Emergent Issues in HP Scattering Research:

Liquids, (melts, fluids) & Solid State Synthesis

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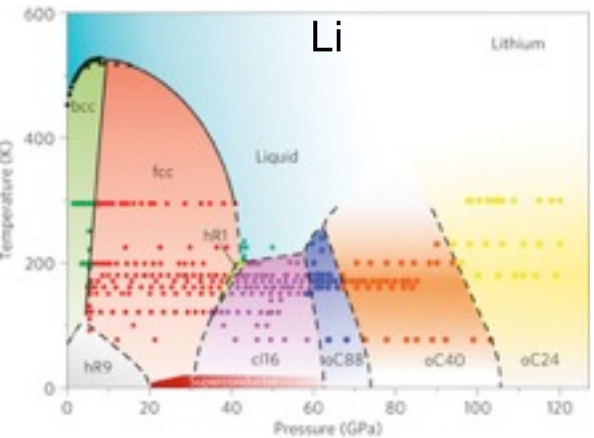
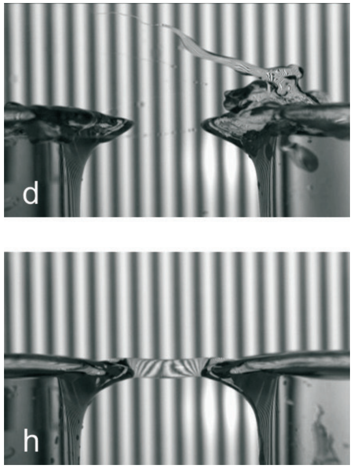
Support: DOE-BES

Two Interesting Challenges

- *Interesting Liquids, Fluids - under pressure or not*
  - **Existence/nature of HP-stabilized liquids, density anomalies etc**
  - **Emergent phenomena in deeply undercooled/supersaturated liquids**

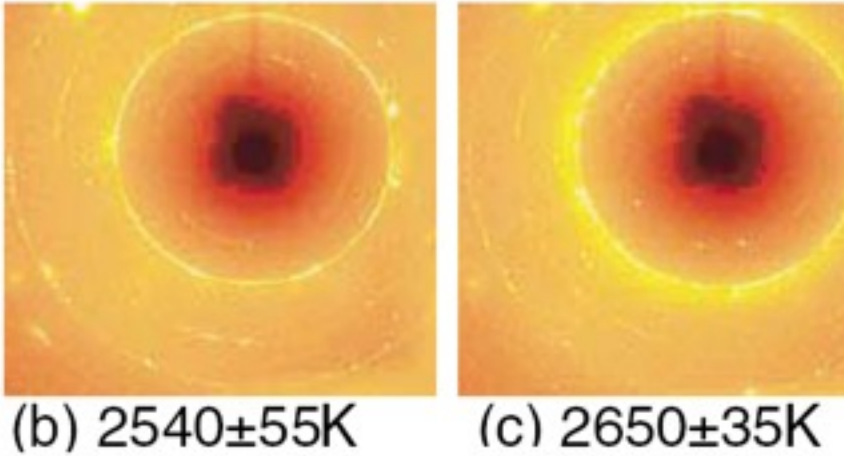


Guillaume et al (2011) Nature Phys., 7, 211



Floating water bridge (30 kV); Fuchs, J Appl Phys D43, 2010

Shen et al., *PRL* **92**, 185701 (2004)



- **Transformational solid state chemistry suited to HP research**
  - **Making new materials, not just poking old ones**
  - **Beyond random walks: speeding discovery**
  - **Simultaneous properties, Å - nm - µm characterization**

The melt - glass transition

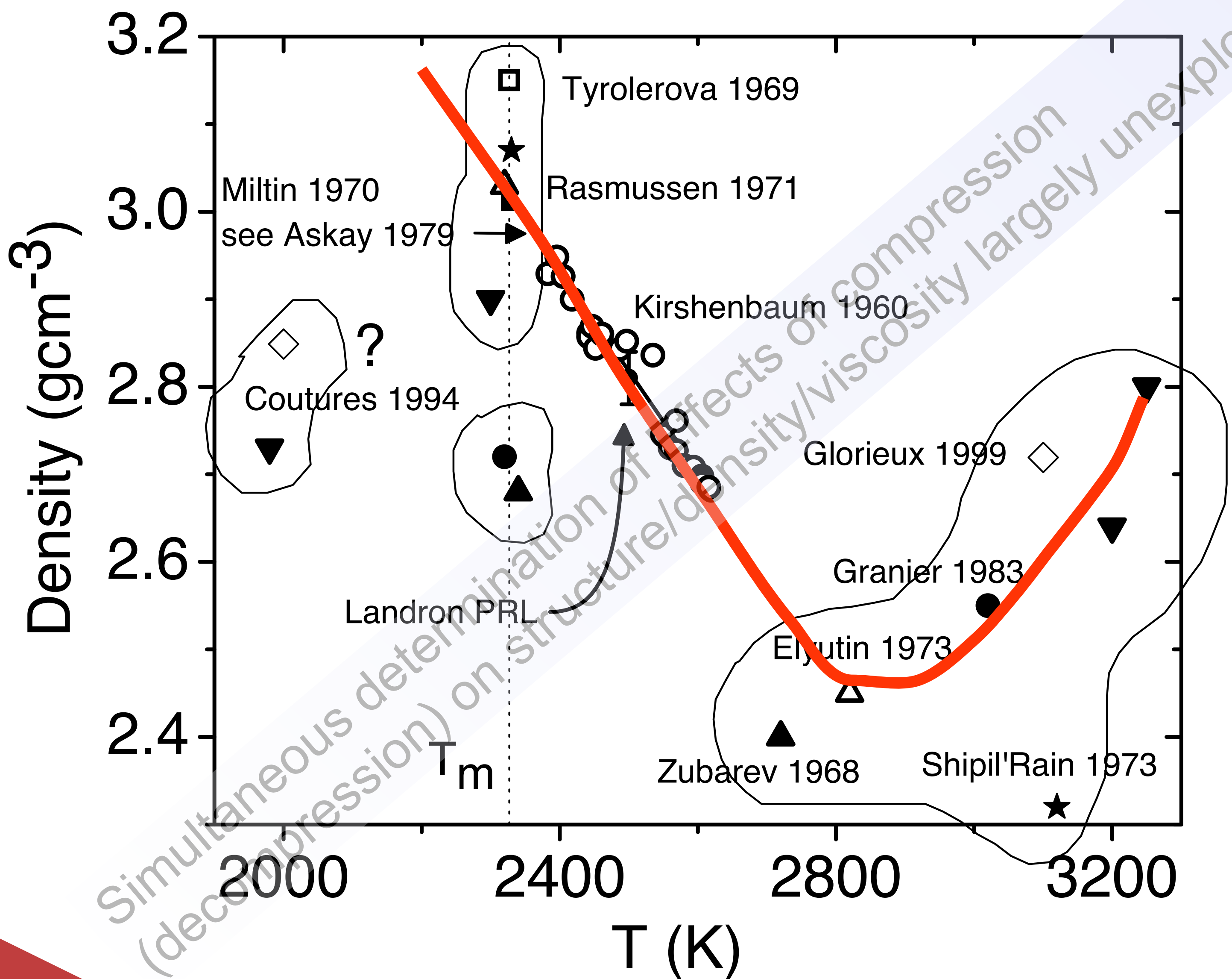
- "The deepest and most interesting unsolved problem in solid state theory" (the glass transition as described by P.W. Anderson (1995), "Through the Glass Lightly", Science 267: 1615)

- Can we study the process experimentally?

