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FIRST APPLICATION OF SIMULTANEOUS SANS AND DIFFERENTIAL SCANNING CALORIMETRY: MICROPHASE SEPARATED ALKANE BLENDS

ELLIOT GILBERT

Instrument Responsible, QUOKKA (SANS)

Leader, Food Structure and Dynamics

MOTIVATION

- PhD, Chemical Physics (1993-97)
  - ‘Phase Behaviour in n-Alkane Systems’

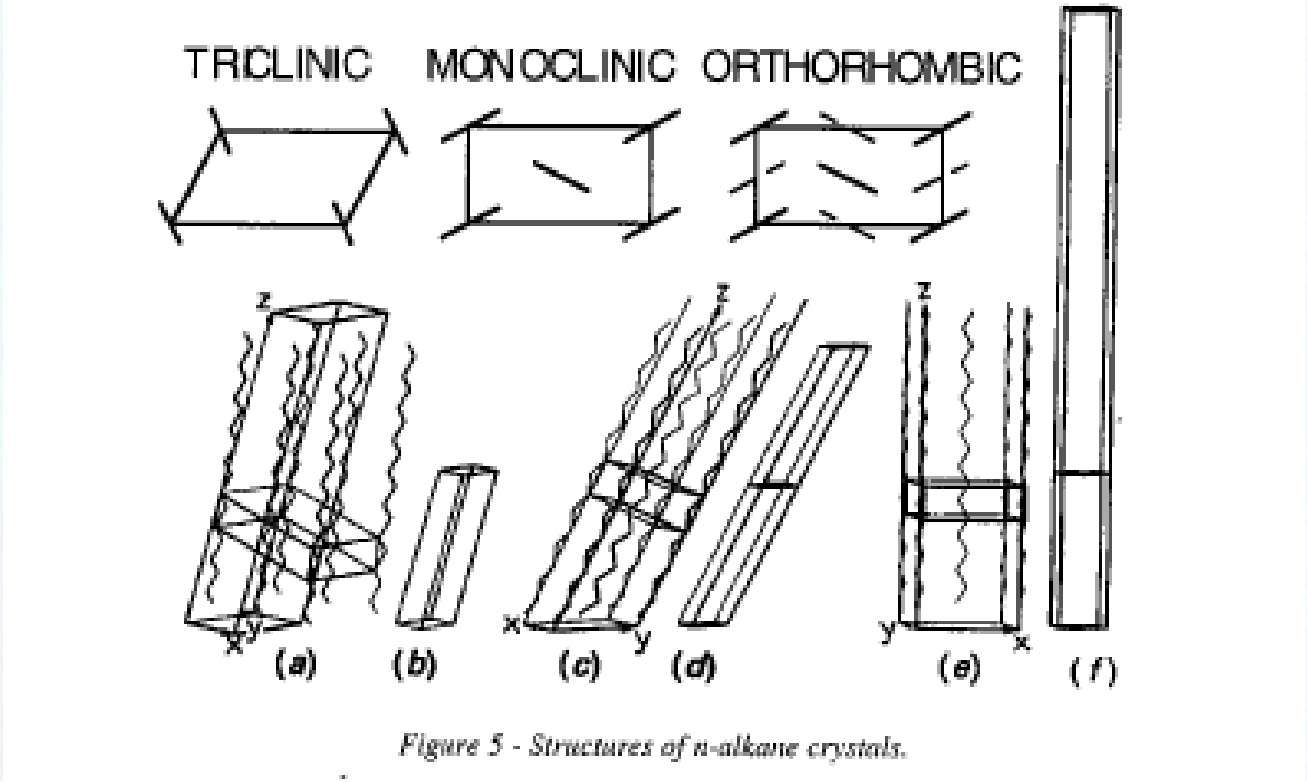
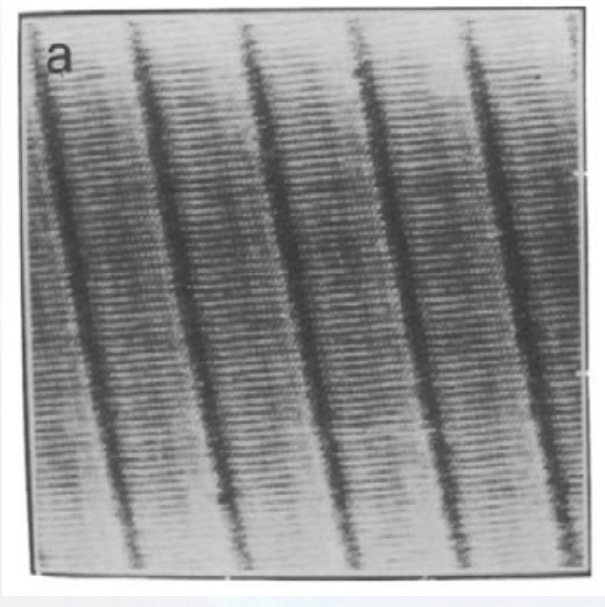


