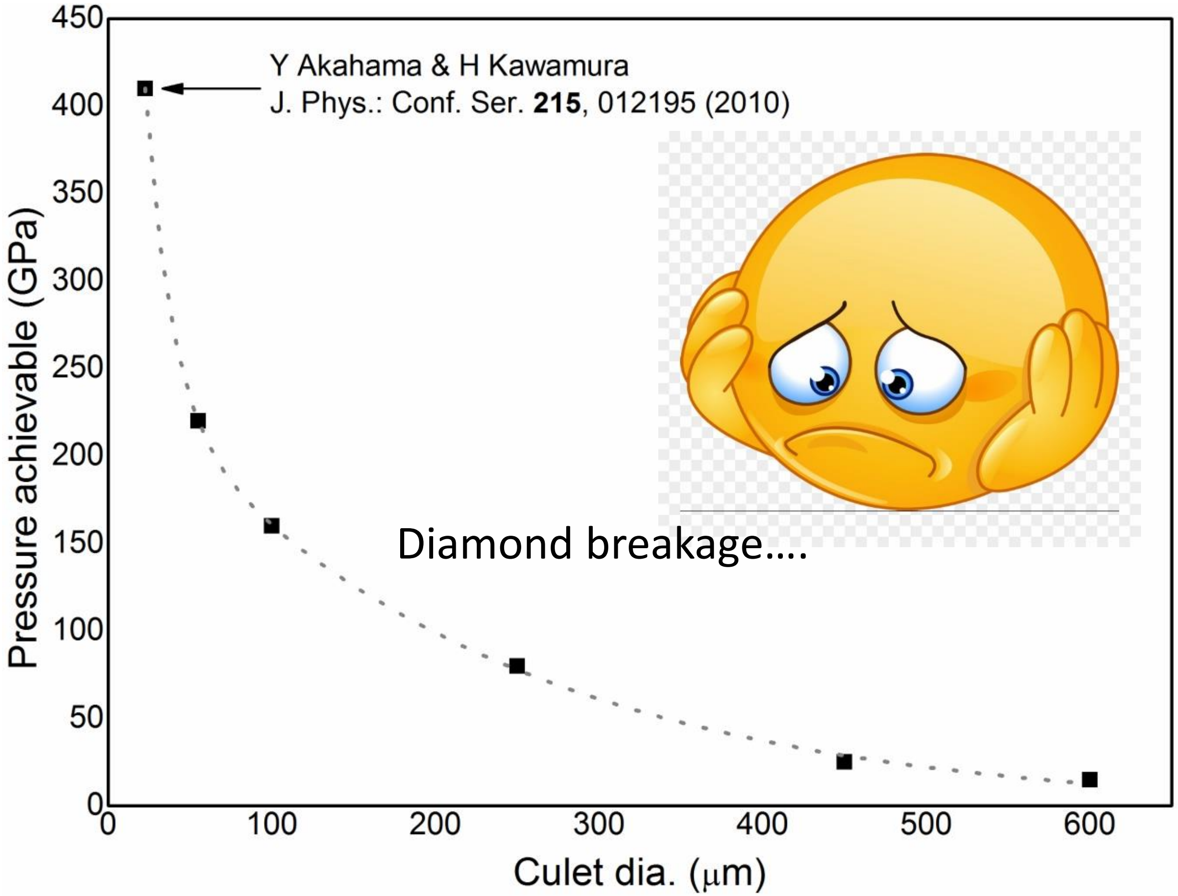
2013 – present: Senior lecturer at the University of Salford

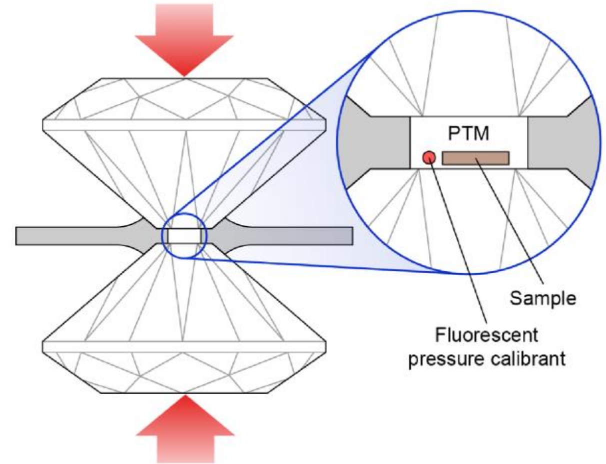
My research here focusses on the behaviour of materials under extreme pressures and temperatures, mostly whilst confined in the diamond anvil high pressure cell.

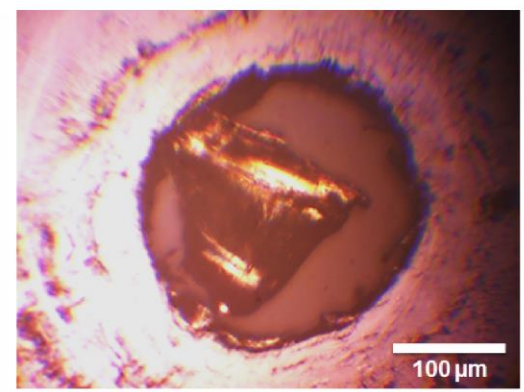
The Diamond Anvil High Pressure Cell



Diamond anvil high pressure cell





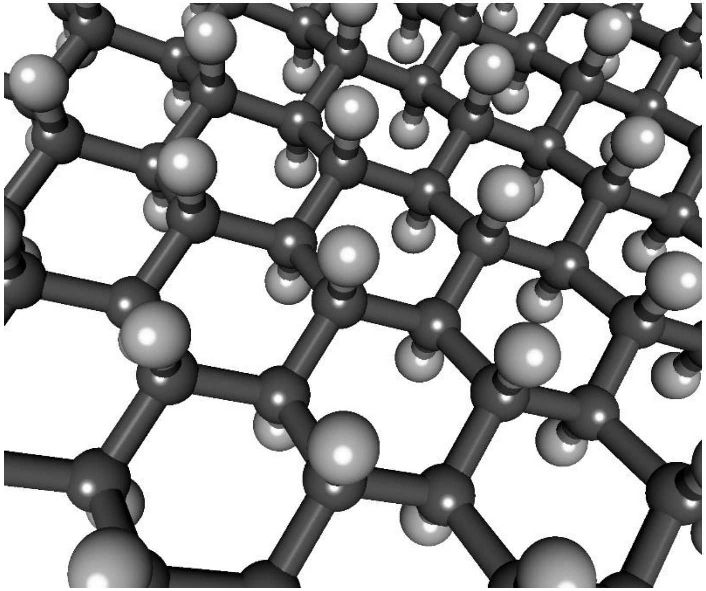


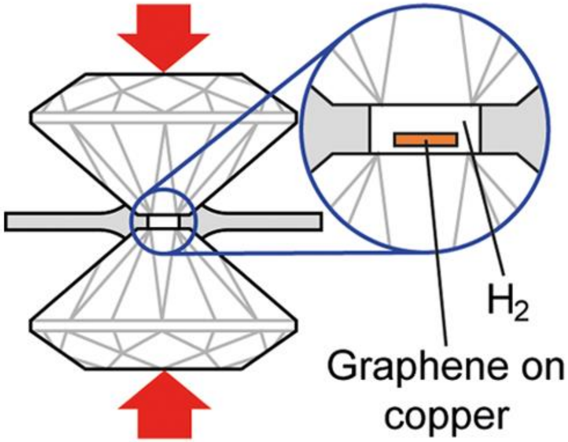
J.E. Proctor and D. Massey, Rev. Sci. Instr. (2018)

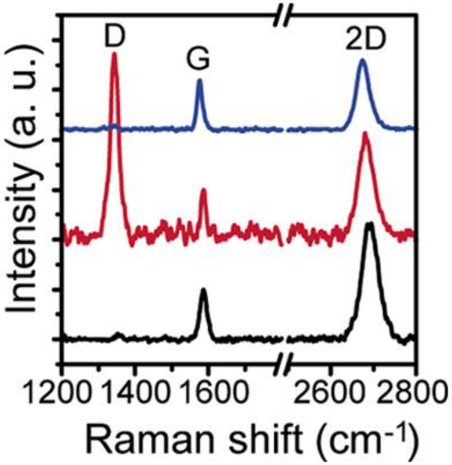
(PTM: Pressure-transmitting medium)

My contributions to graphene science

- First use of high pressure to study graphene (work published in 2009 whilst I was at Edinburgh). J.E. Proctor et al., Phys. Rev. B (2009).
- First use of high pressure (combined with high temperature) to hydrogenate graphene (work conducted in 2013 – 2015 at Salford).