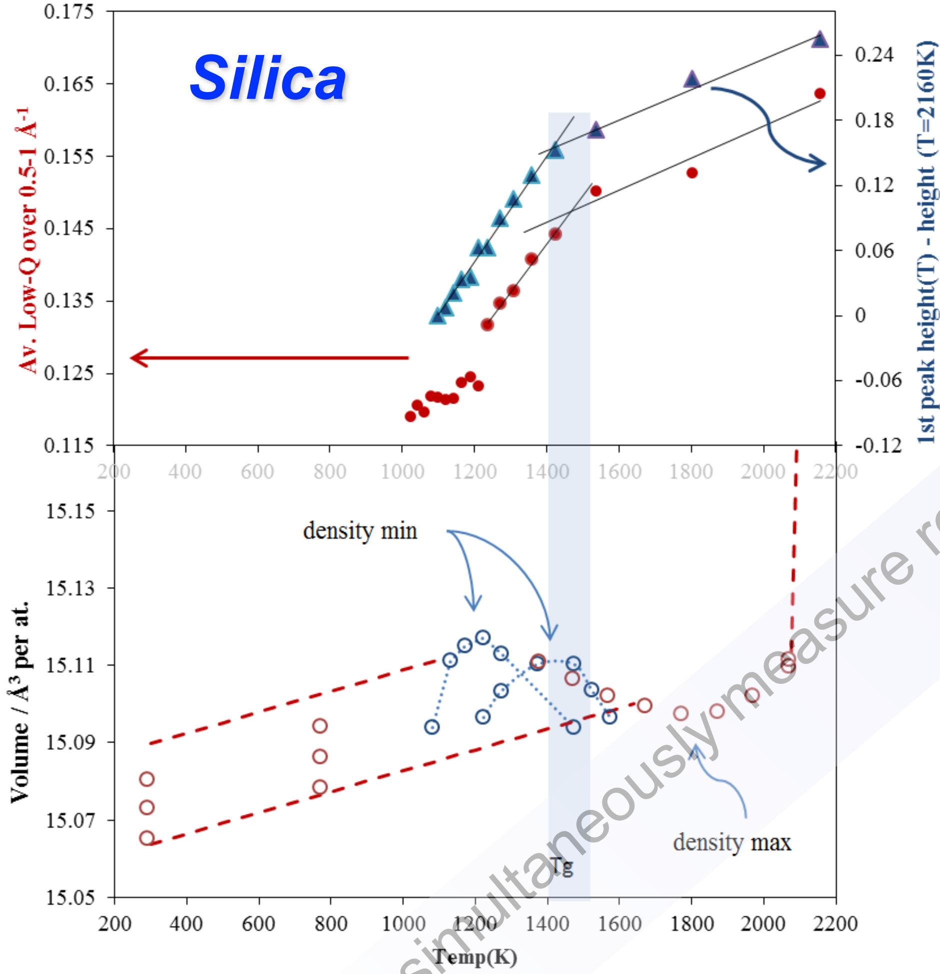
- Observable change in the under-cooled regime?

- Any indication experimentation might be worthwhile?

Density anomalies: Liquid Al_2O_3 - literature survey



Origin of density maxima and minima: Ambient P



Preliminary measured structural change and relation to density anomalies.

Volume (density) data from Sen (2004), and Bruckner (1970).

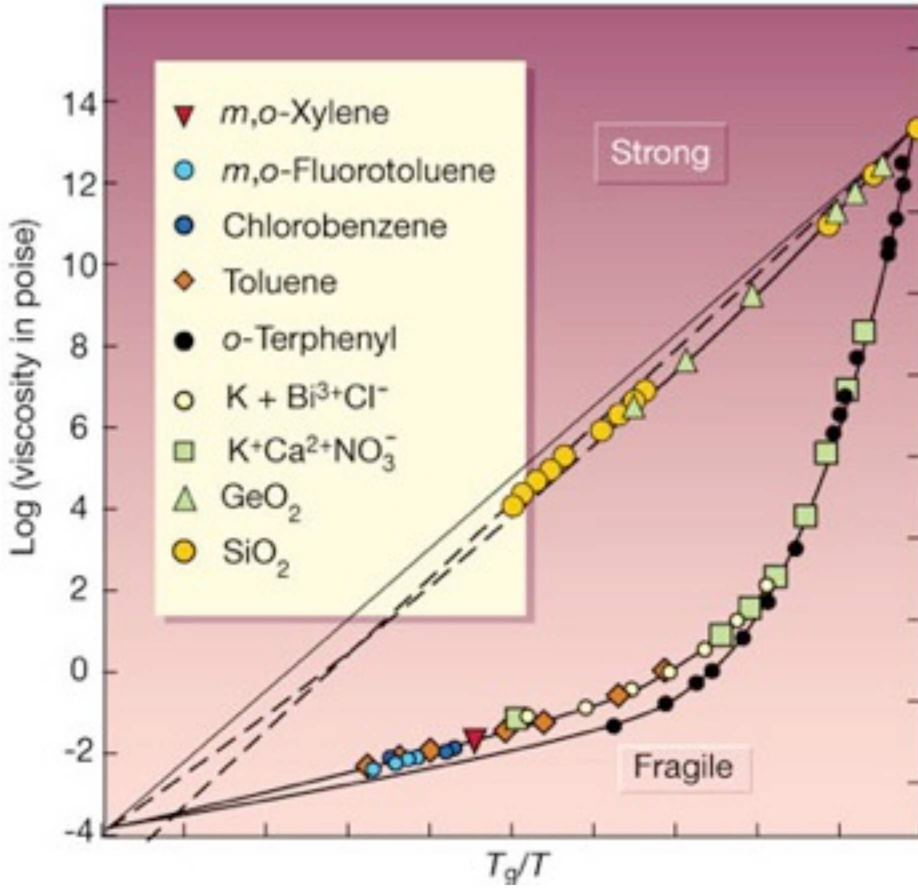
The two density minima are from two different measurements.
Tg = glass transition temperature.
Left side dashed lines are linear expansion of glasses quenched from different temperature liquid.

Can we simultaneously measure reliable scattering and measure density?

Melt Fragility, changes in physical properties

- Interesting phenomena at long relaxation time (τ).

- This Angell plot describes structural relaxation of all liquids on the same scale.



Angell, Nature, 1995

Melt Fragility and Structural Changes

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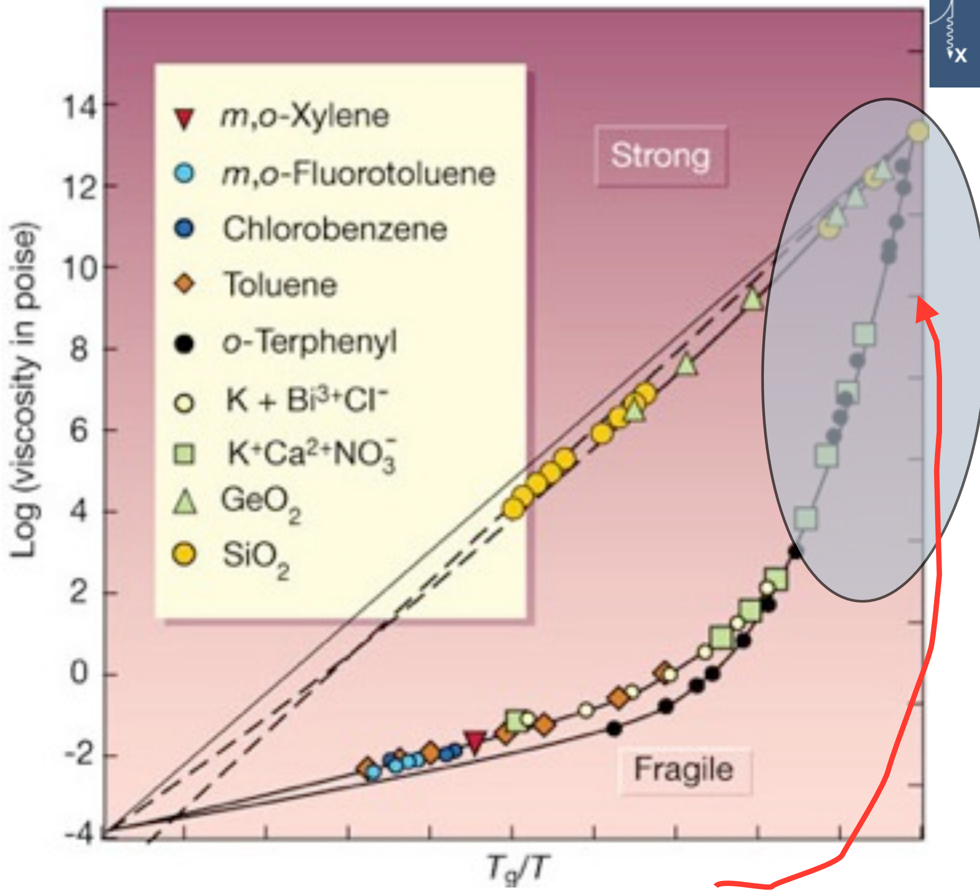
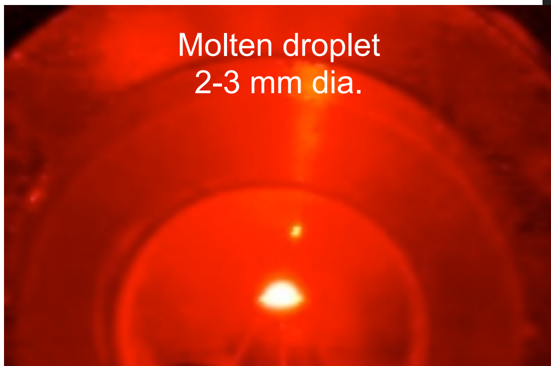
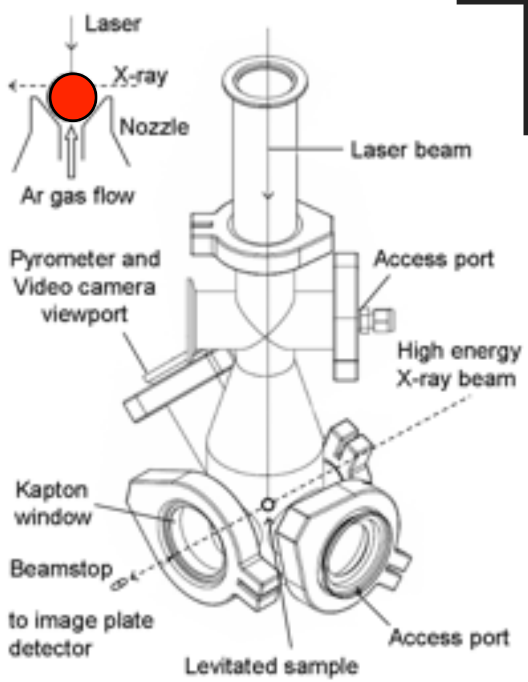