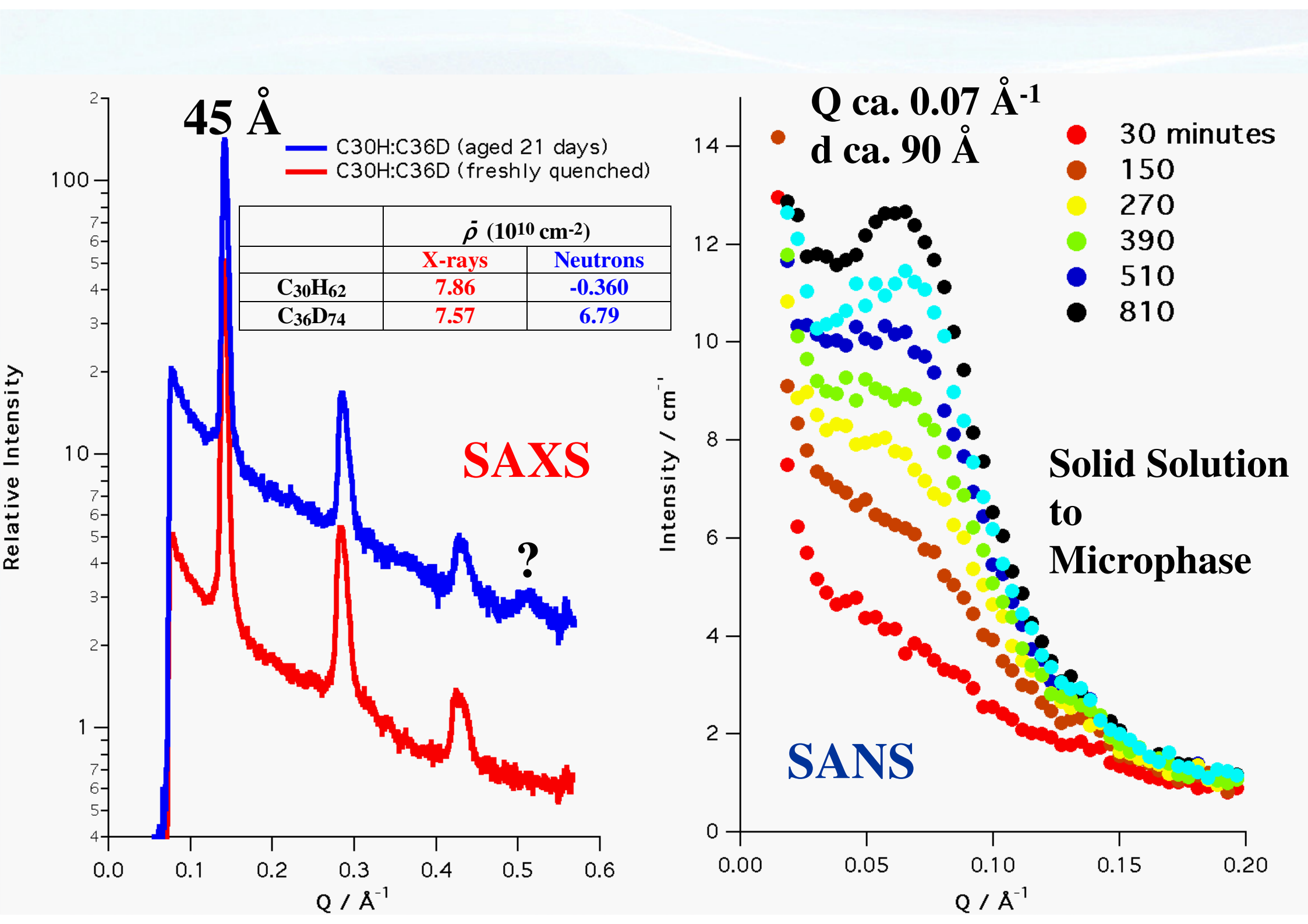
Figure 5 - Structures of n-alkane crystals.

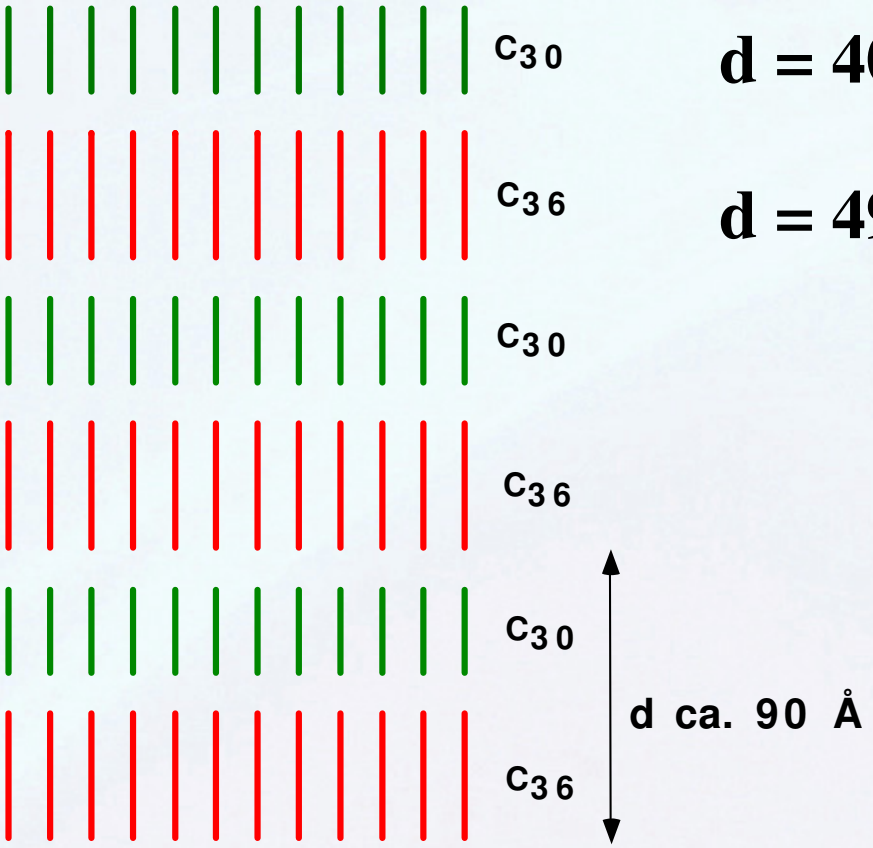


Gilbert, Senden and White
Chem Phys Lett 1994

1:1 C_mH_{2m+2} + $C_nD_{2n+2,}$ effect of changing (n-m)?

within thesis: $20 \leq m \leq 34$ with $n = 36$


45 Å
C30H:C36D (aged 21 days)
C30H:C36D (freshly quenched)
$\bar{\rho}$ (10^{10} cm^{-2})
X-rays
Neutrons
$C_{30}H_{62}$ 7.86 -0.360
$C_{36}D_{74}$ 7.57 6.79
SAXS
?
Relative Intensity
Q / Å^{-1}
Q ca. 0.07 Å^{-1}
d ca. 90 Å
30 minutes
150
270
390
510
810
Solid Solution
to
Microphase
SANS
Intensity / cm^{-1}
Q / Å^{-1}