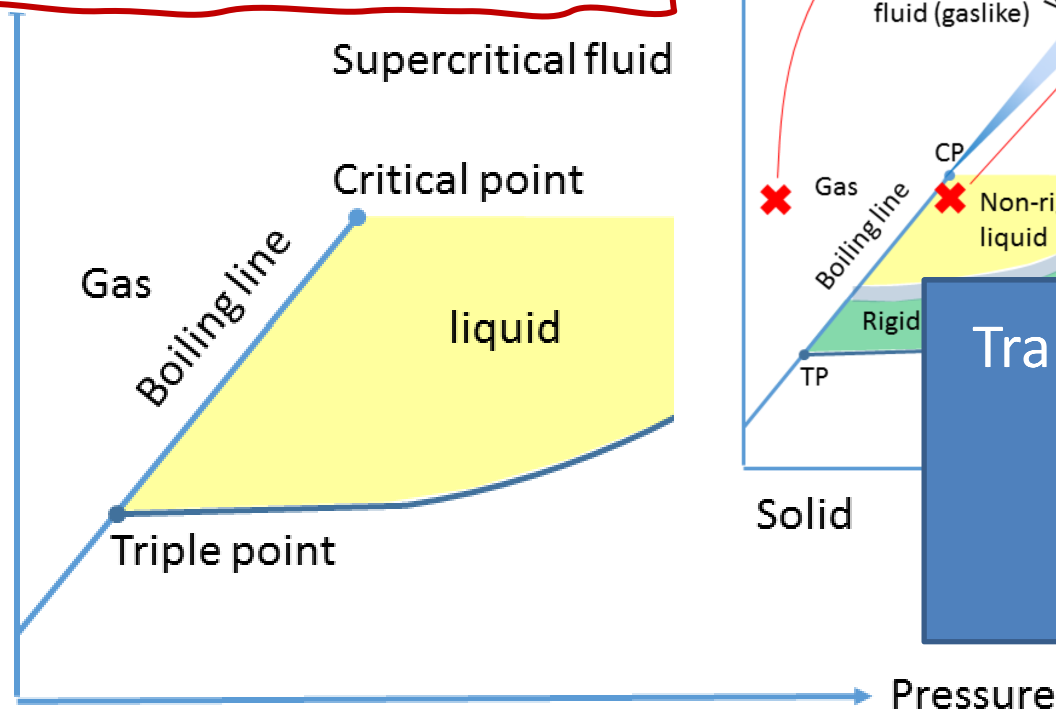


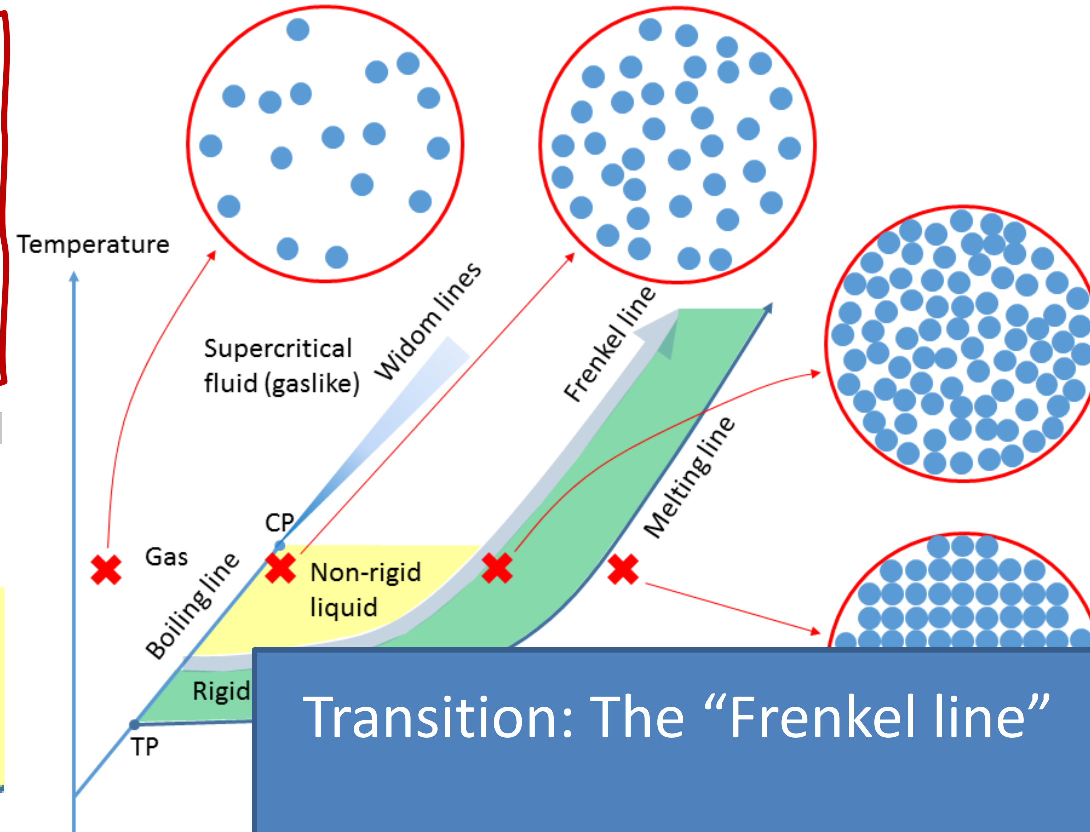
D. Smith et al., ACS Nano (2015)

← Ideal hydrogenated graphene (or graphene) would look like this (hydrogen atoms are lighter grey). Real hydrogenated graphene (both from our lab and from other groups) has nowhere near this level of order or hydrogen coverage.

Discovery of new transition between basic states of matter

Most of the experimental evidence for the existence of the Frenkel line has been obtained here at Salford, including the first study recognised to be correct by the scientific community.





Transition: The “Frenkel line”

Planetary science implications?