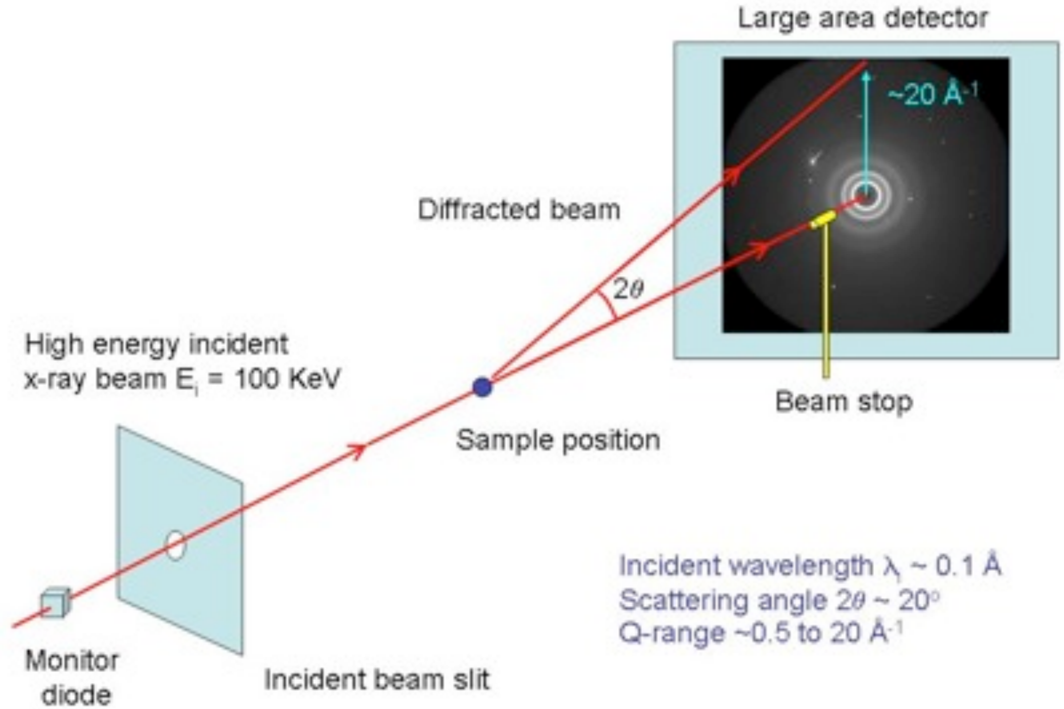
The region of the greatest change in viscosity (relaxation time) is the most inaccessible for XN scattering, the deeply supercooled regime.

Angell, Nature, 1995

Access to deeply undercooled melts
Levitation + HE x-rays + "fast" detectors (30 Hz)

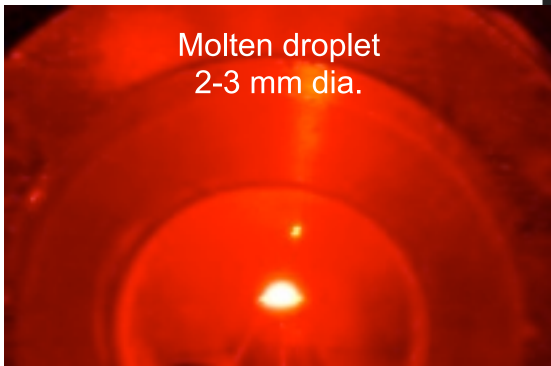


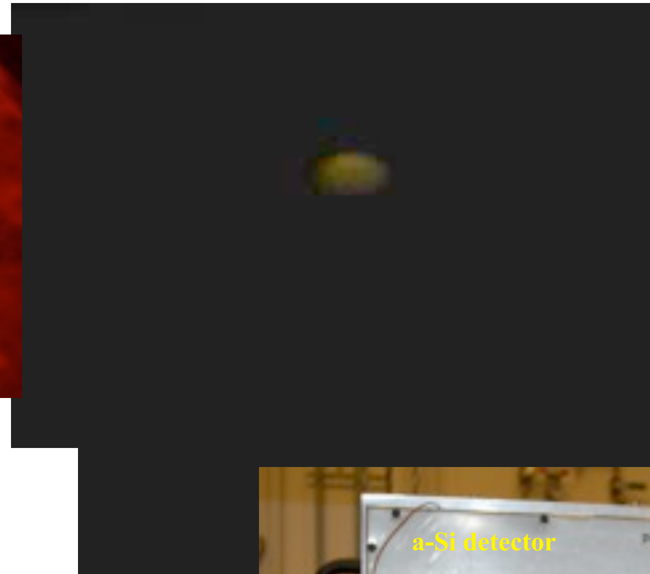


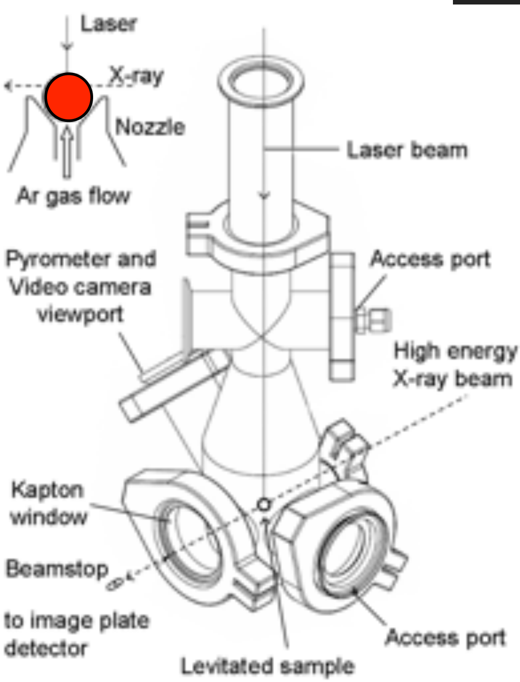


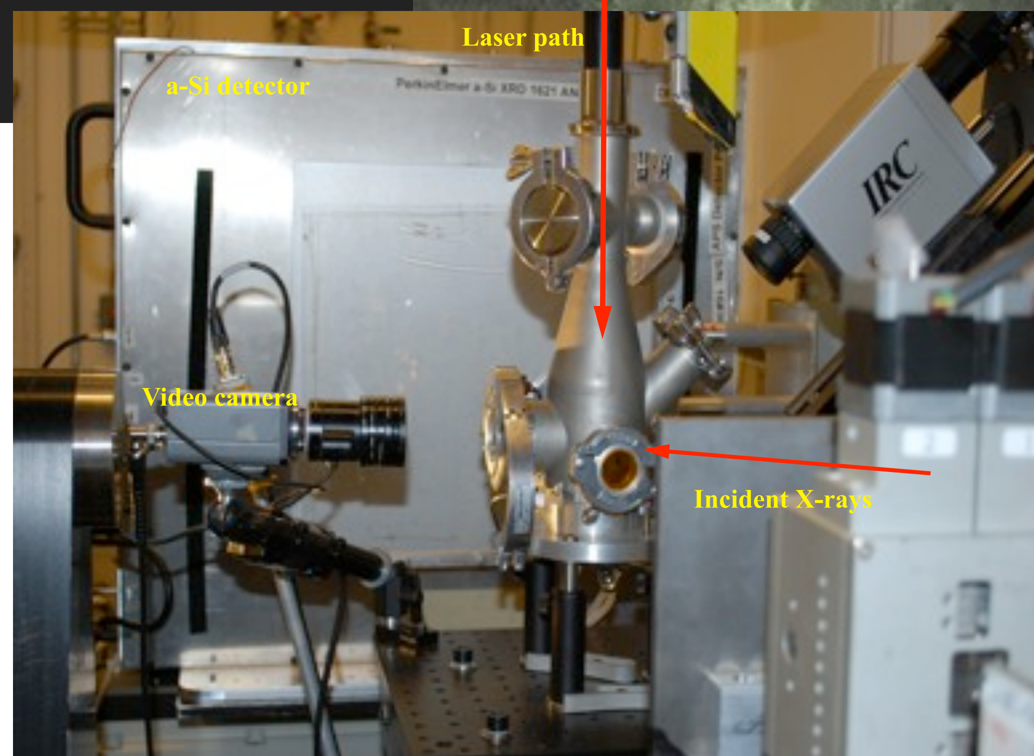
Incident wavelength $\lambda_i \sim 0.1$ Å
Scattering angle $2\theta \sim 20^{\circ}$
Q-range ~0.5 to 20 $Å^{-1}$