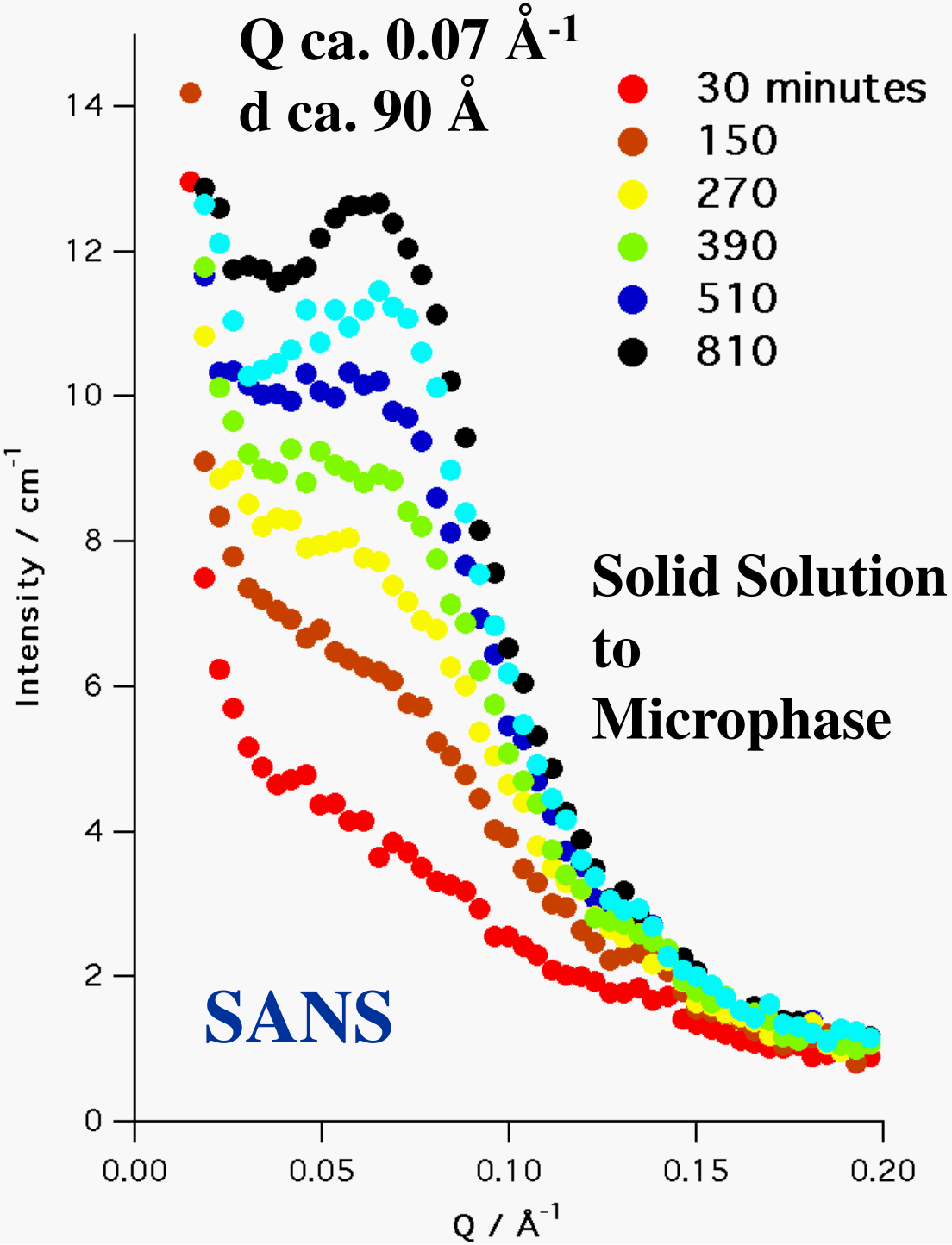
d = 40 Å

d = 49 Å

Microphase cf. block copolymers – doubling of unit cell

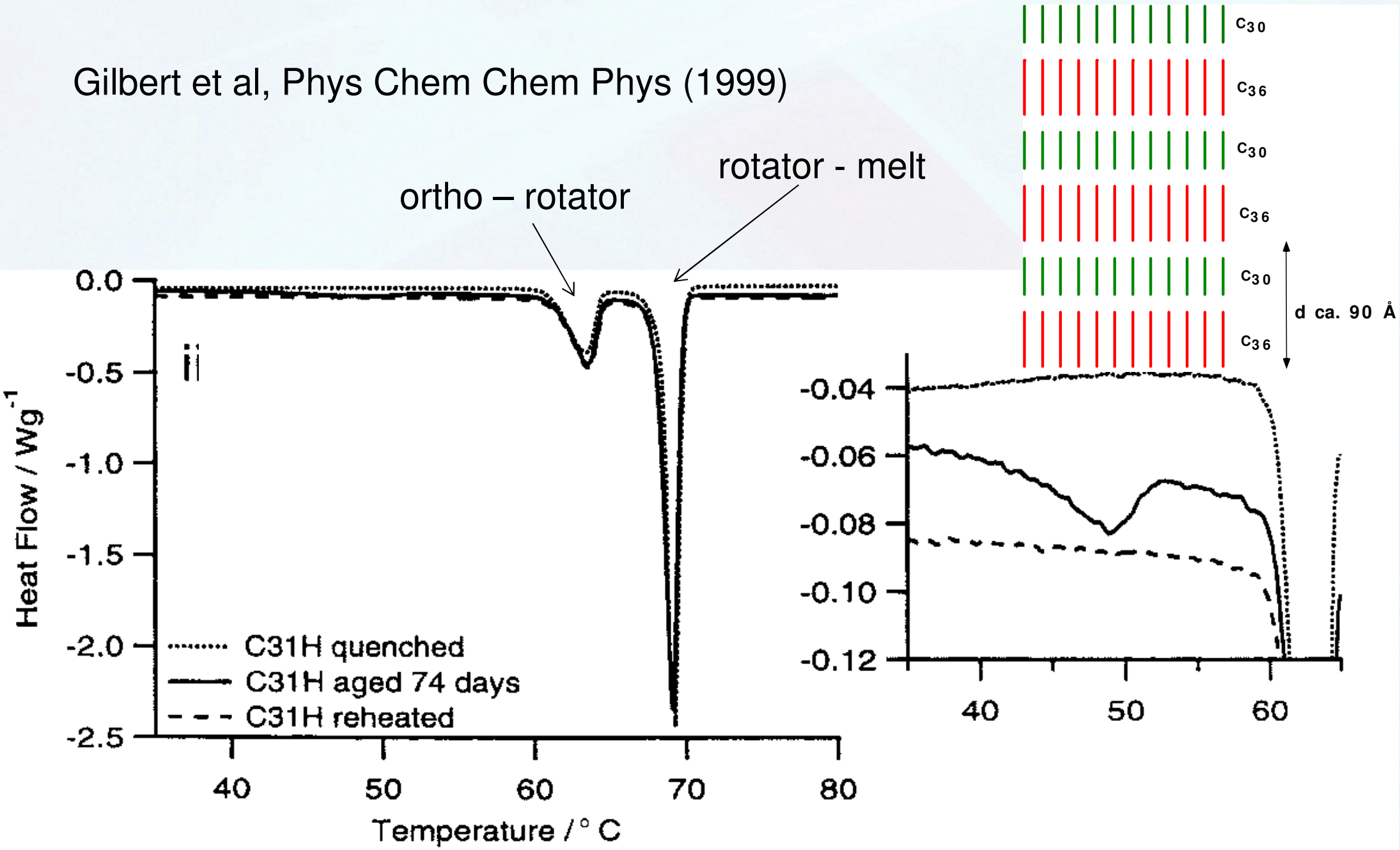
SAXS – average dimension

Mazee (1958) C_{30}:C_{35} ca. 1 year

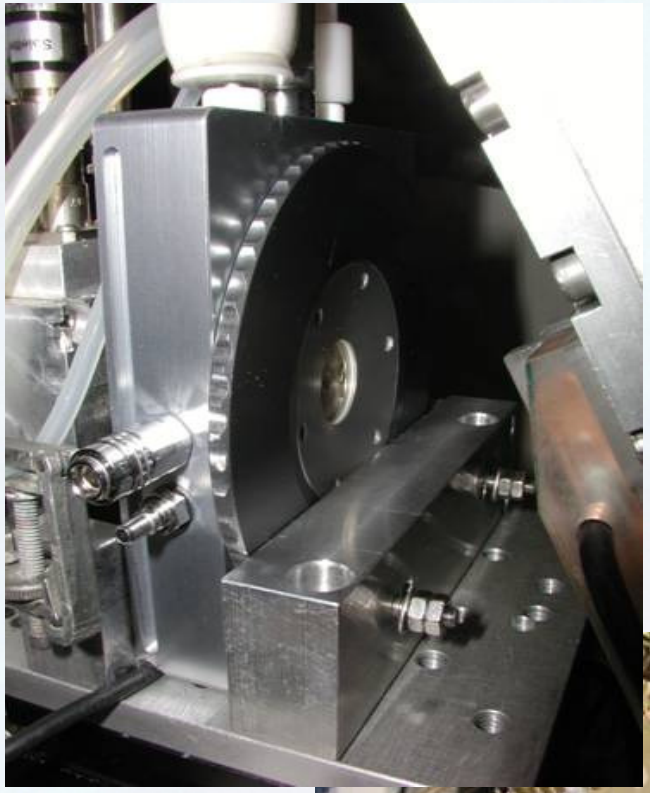


MICROPHASE SEPARATION AND DSC

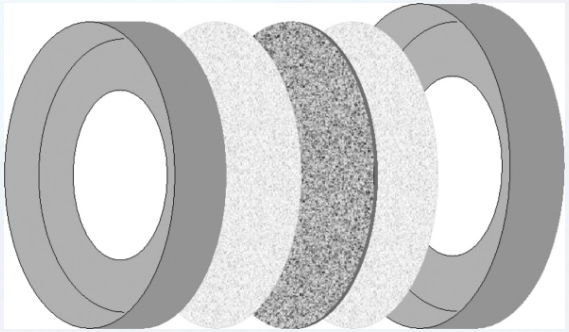
Gilbert et al, Phys Chem Chem Phys (1999)