Frenkel line: Optical Spectroscopy

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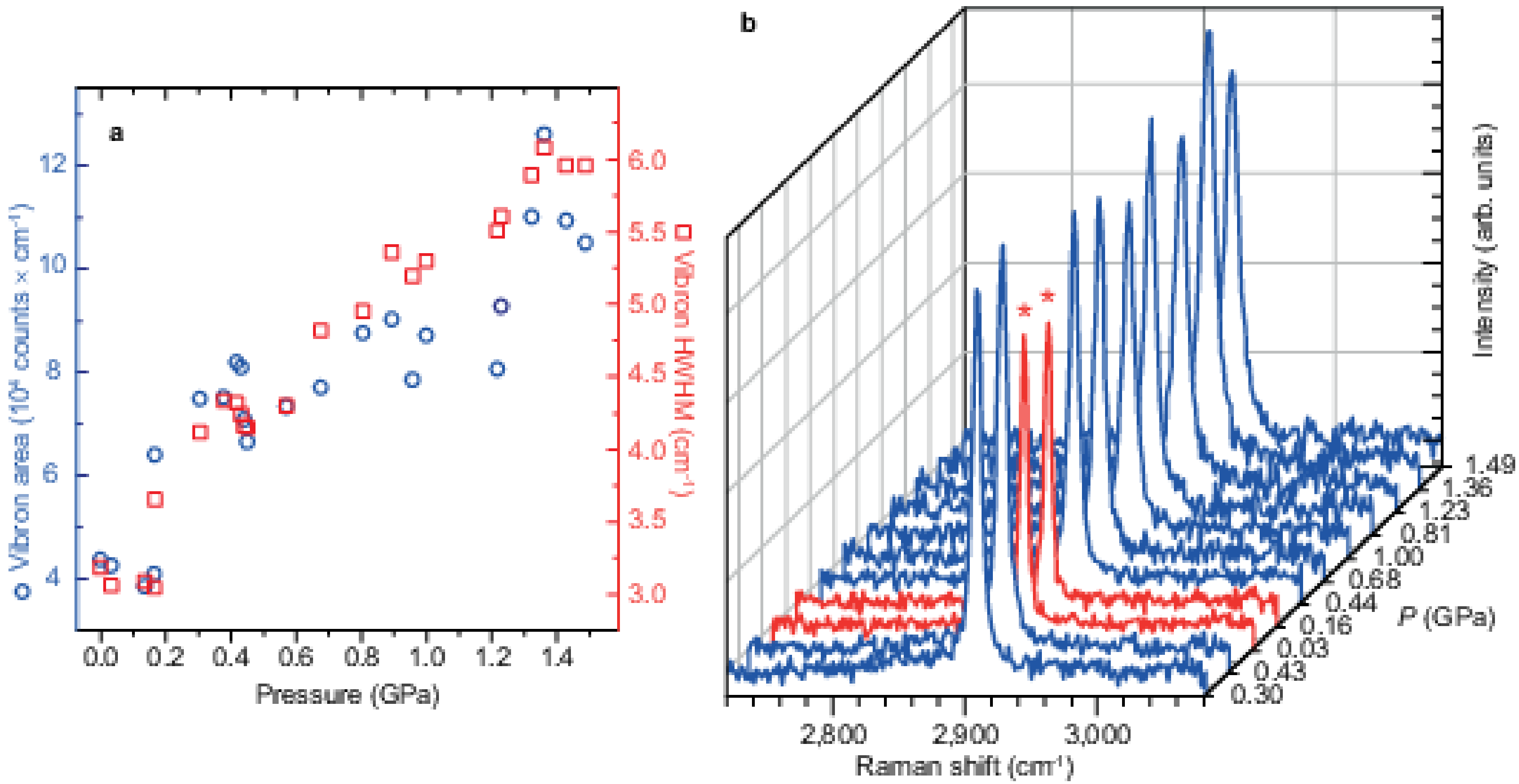
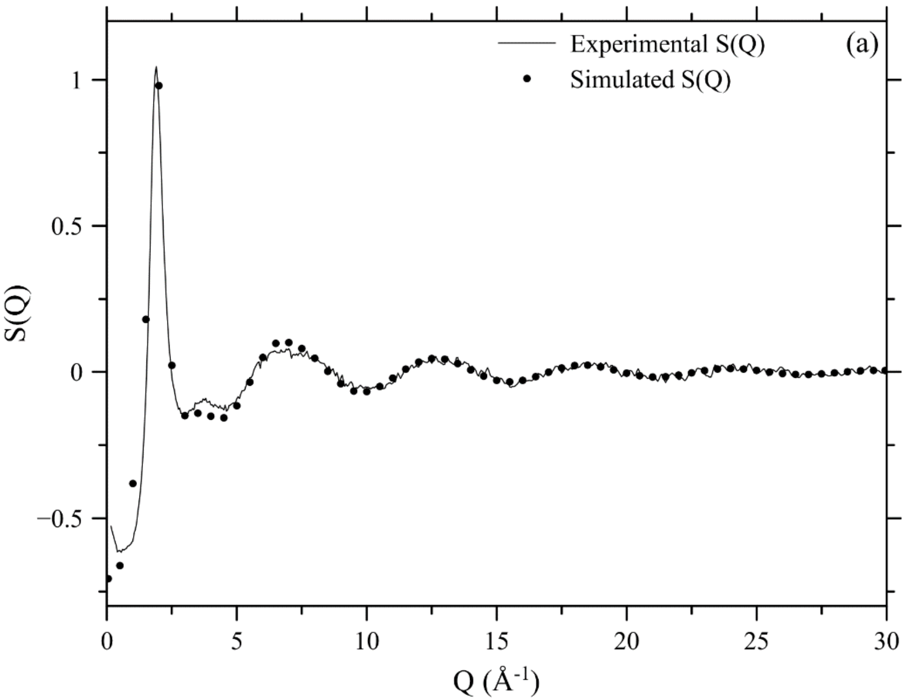


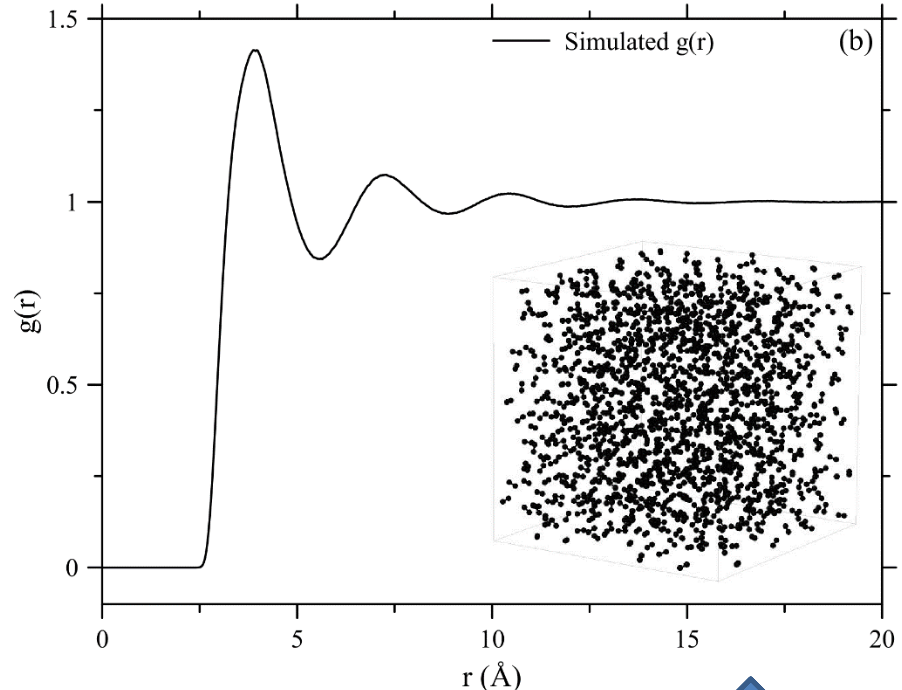
We find that behaviour on the gaslike and liquidlike sides of the Frenkel line is <u>fundamentally different</u>; conclusions do not rely on validity of any background subtraction or Fourier transform procedure etc. It is evident from the raw data.

D. Smith et al., Phys. Rev. E (2017).

Frenkel line: Co-ordination number

Neutron diffraction and EPSR on fluid nitrogen (300 K, 300 MPa)





“Box” of atoms used by EPSR. In reciprocal space (a), $S(Q)$ from this box is compared to $S(Q)$ diffraction data.

$g(r)$ (giving information about sample structure in real space, (b)) is then obtained from the box once process of fit improvement (refinement) is complete.

Frenkel line: Co-ordination number

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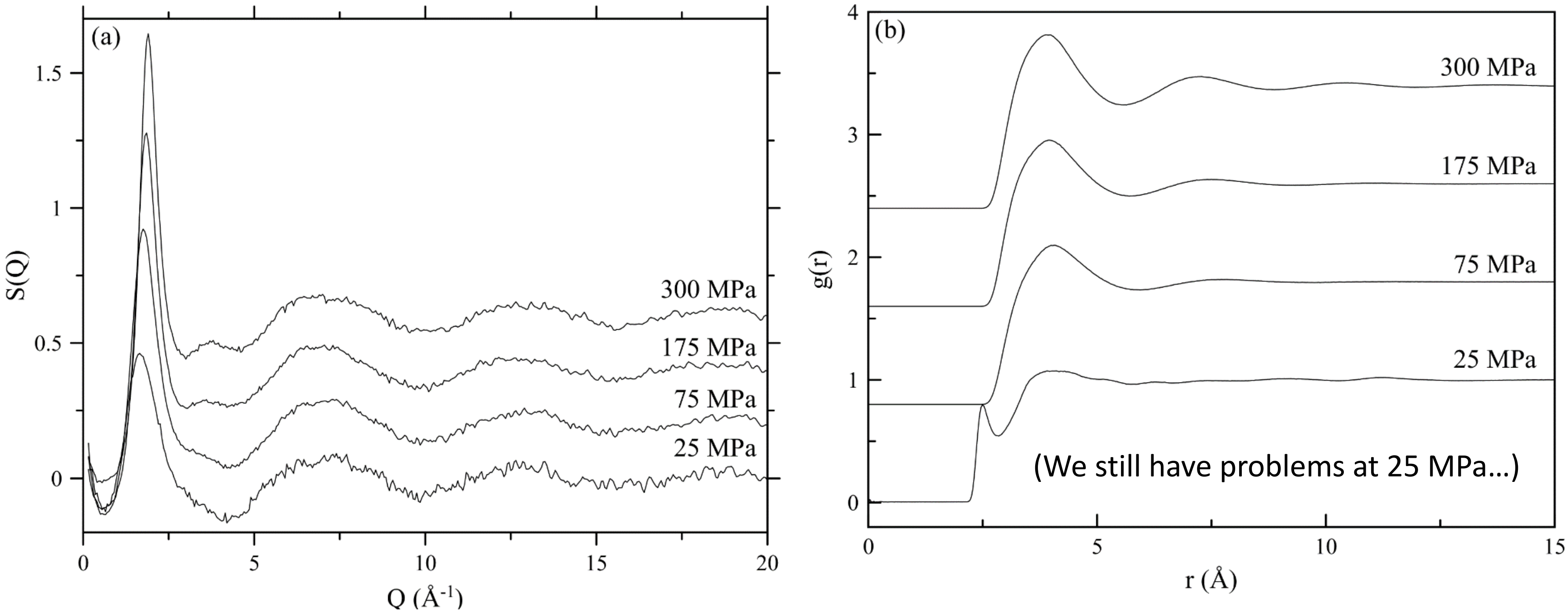
Neutron diffraction and EPSR on fluid nitrogen (300 K, 300 MPa)



All parameters we can extract from $S(Q), g(r)$ vary smoothly and monotonically, albeit with some scatter in the data.