Levitation + HE x-rays + "fast" detectors (30 Hz)

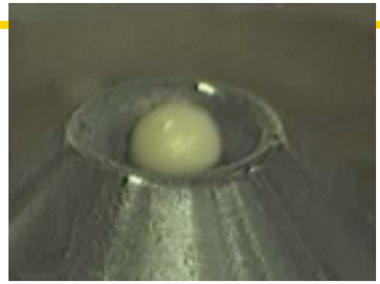




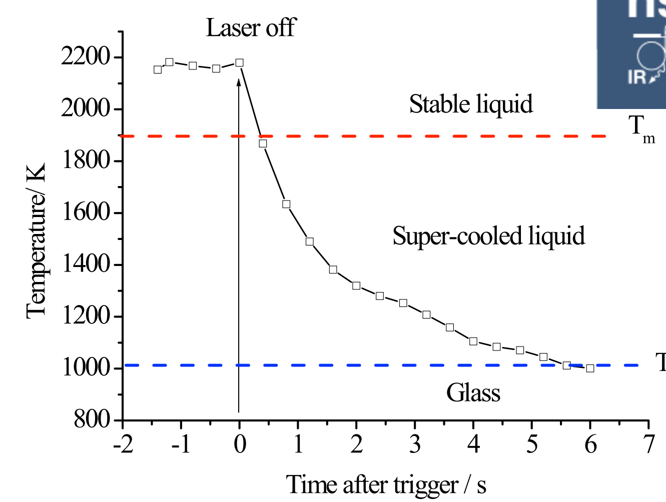




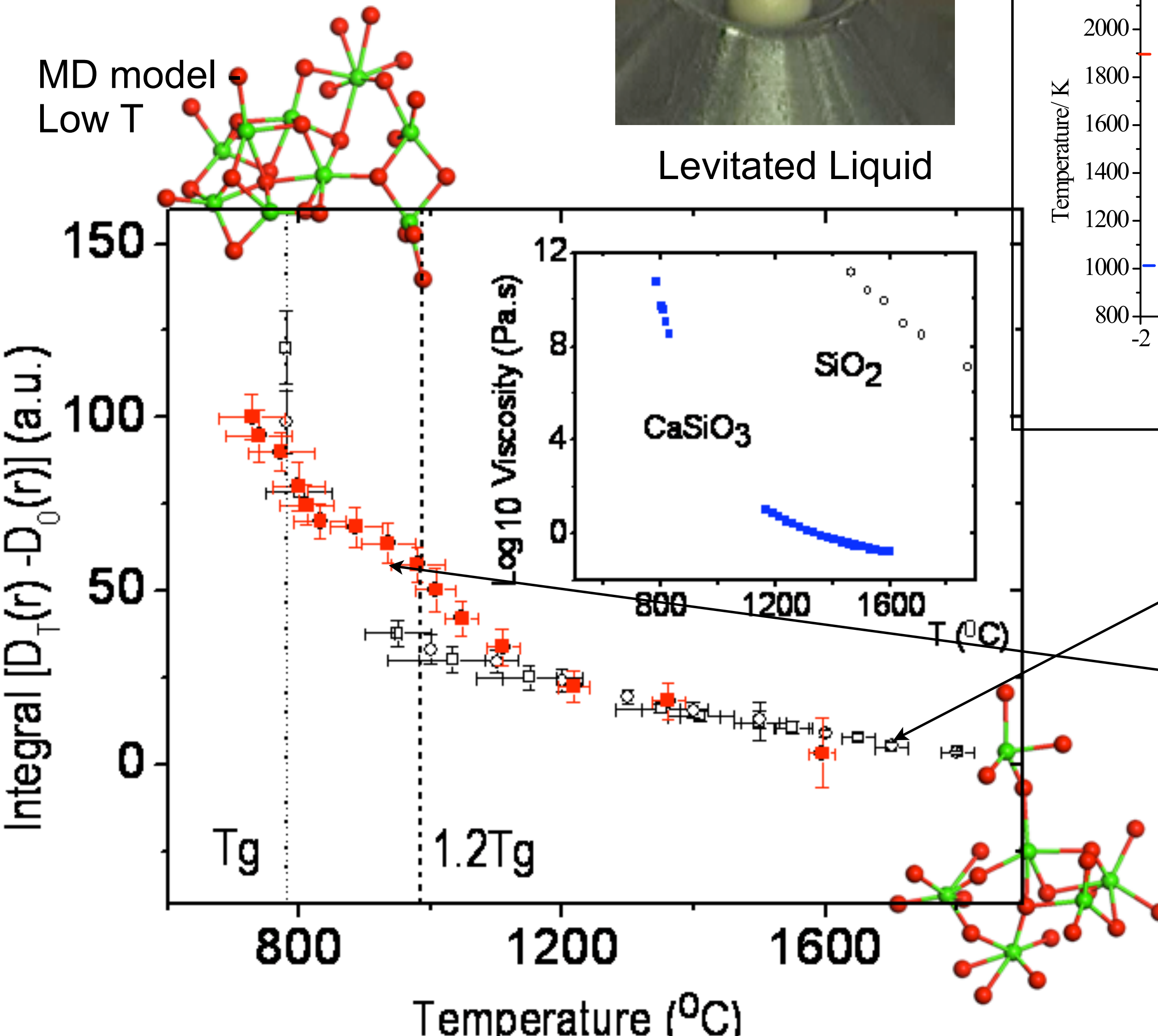
State of the art liquids: TR total scattering in drastically under cooled regime