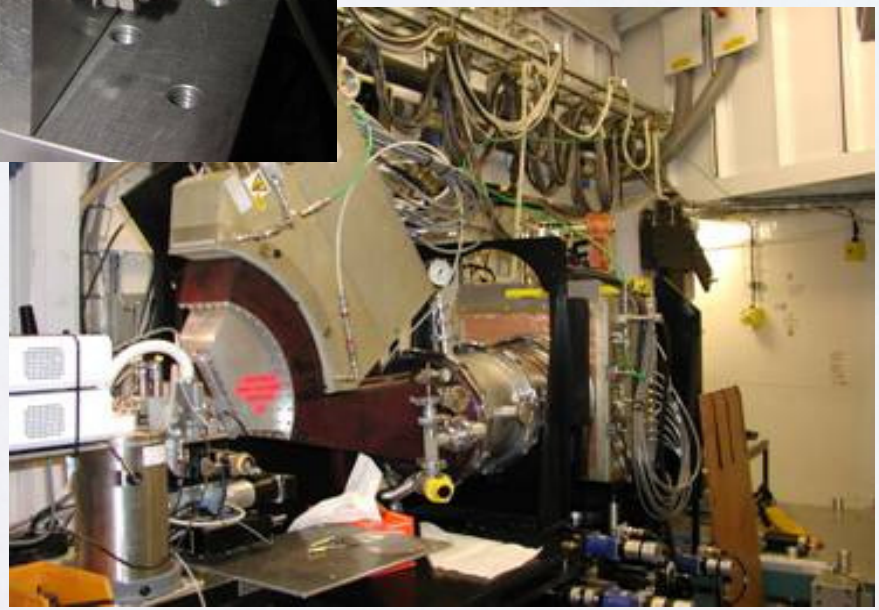


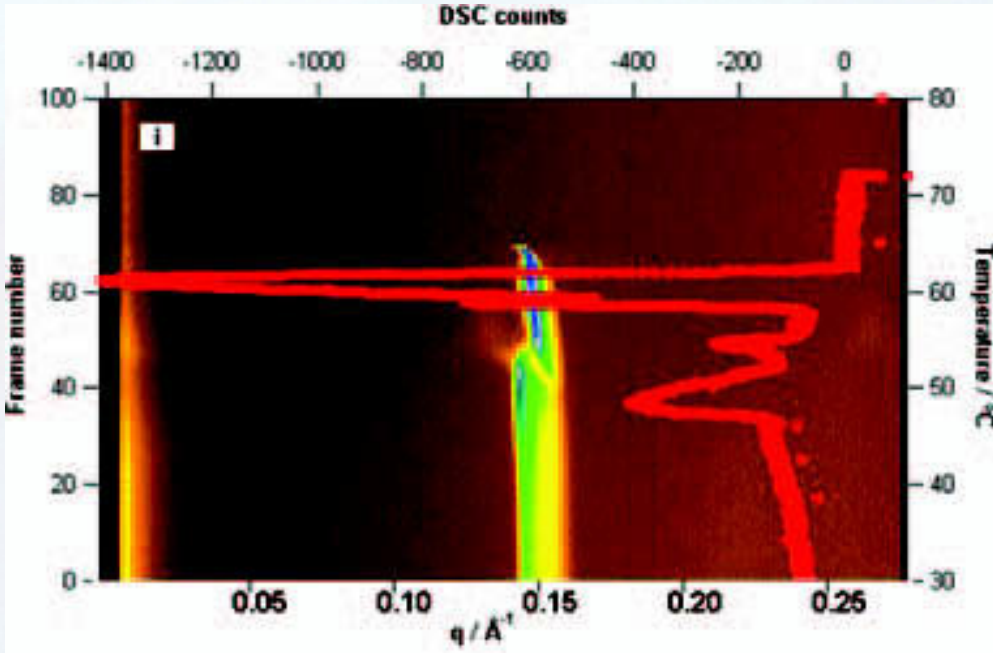
COMBINED SAXS/DSC

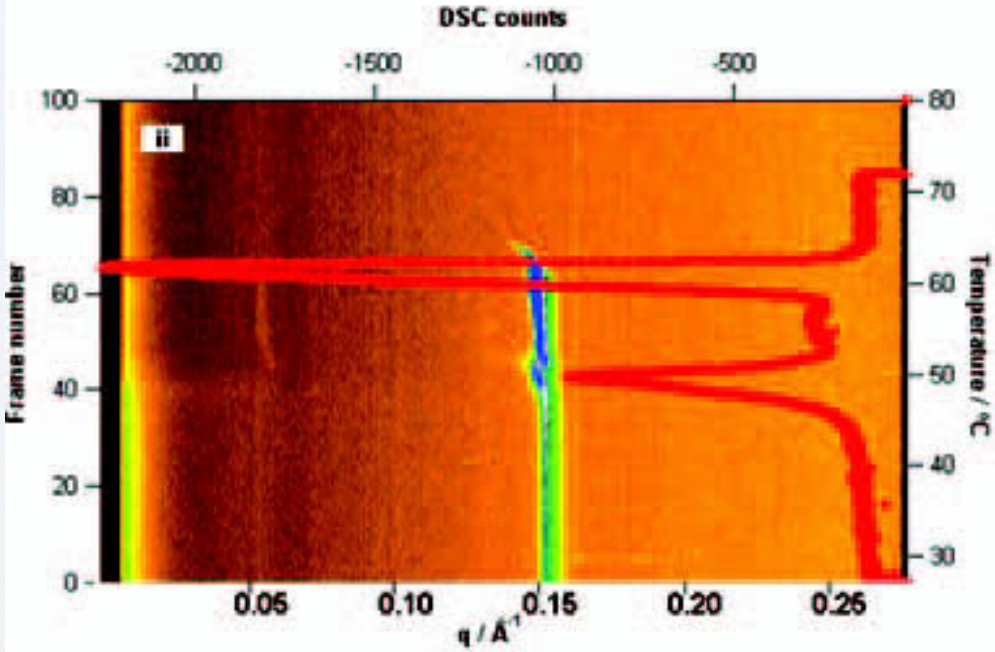


2:1 $C_{28}H_{58}$:$C_{36}D_{74}$
i) 100C/min (aged 5 h)
ii) 0.1C/min (aged 3 w)







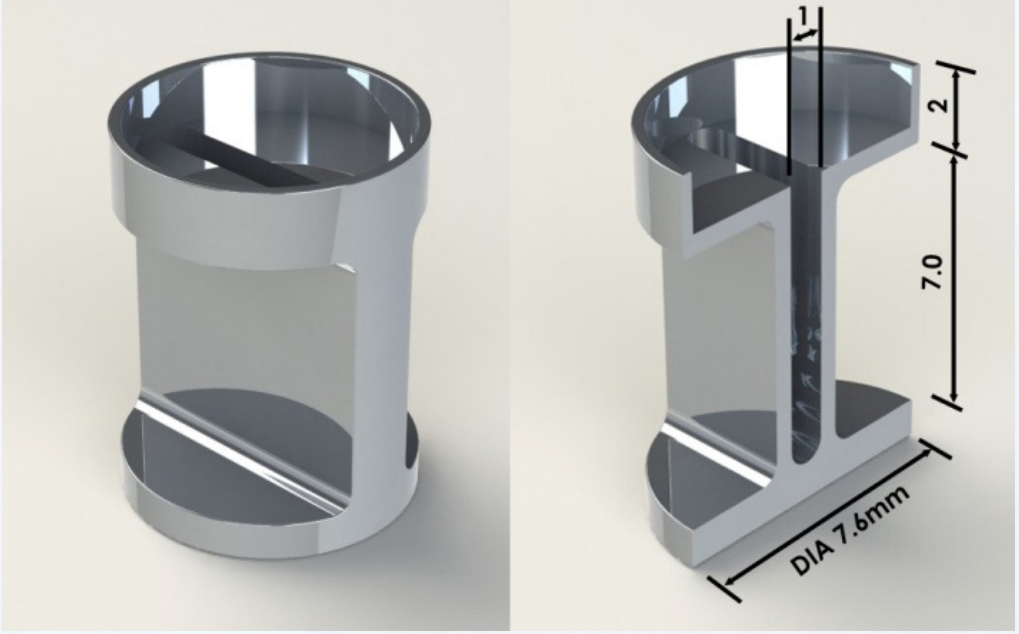


Gilbert et al., Mol. Cryst. Liq. Cryst. 440 (2005) 93

SANS/DSC FACTORS

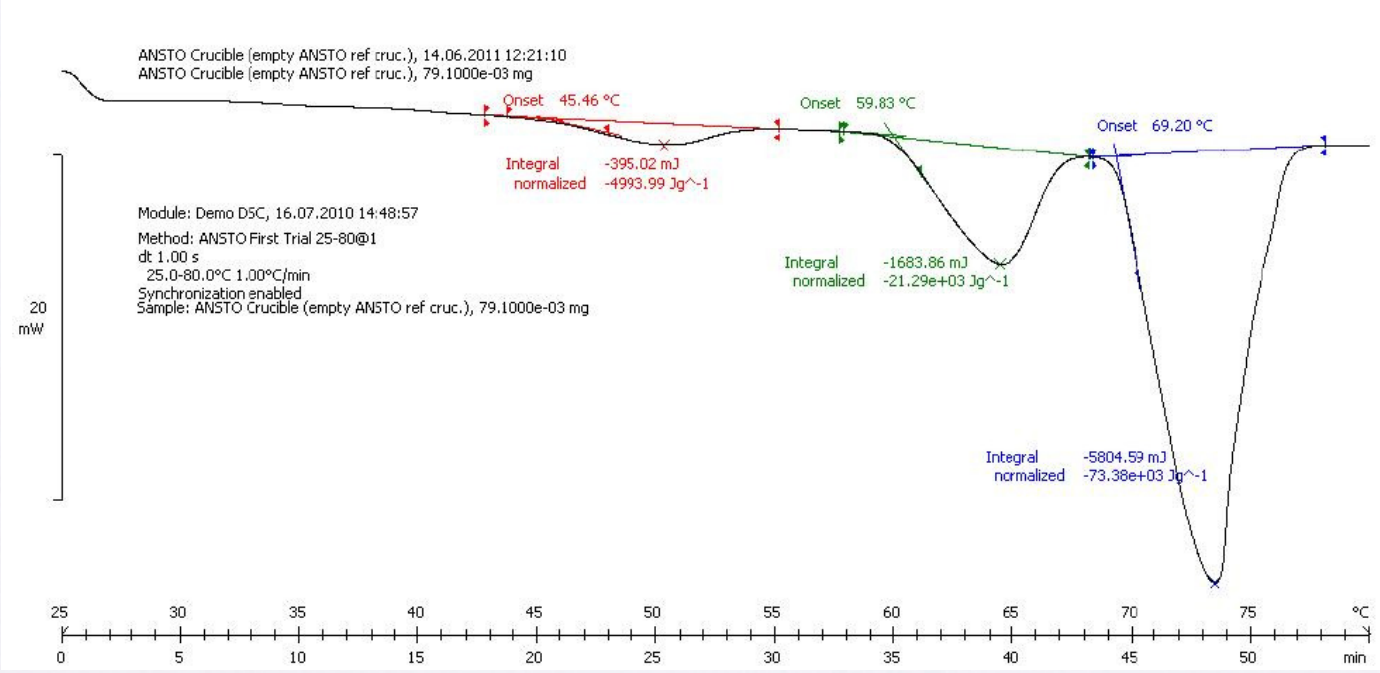
- flux versus scan rate (and sample size)
- need for novel crucible design
  - size – 5 mm diameter
  - material selection (attenuation, shielding, activation)
- extent of compromise on thermal response and control
  - in-house or (staged) customisation of commercial unit?
- space at sample position
- maximum scattering angle
- instrument control and synchronisation