Except…the co-ordination number!

J.E. Proctor. C.G. Pruteanu, I. Morrison, I.F. Crowe and J.S. Loveday, J. Phys. Chem. Lett. **10**, 6584 (2019)

Co-ordination number definition

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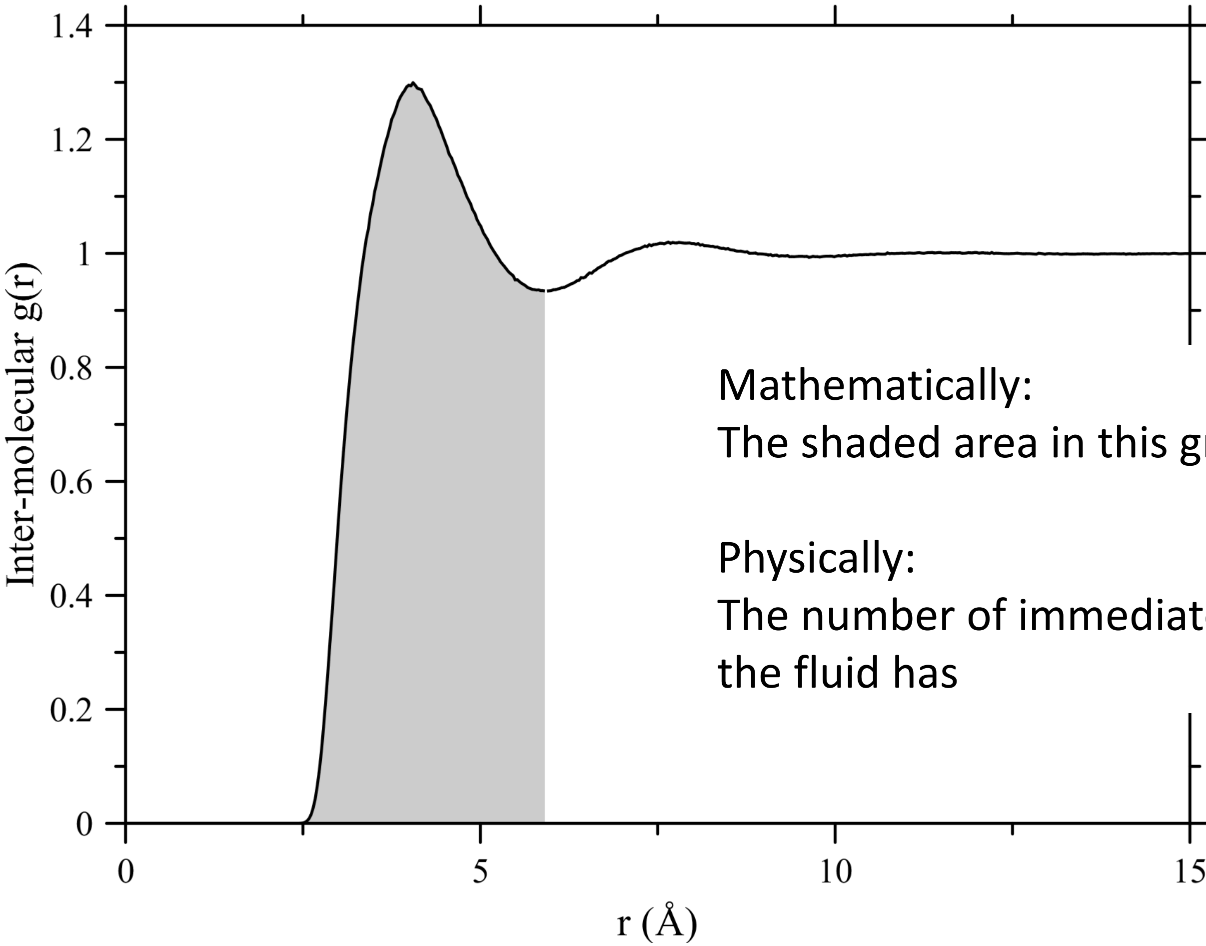
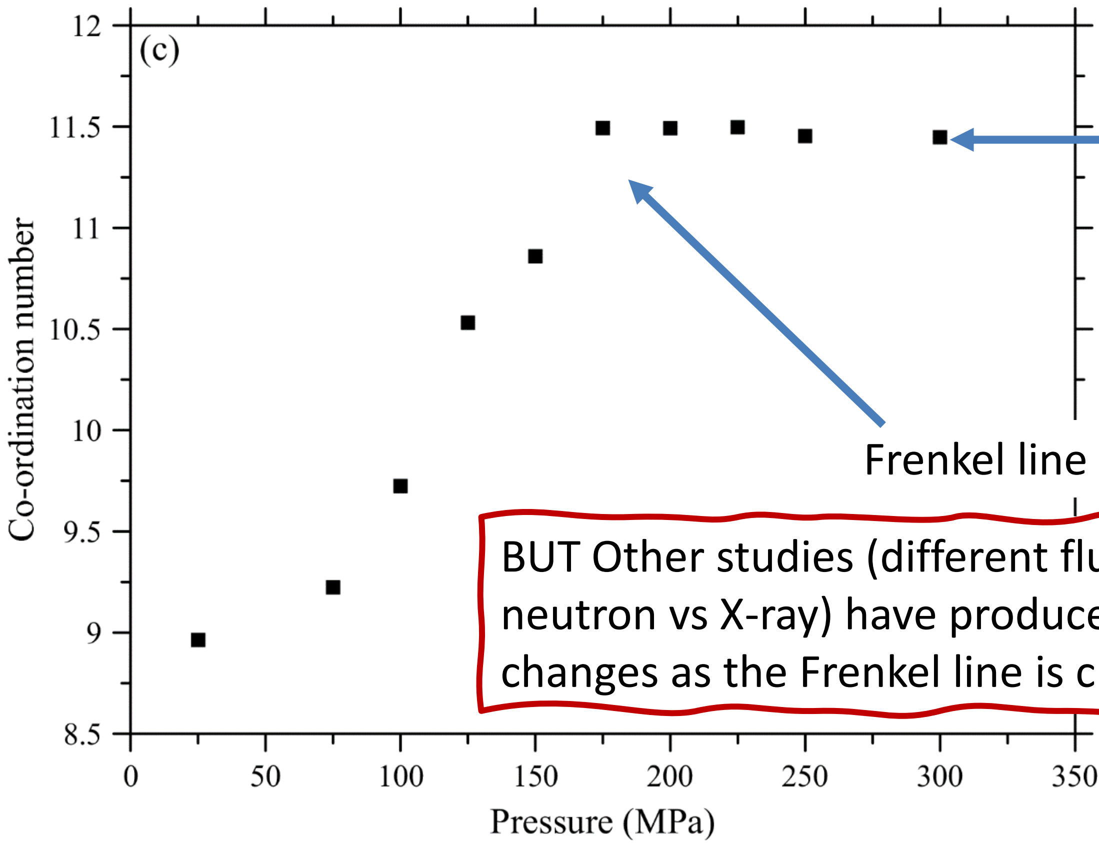


Mathematically:
The shaded area in this graph

Physically:
The number of immediate neighbours a particle in the fluid has

Frenkel line: Co-ordination number



CN plateau is just below solid-state value of 12.