Levitated Liquid



MD model - Low T

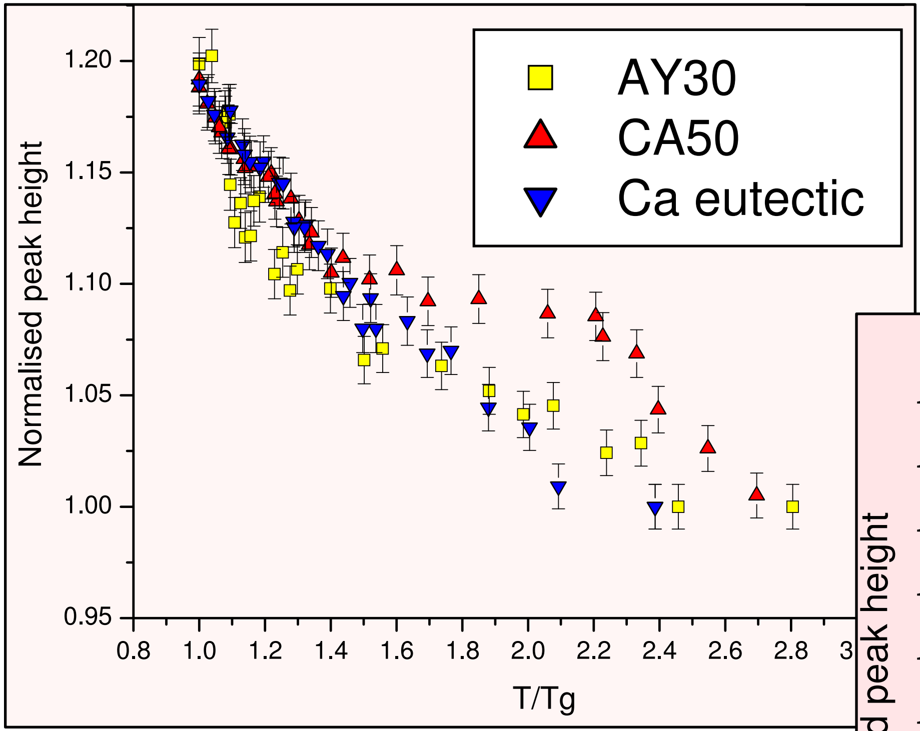


Black points collected in static mode

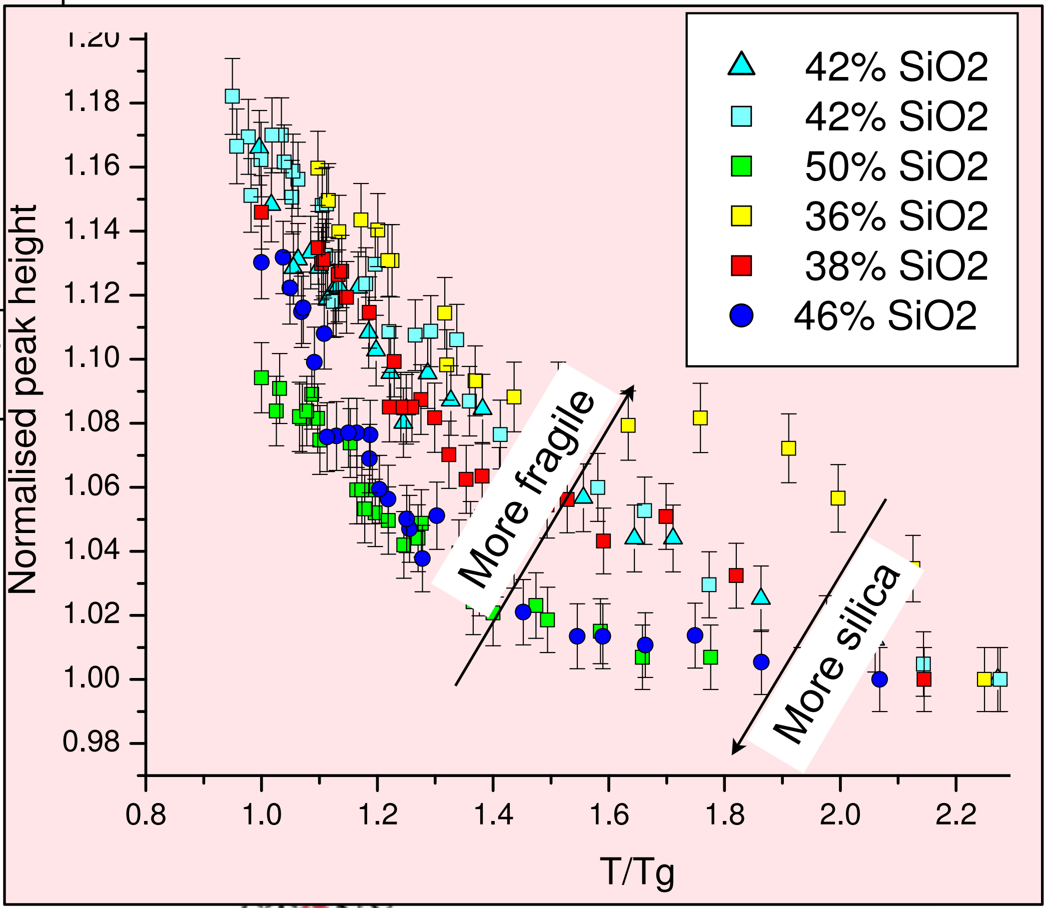
Red points collected with 100 msec TR

MD model fitted to scattering data - High T

A general result?



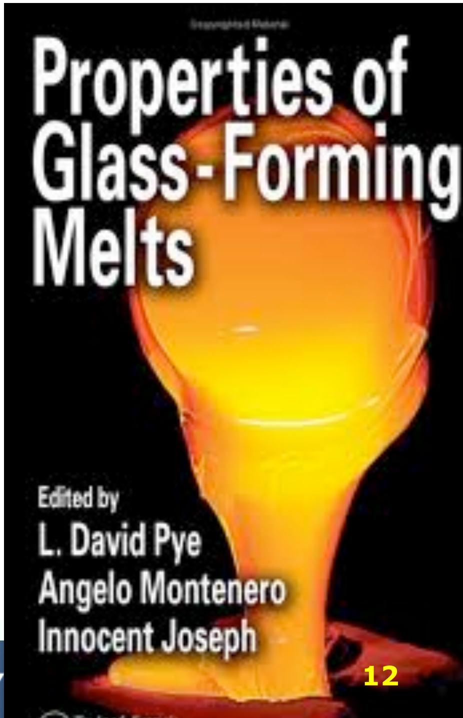
at least systematic?



The problem(s) for HP conditions

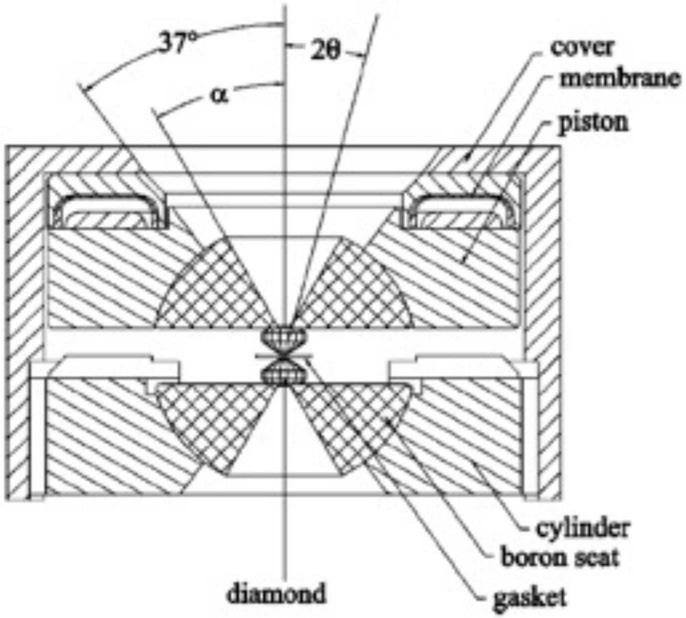
- *Simultaneous* density (viscosity) + "structure"
  - Especially in under-cooled regime - real time
  - How reliable is *G*(*r*) slope at low r?

- Following structure evolution with scattering
  - parasitic scattering and nucleation from container
  - melting of container
  - insufficient Q-coverage/normalization of S(Q)

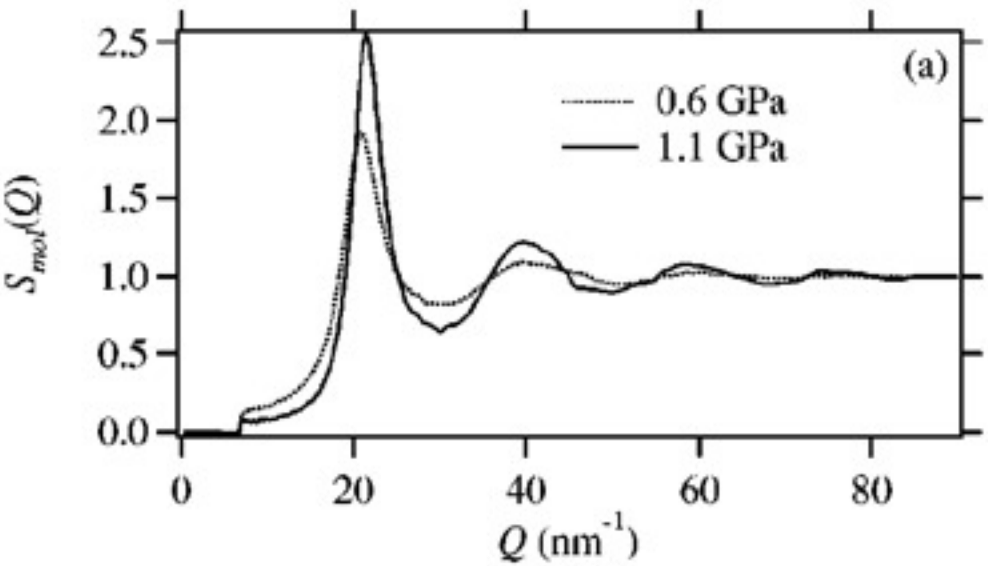


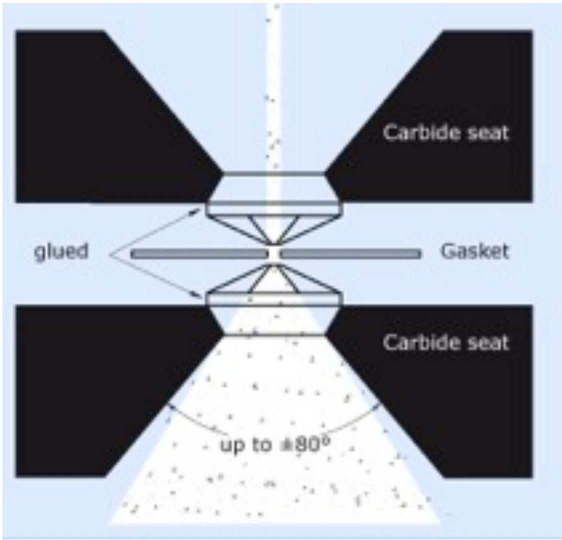
Structure of liquids – DAC experiments

Eggert et al., *PRB* **65**, 174105 (2001)