CRUCIBLE DESIGN AND THERMAL VALIDATION



1370F Al - 1 mm slot, 0.5 mm wall
49µL (ca. 20% of std 1 mm cuvette) sample in base and in vertical region

1. Verify transitions observable with novel crucible in commercial DSC unit (‘true’ and sequential mode cf. SANS)



FIRST SCATTERING TEST ON QUOKKA (ex-DSC)

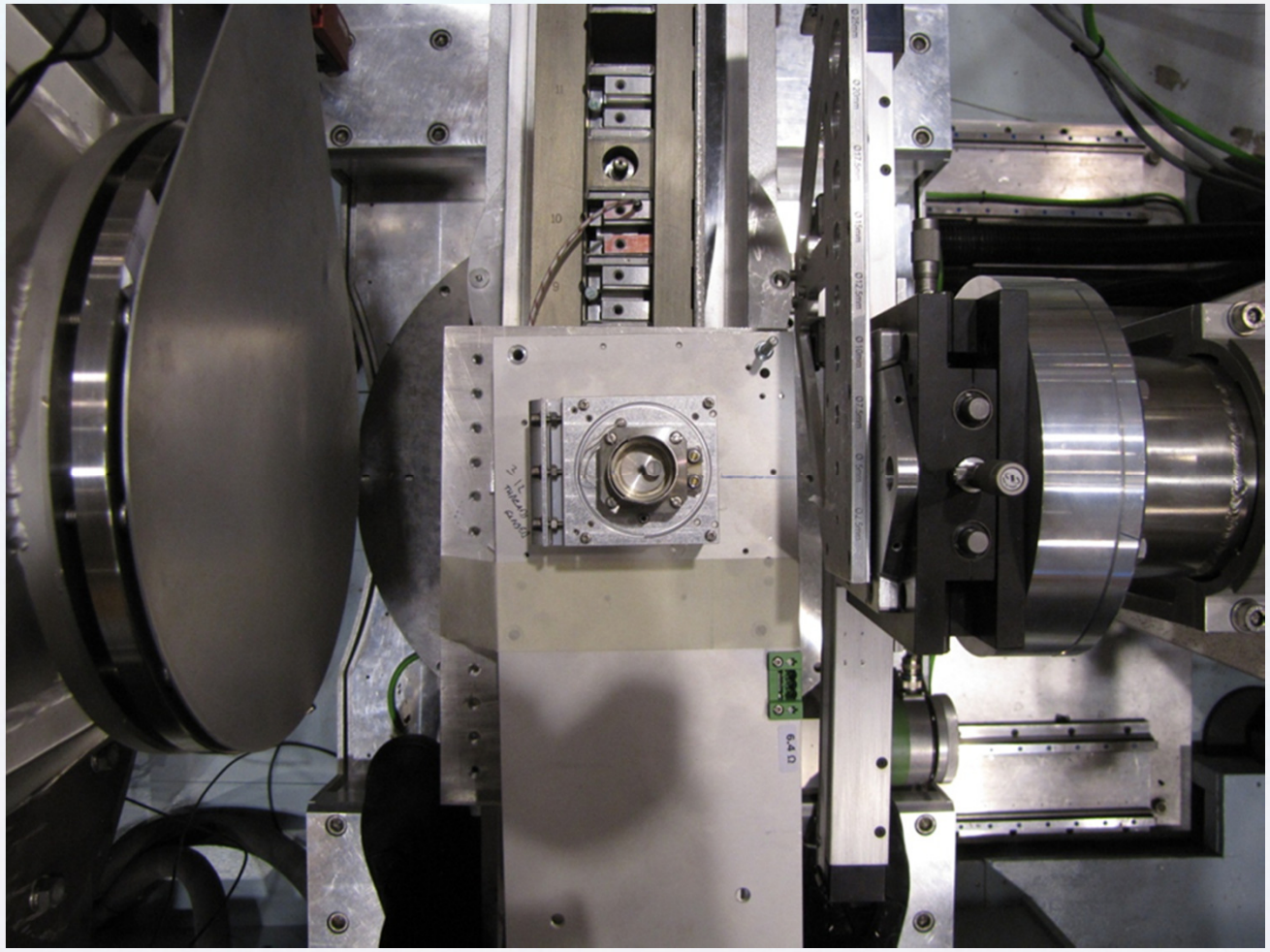
2. Verify Scattering - ex-furnace

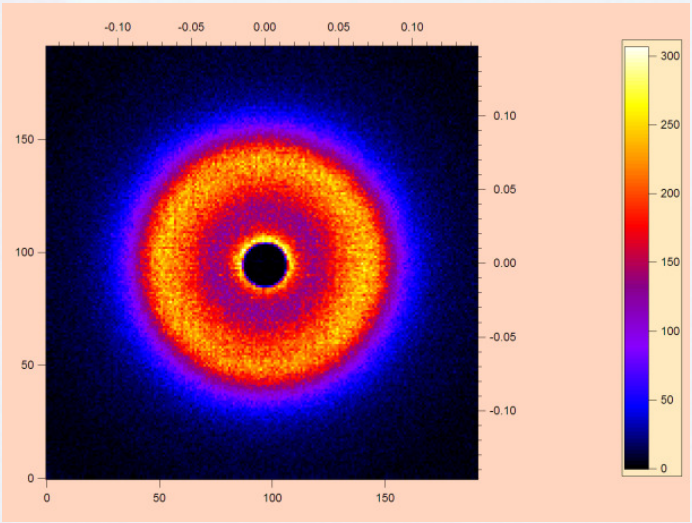
SSD = SDD = ca. 4 m; D_1 = 50 mm; **D_2 = 2.5 mm !**