Frenkel line transition

BUT Other studies (different fluids, different analysis methods, neutron vs X-ray) have produced different conclusions on what changes as the Frenkel line is crossed…

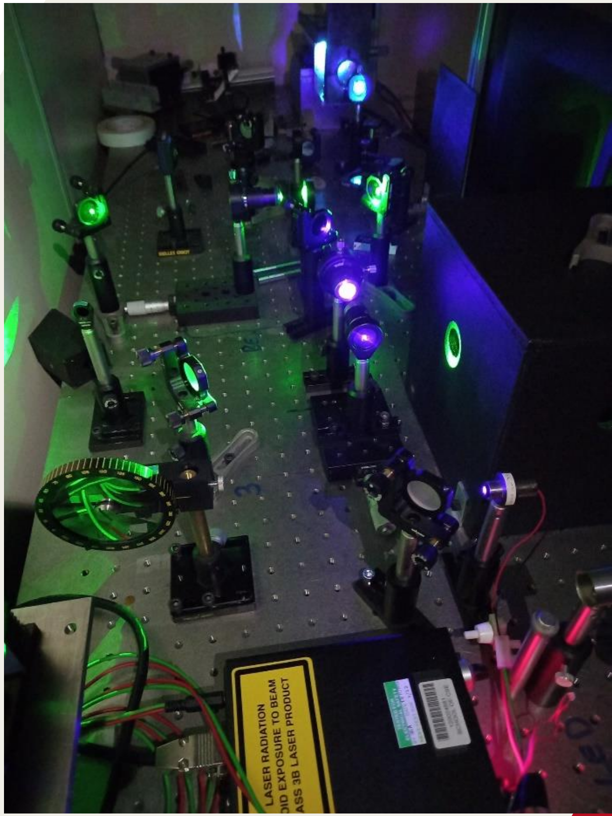
J.E. Proctor. C.G. Pruteanu, I. Morrison, I.F. Crowe and J.S. Loveday, J. Phys. Chem. Lett. **10**, 6584 (2019)

Frenkel line: References

Krypton and the Fundamental Flaw of the Lennard-Jones Potential
C.G. Pruteanu et al., J. Phys. Chem. Lett. (submitted).
Phase diagram of ethane above 300 K
J.E. Proctor et al., J. Phys. Chem. C (accepted).
Structural Markers of the Frenkel Line in the Proximity of Widom Lines
C.G. Pruteanu et al., J. Phys. Chem. B **125**, 8902 (2021).
Modelling of liquid internal energy and heat capacity over a wide pressure-temperature range from first principles
J.E. Proctor, Phys. Fluids **32**, 107105 (2020).
On the Transition from Gas-like to Liquid-like Behaviour in Supercritical N_2
J.E. Proctor. C.G. Pruteanu et al.,, J. Phys. Chem. Lett. **10**, 6584 (2019).
Observation of liquid-liquid phase transitions in ethane at 300 K
J.E. Proctor et al., J. Phys. Chem. B **122**, 10172 (2018).
Dynamics, thermodynamics and structure of liquids and supercritical fluids: crossover at the Frenkel line
Yu.D. Fomin et al., J. Phys.: Cond. Mat. **30**, 134003 (2018).
Crossover between liquidlike and gaslike behaviour in CH_4 at 400 K
D. Smith et al., Phys. Rev. E **96**, 052113 (2017).

In-house experimental facilities at Salford

Optical spectroscopy and sample preparation: Here in the Newton building.



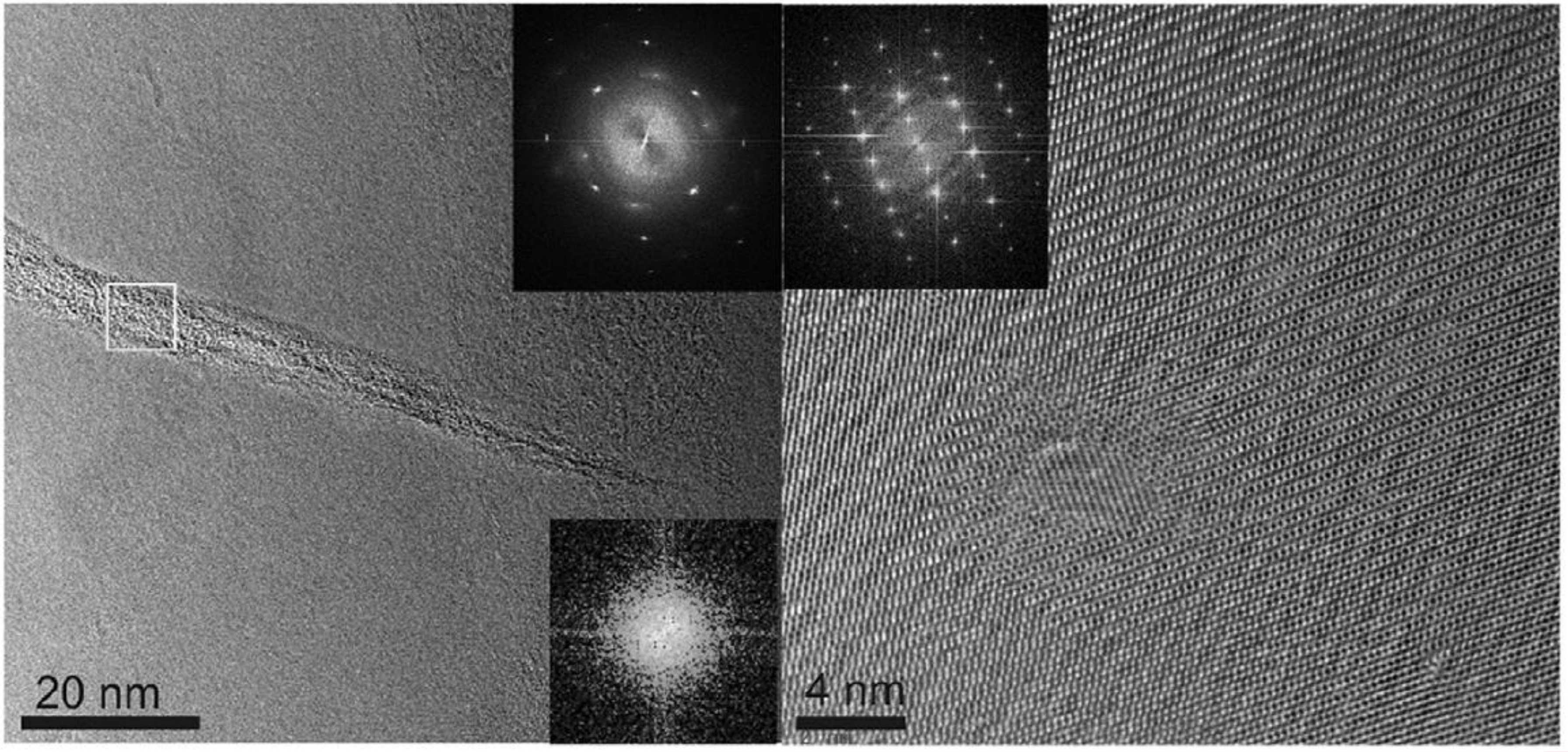
Central facility use

X-ray diffraction: Diamond Light Source (Oxford). (August 2021)

Neutron diffraction: ISIS pulsed neutron source (Oxford) (May 2021)