Liquid Ar





Boehler-Almax anvils

Slide C/- Chrystele Sanloup,
UPMC & CSEC, Edinburgh

Getting the density from g(r)

Kaplow et al., *Phys. Rev.* **138**, A1336 (1965)

$$I_{coh}(Q) = \alpha I_{samp}(Q) - I_{incoh}(Q)$$

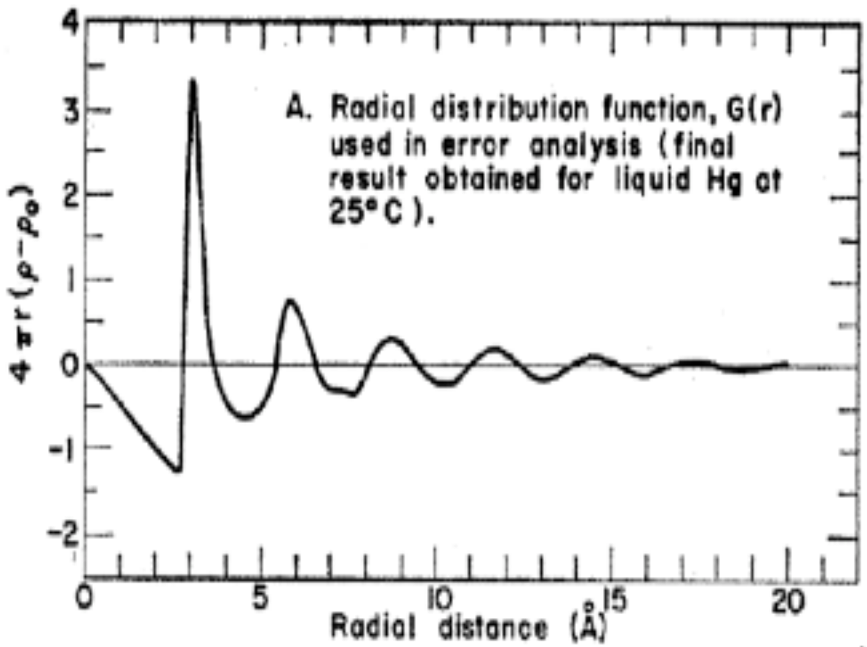
$$S(Q) = \frac{I_{coh}(Q)}{\alpha f(Q)^2}$$

α, normalization factor such as

$$\lim_{Q \to \infty} S(Q) = 1$$

$$F(r) = 4\pi r\rho\left(g(r)-1\right) = \frac{2}{\pi}\int_0^{Q_{max}} Q\left(S(Q)-1\right)\sin(Qr)\,dr$$

⇒ Initial slope gives ρ



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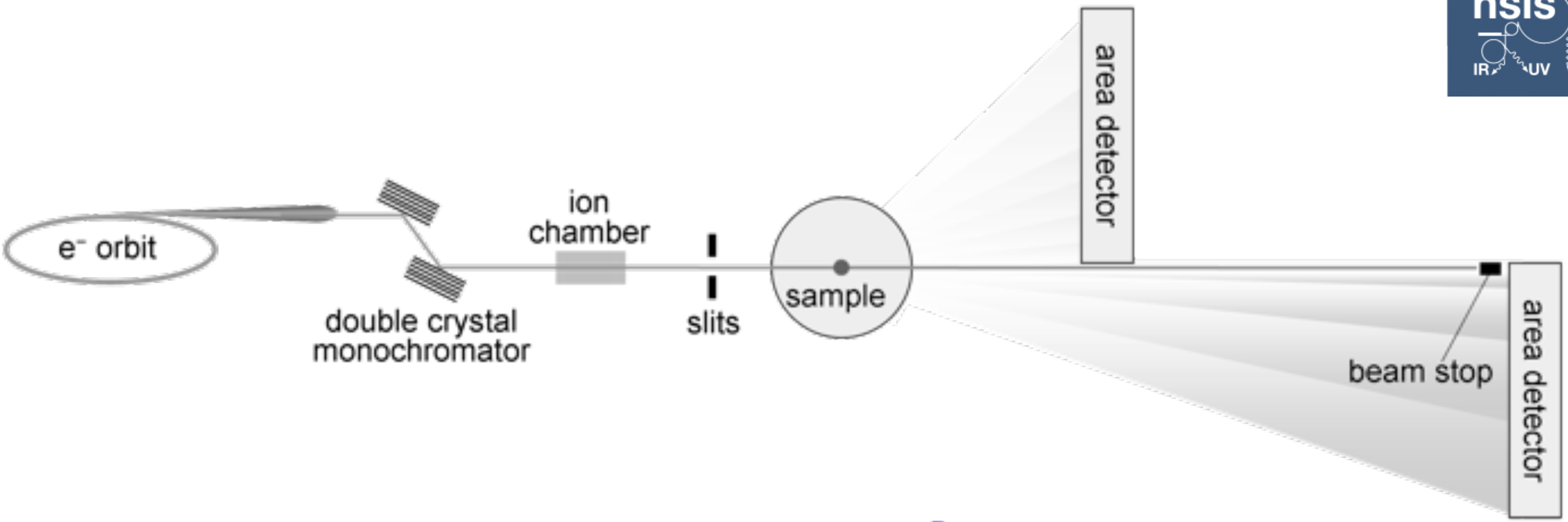
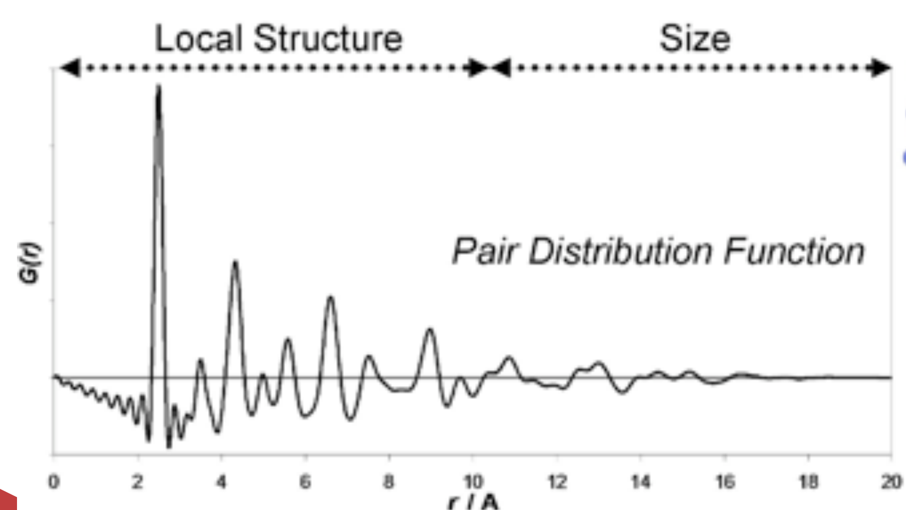
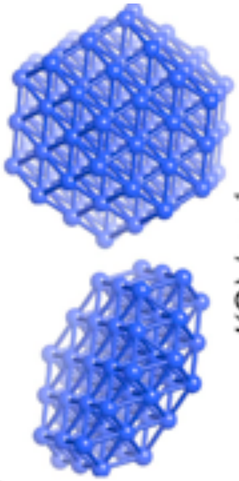
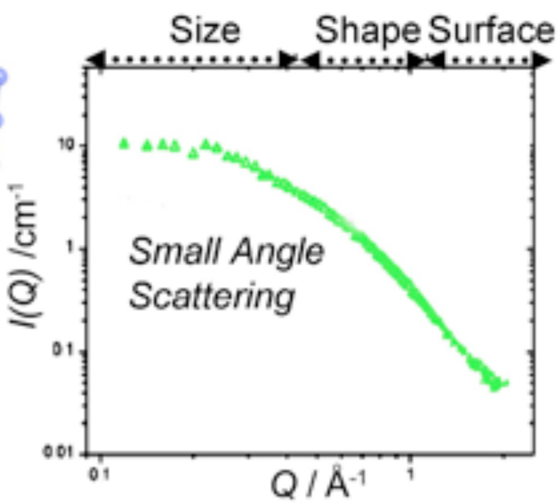
UPMC & CSEC, Edinburgh