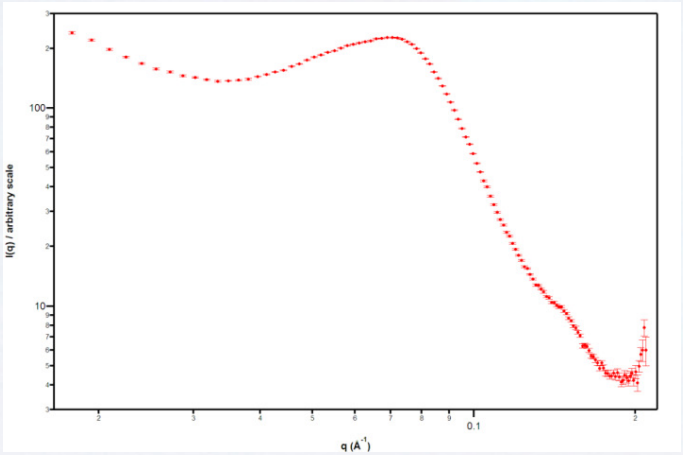
(1/2 diameter, 1/4 area of design criterion)

(cf. ramp rates of 1 – 5C/min – data in acceptable period)

2 mins data **& attenuated by factor of 2 i.e. using 1/8th neutrons**

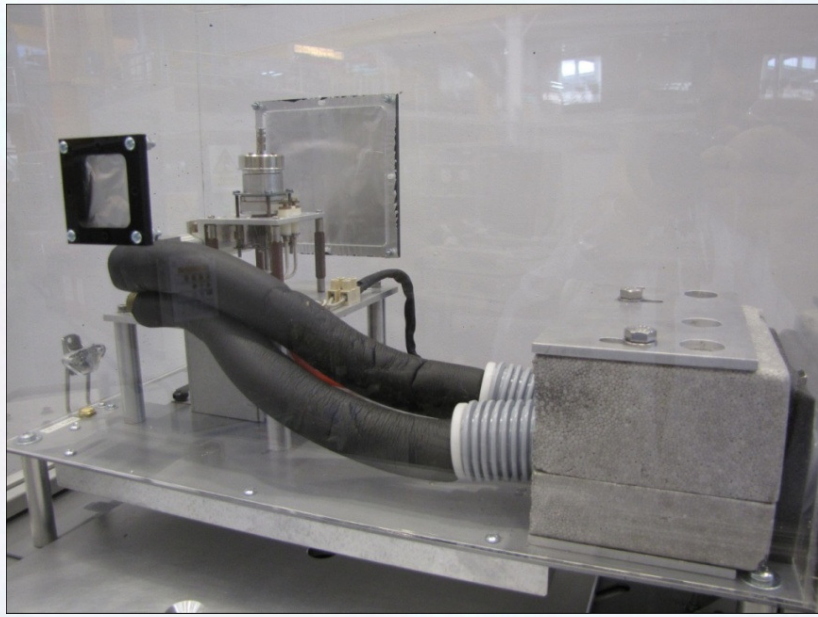






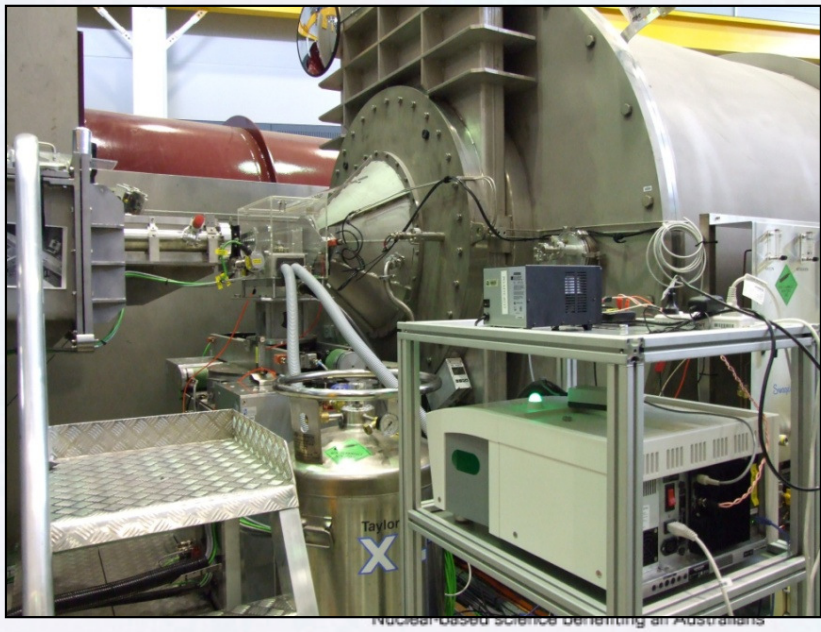
FURNACE AND HARDWARE MODIFICATION

- Furnace walls
  - Inner (Ag): holes @ 3/9 o'clock, 6 mm entrance, 11.3 mm exit (+/- 22° V; 36° horiz H)
  - Outer (Ag to 5 mm Al – min. convective loss)
  - Cd apertures (shielding, alignment)



- <u>DSC tests repeated</u>
  - Added draught shield
  - Indium: agree with unmodified DSC

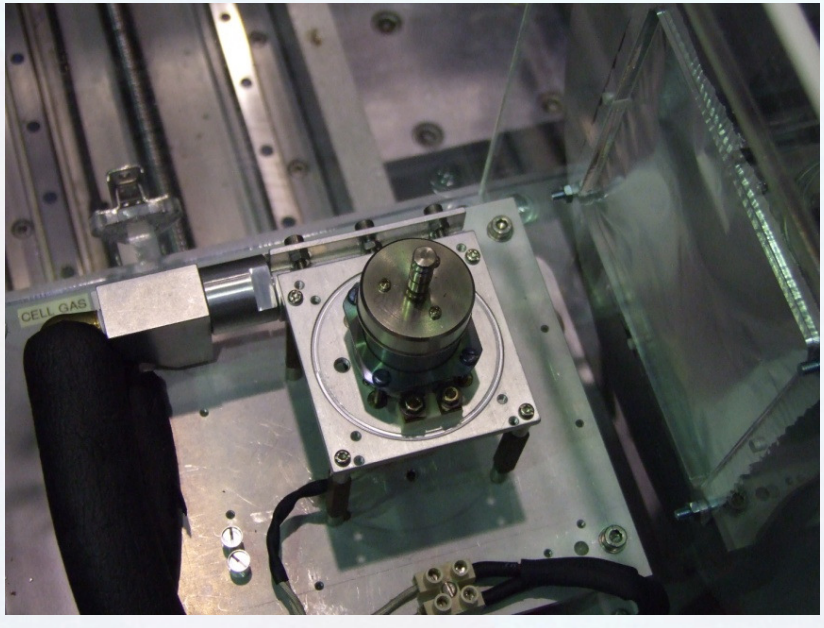
- Heating pan, electronics removed from DSC body
- Power, gas services to furnace, analogue board, liq N_2 cold finger extended
  - furnace, DSC board separated (ca. 2m)
- Perspex box: inert atmosphere, flush with dry N_2