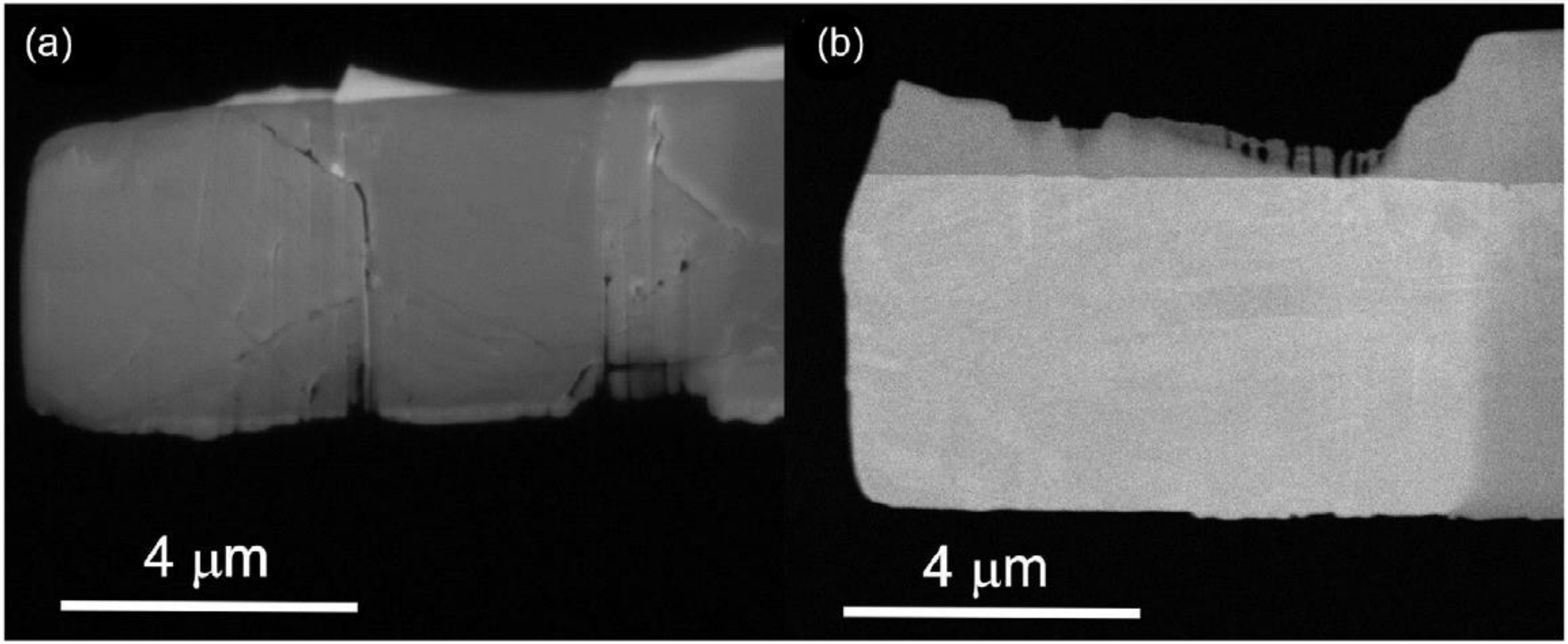
Current and future synergies between electron imaging and extreme conditions research

Characterization of samples following high-pressure treatment



TEM images of pure (left) and Si-doped (right) B4C following 50 GPa pressure treatment
JE Proctor et al., J. Phys.: Cond. Mat. **27** (2015), 015401

Characterization of samples following high-pressure treatment



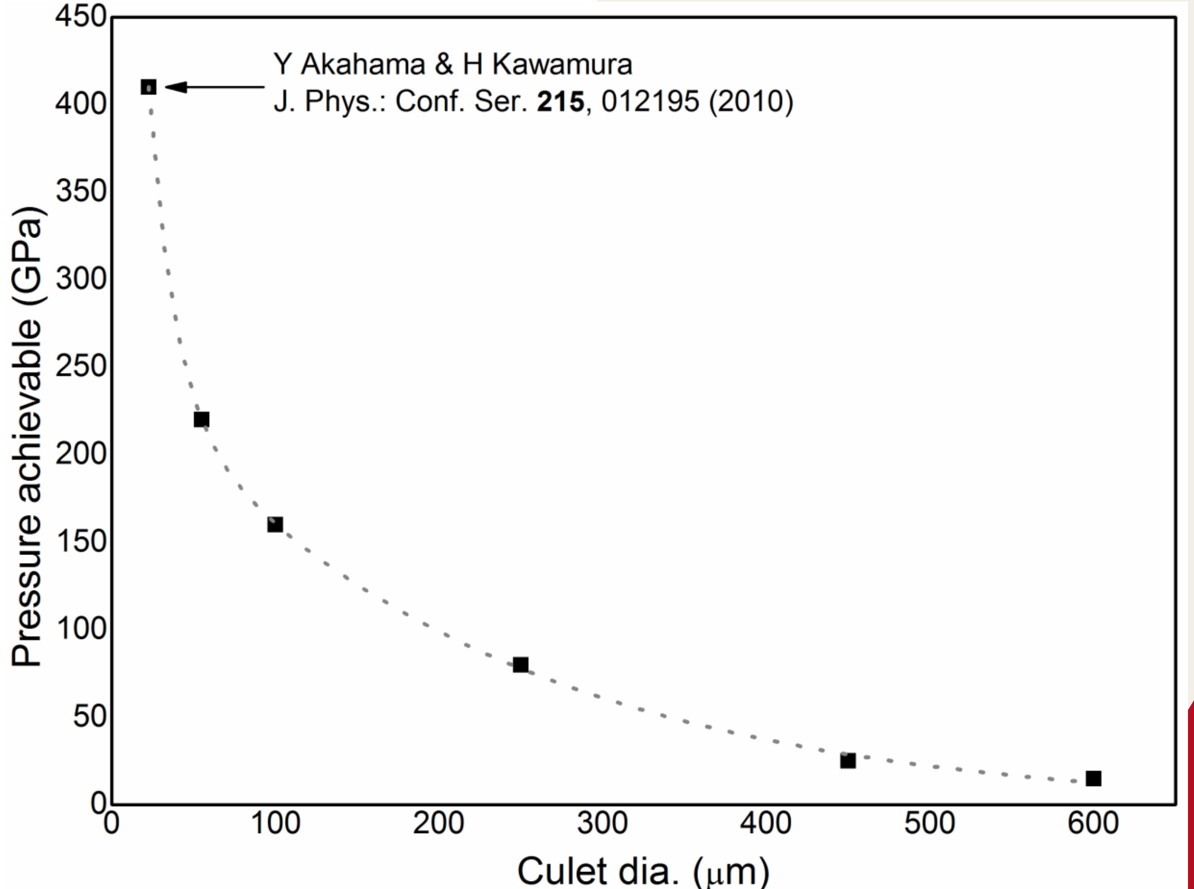
SEM images of pure (left) and Si-doped (right) B4C following 50 GPa pressure treatment
JE Proctor et al., J. Phys.: Cond. Mat. **27** (2015), 015401

Post-pressure TEM and SEM was critical to demonstrating the stabilizing effect of silicon-doping on this ceramic armour material

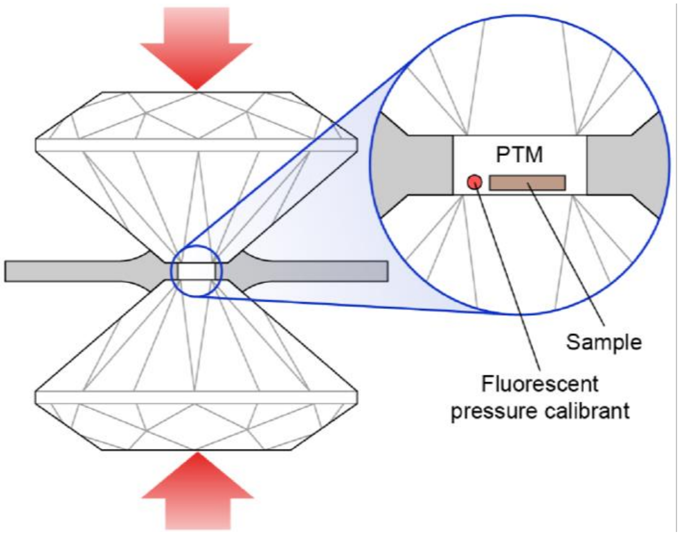
Miniaturization of the diamond anvil high pressure cell

(*Or*, to be more precise, of the diamond tips)

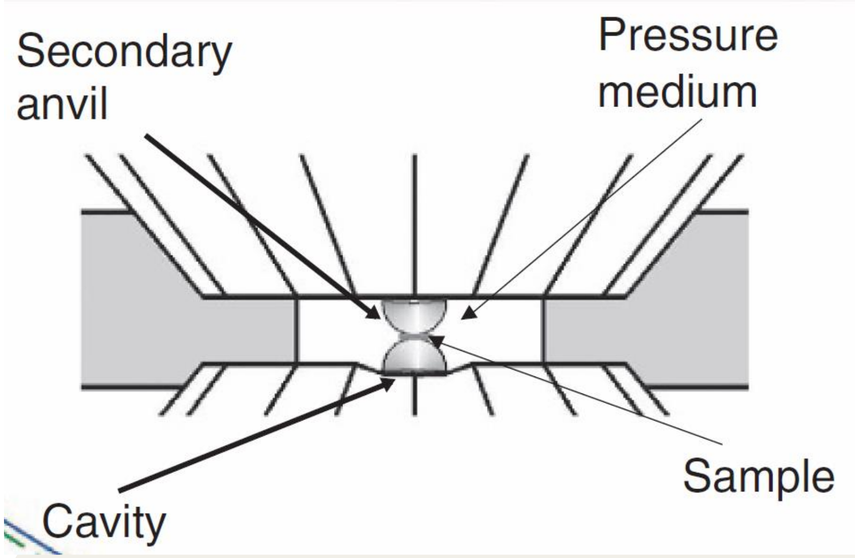
Higher pressures than this have recently been obtained using double-stage DACs with FIB machining to manufacture the tip approx. 1 μm diameter.