The Future:
Combined PDF and SAXS measurements









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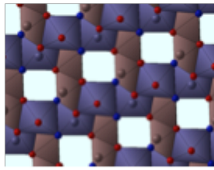
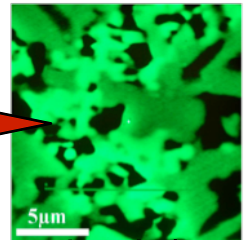
HP Synthesis and optimization 1.0 - state of the art

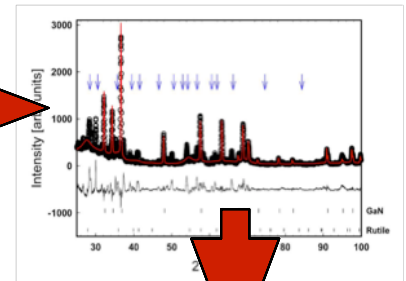
- (1) Find something valuable only made at high P



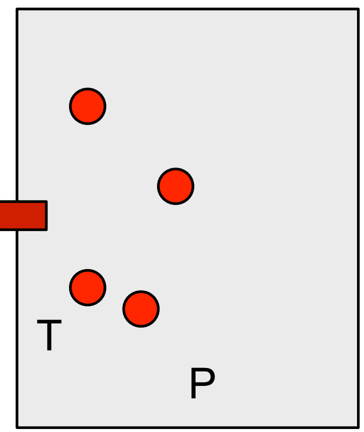
Prediction



synthesis/composition
multiphase

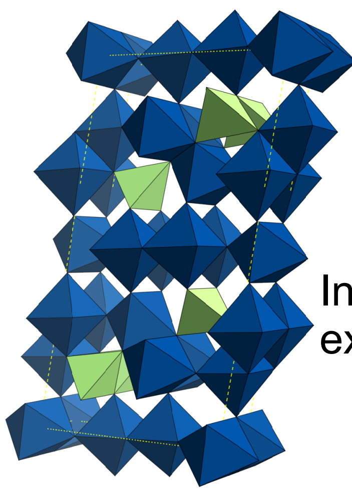


multiphase fit



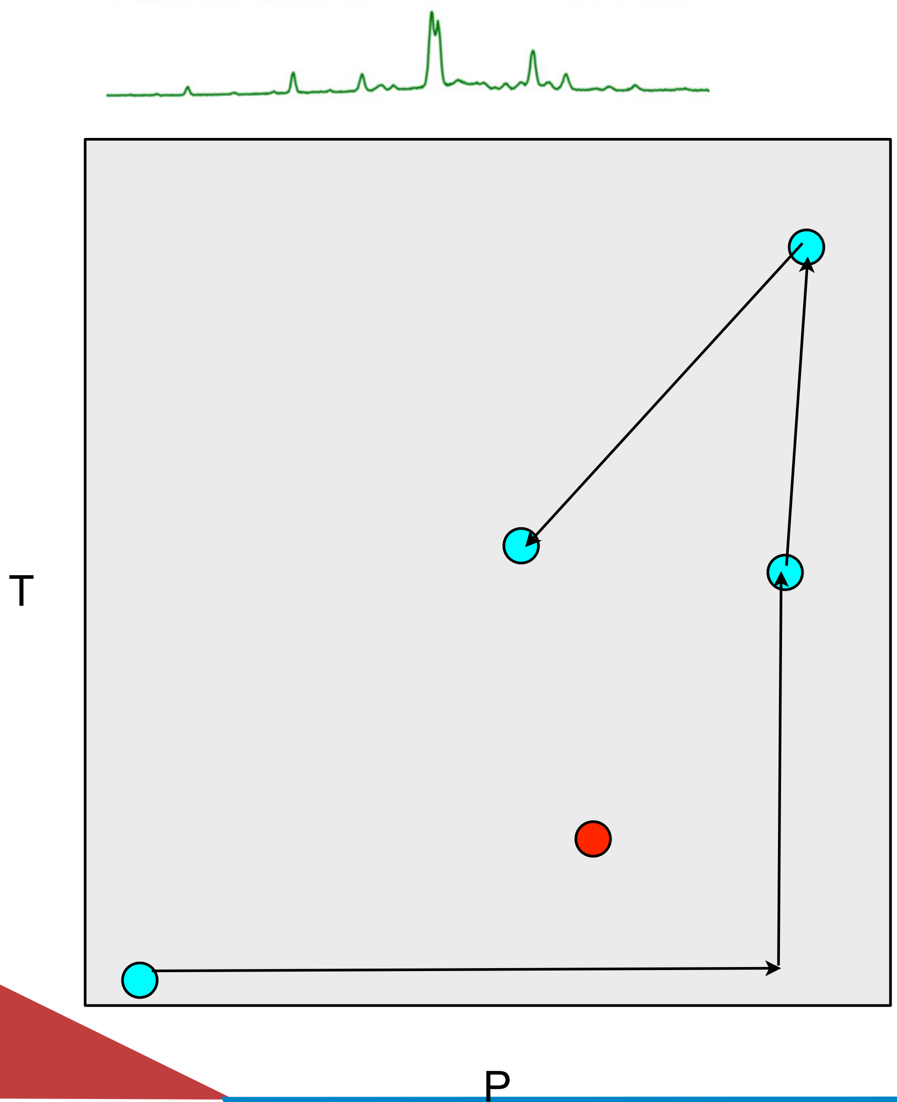
Individual quench
experiments

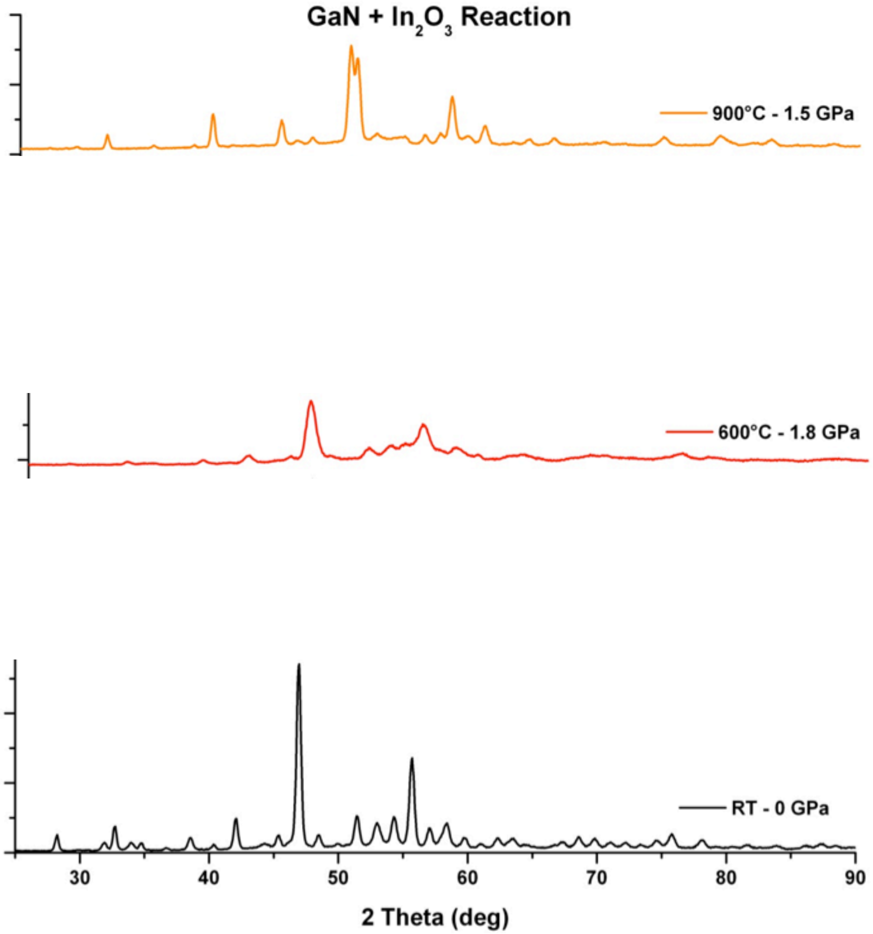
Cycle time
~ 1 month



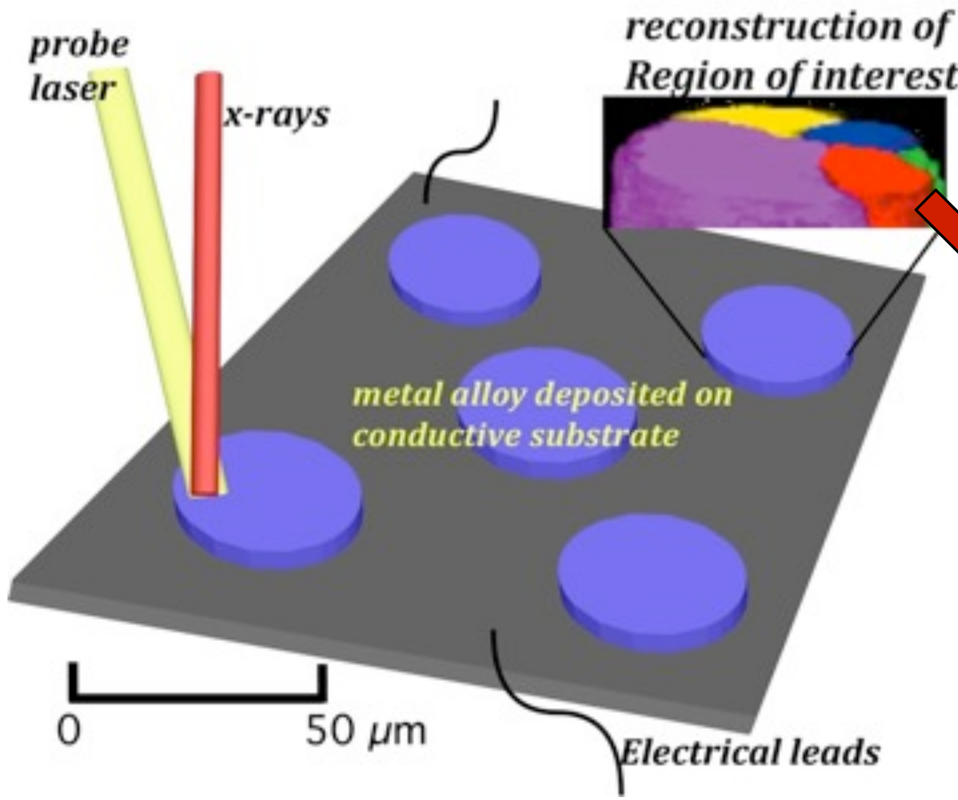
Actual new phase

HP Synthesis and optimization 2.0

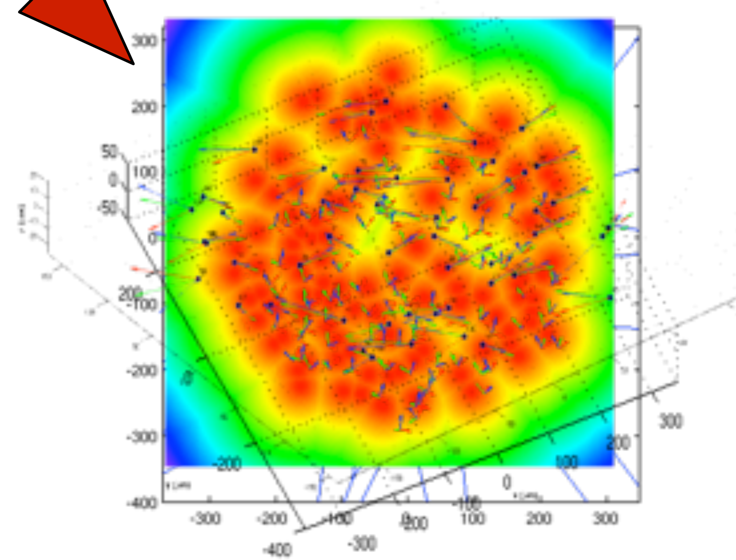




HP Synthesis and optimization 3.0



Total Crystallography: Phase ID, Structure Solution, grain maps, strain mapping, KINETICS

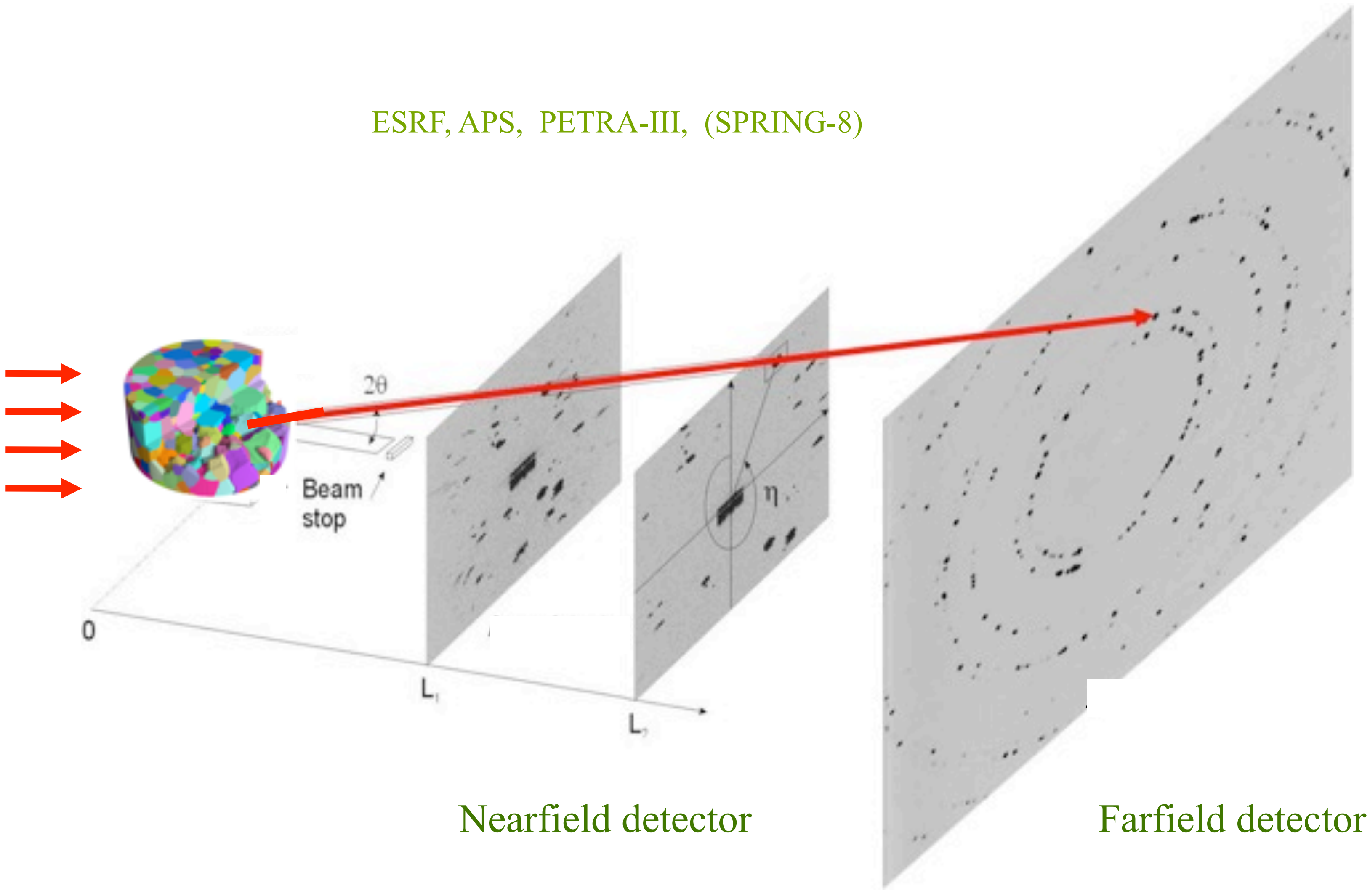


Simultaneous measurement of properties and Phase ID
Put solid state kinetics on a fundamental footing grain maps, grain boundary effects, size strain

Vaughan, Wright et al., in progress; http://www.esrf.eu/UsersAndScience/Publications/Highlights/2006/MAT/MAT10

3DXRD set-up - high energy

ESRF, APS, PETRA-III, (SPRING-8)



Nearfield detector

Position

Farfield detector

Orientation and strain

H.F. Poulsen: **Three-Dimensional X-ray Diffraction Microscopy** (Springer, 2004).

Necessary developments - supercooled liquids

- Goal: better understanding of liquids in transition to glass/crystal close to T_g or $<T_g$
- Simulations suggest dynamically heterogeneous behavior, related to sampling potential energy landscape
  - Fast measurement in container for limited undercooling
  - Extended S(Q) - high energy
  - Simultaneous measurement of density/structure to discover/study anomalies
    - Errors in using low-r region of G(r) for density
  - Measurement of S(Q,w) as well as S(Q) in real time (Egami group, PRL, 106, Art:115703).

Necessary developments - Solid State HP chemistry

- Goals: Real time evaluation
  - 1) New materials by design at extreme conditions
  - 2) Total crystallography for structure/texture/strain
  - 3) Metastable processes/quenchability
- Strong theory coupling to focus synthesis
- Massively parallel measurement/optimization
- Deposited sample/circuit in one sample loading
- Measure response signal, *then* phase optimize
- High energy beams
- Dynamic control of energy and beam size (nm - μm)
- High spatial/energy resolving detectors