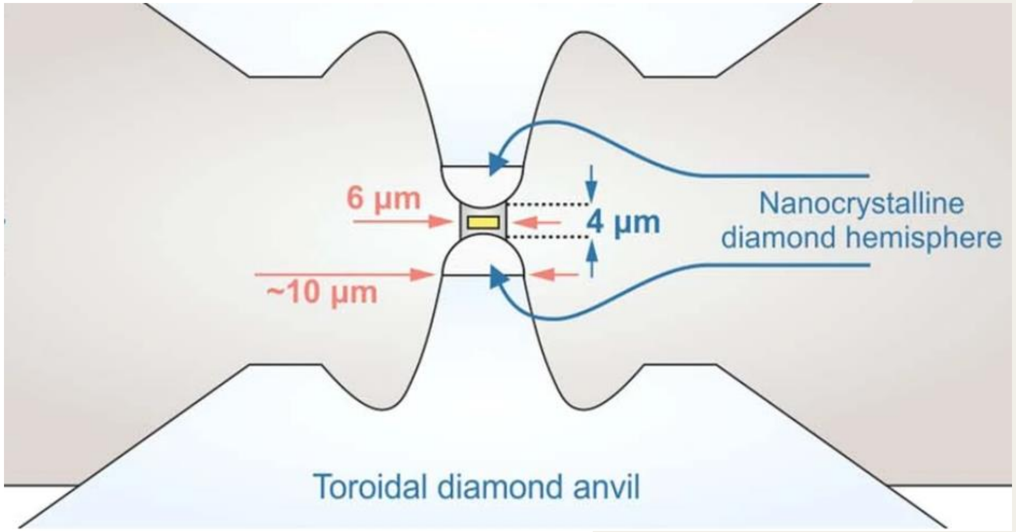
Miniaturization of the diamond anvil tips in the DAC



Conventional DAC



Double stage DAC design 1 (Dubrovinsky, Dubrovinskaia et al. Nat. Comms. 2012)



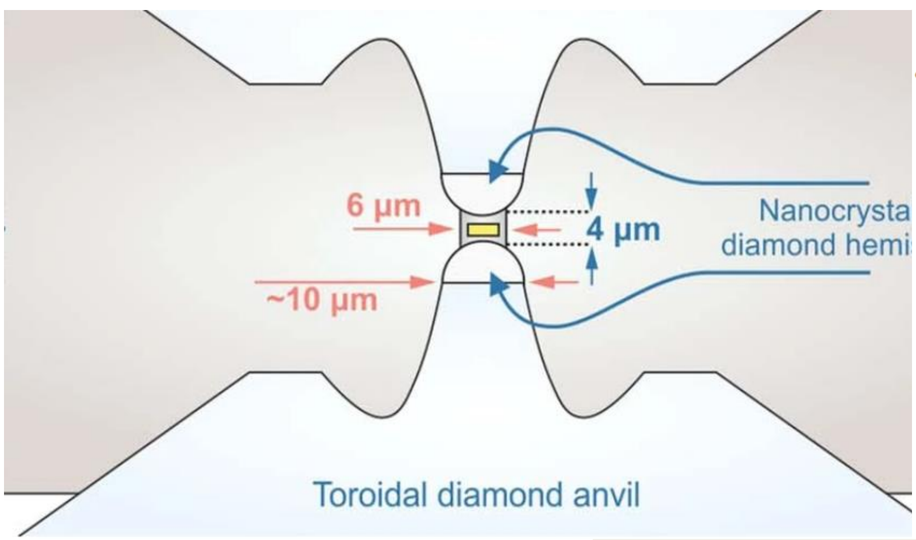
Double stage DAC design 2 (Dubrovinsky et al. Nature 2022)

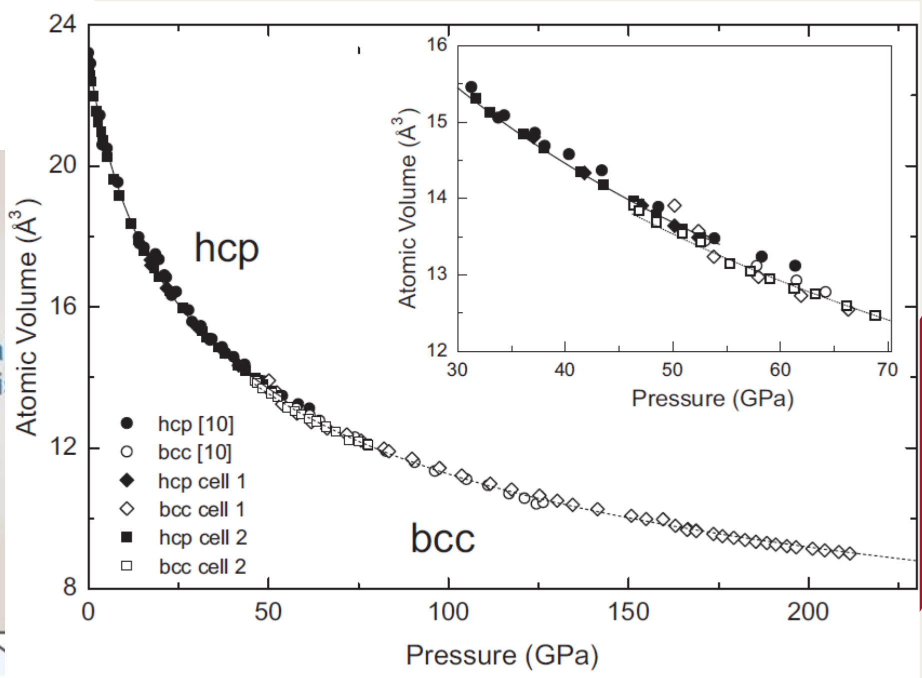
Miniaturization of the diamond anvil tips in the DAC

Static pressures up to 1 TPa have been obtained

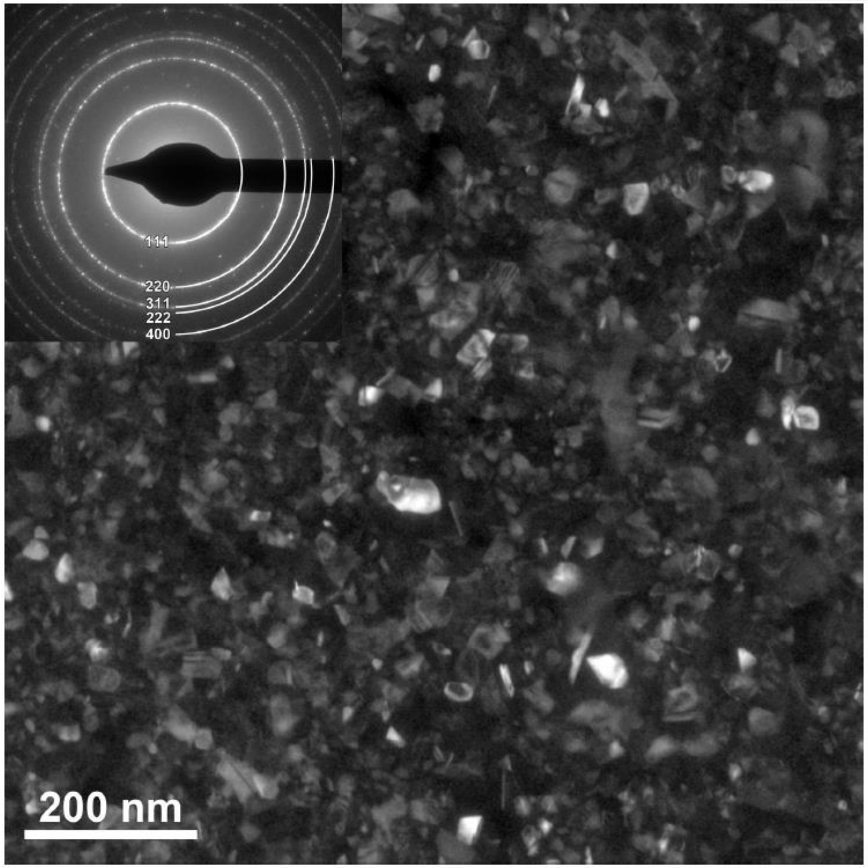
Combined with laser heating to generate high temperature (low temperature should also be possible)

Accurate pressure measurement is a problem due to low compressibility of pressure markers at TPa pressures





Miniaturization of diamond anvil tips: Applications of electron imaging



TEM image of nanocrystalline diamond tip (Dubrovinsky, Dubrovinskaia et al. 2012)

Nanotube high pressure cylinders

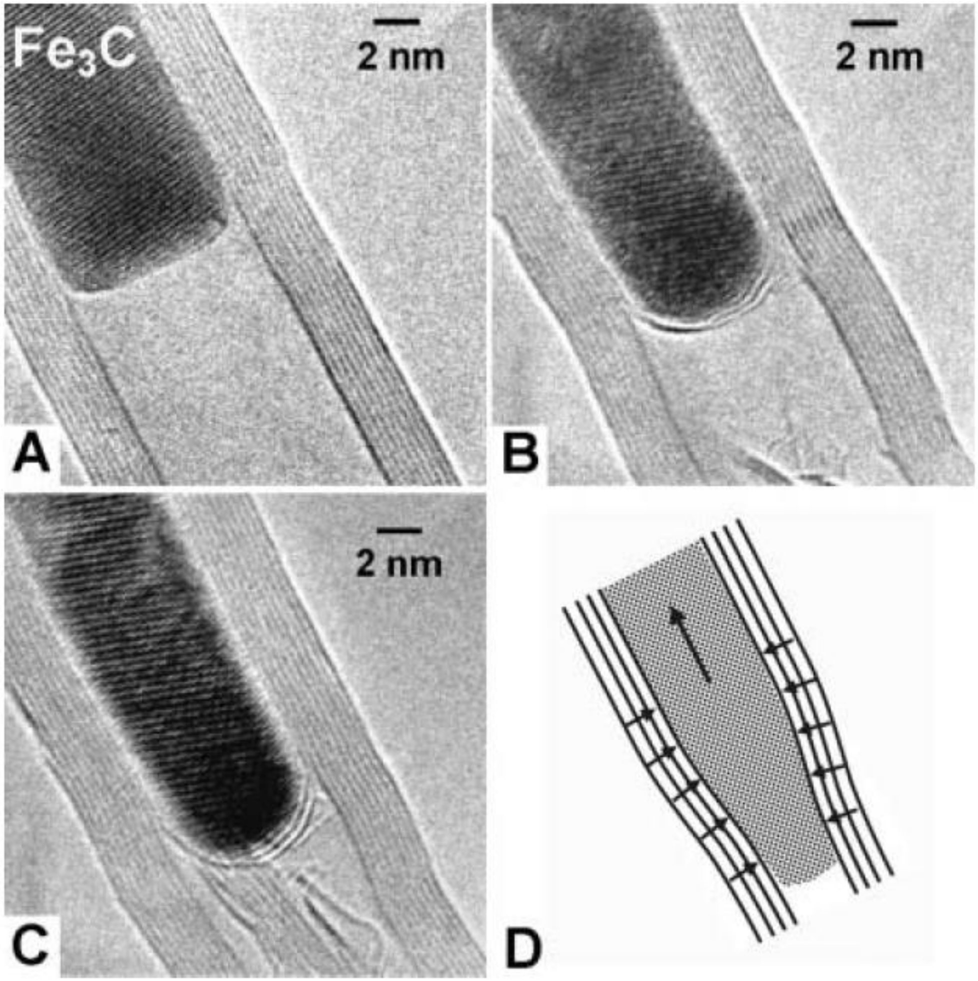


Fig. 1. MWNT with a Fe_3C crystal (dark region) in the inner core under electron irradiation at a specimen temperature of 600°C. The shrinkage of the tube leads to a deformation (thinning) of the Fe_3C crystal. Tubes before irradiation (**A**) and after 12 min (**B**) and 21 min (**C**) of irradiation are shown. The lattice fringes in (A) and in (B) and (C) originate from different sets of lattice planes because of a slight rotation of the tube under irradiation. (**D**) Simplified geometry of the system. Compressive forces (indicated by the small arrows) from the tube shells lead to a thinning of the crystal and its sliding along the tube axis (indicated by the large arrow).

L. Sun et al. (Science, 2006).

Nanotube high pressure cylinders

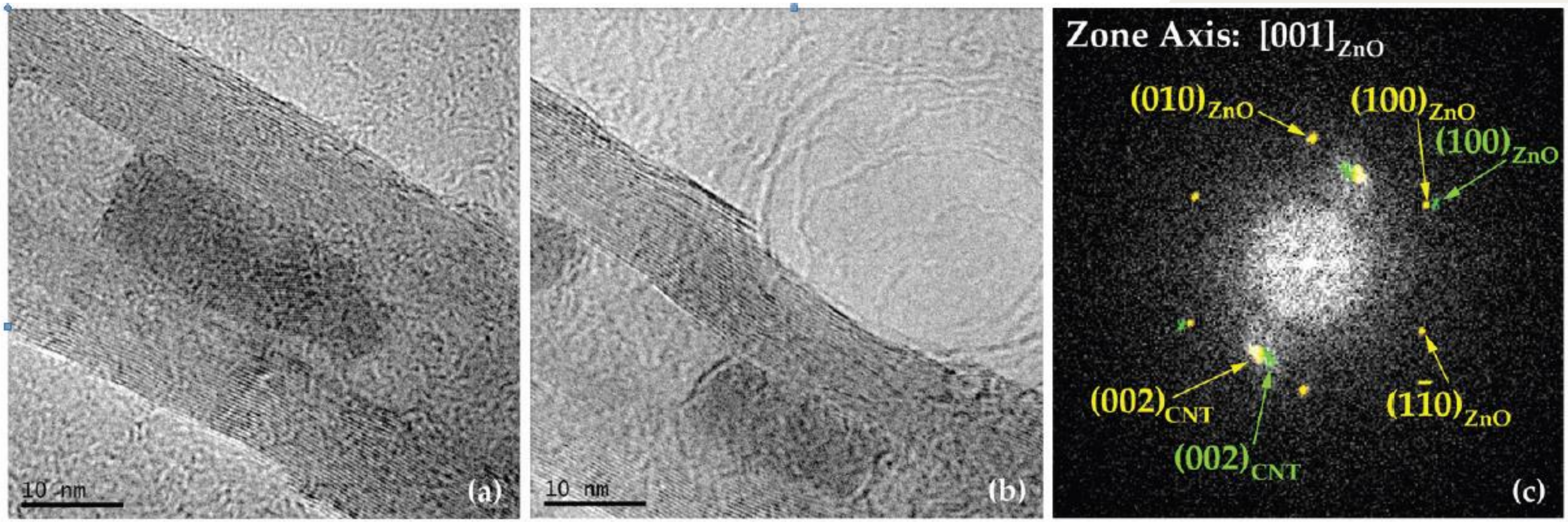


Figure 8. Radiation-induced compression of a zincite (ZnO) nanocrystal in a CNT at 500 °C. (**a**) The crystal prior to irradiation. (**b**) Same crystal after irradiation for 5 min. (**c**) Superimposition of FFTs from **a** in yellow and **b** in green. Compression is indicated by an approximately 6% decrease in the (100) lattice spacing. (Color online.)

Wu and Buseck (Am. Miner. 2014).

Nanotube high pressure cylinders

Pressures up to 40 GPa (and high temperatures up to 1500°c) claimed (Wu and Buseck, Am. Miner. (2014)).

TEM allows imaging of samples *in-situ* at high pressure on an atomic level in real space:

This will *never* be possible in any version of the diamond anvil cell!

This can be complemented by electron diffraction (as opposed to X-ray diffraction in the diamond anvil cell).

Acknowledgements

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Final year project students: Too many to mention!

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University of Edinburgh: Cip Pruteanu, Graeme Ackland, John Loveday, Eugene Gregoryanz

Funding: Royal Society, DSTL

Central facility use: ISIS pulsed neutron source, Diamond light source, European synchrotron radition facility

Thanks for listening…

Questions?