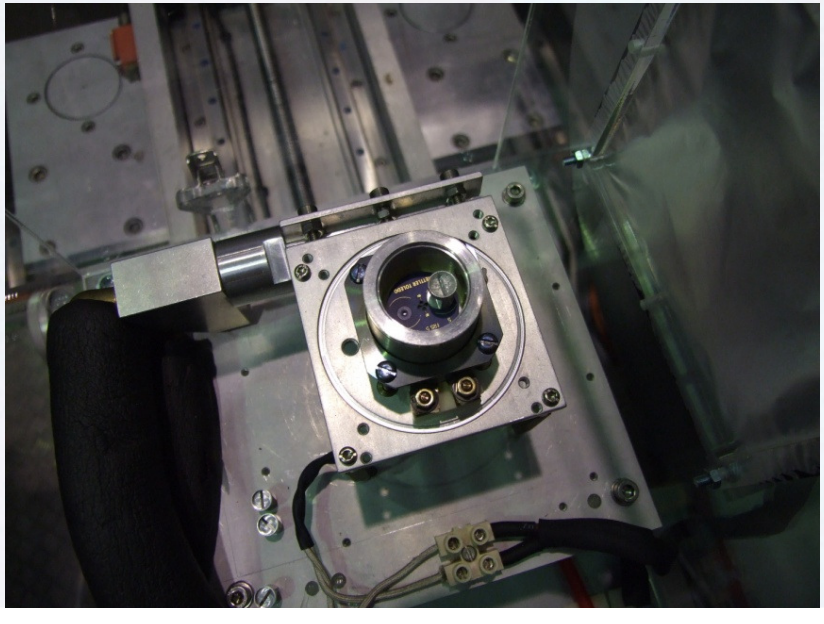


- <u>DSC tests repeated: calibrate with In, checked: phenyl salicylate, naphthalene and benzoic acid</u>

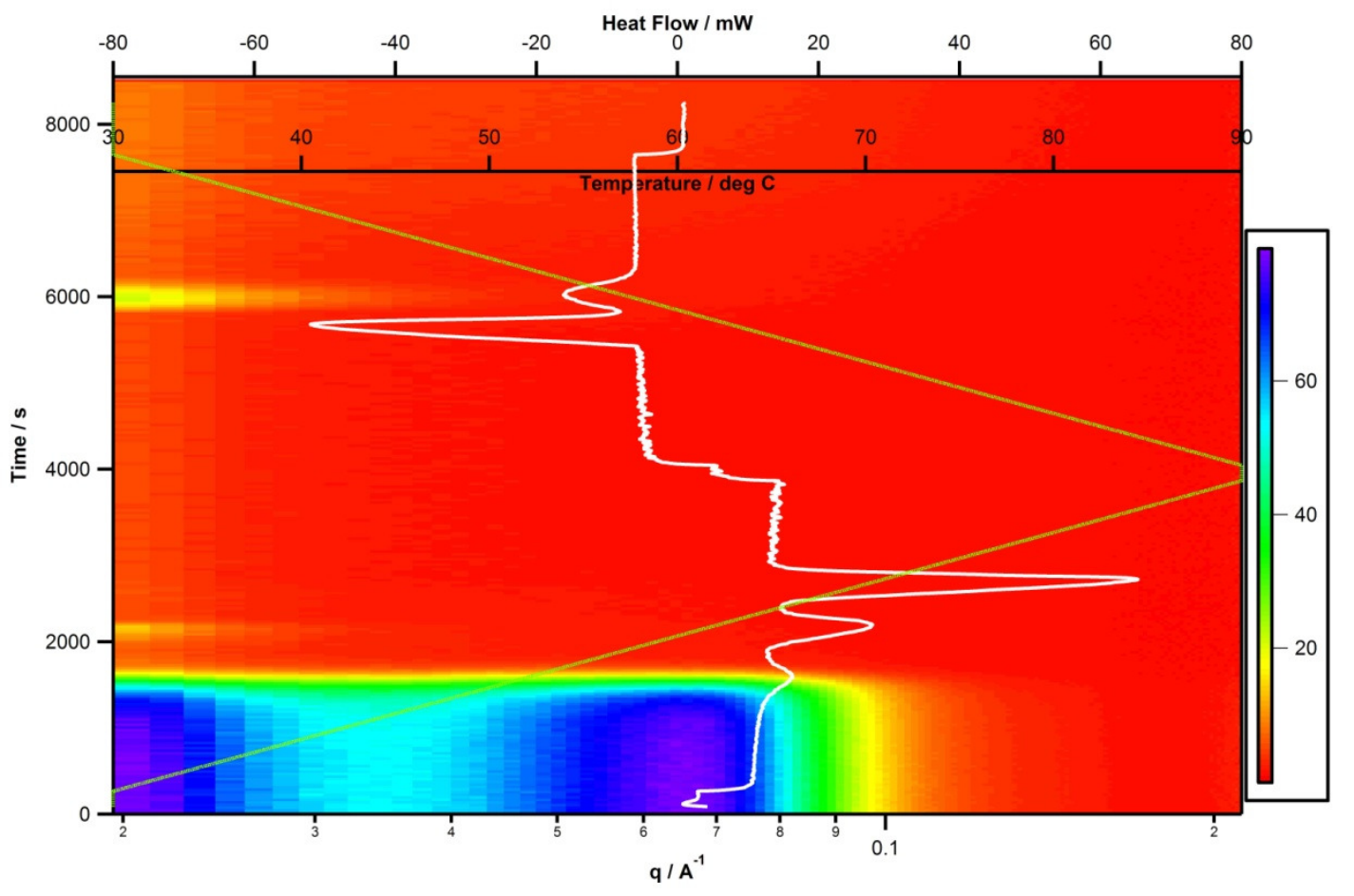
FIRST SIMULTANEOUS SANS AND DSC

- Trigger O/P from DSC via Protek voltmeter set up for RS232
- Trigger monitored by QUOKKA software
- DSC data collected every second
- Correlated to +/- 1 sec post-expt
- SANS in event mode acquisition





FIRST SIMULTANEOUS DATA:
1:1 $C_{30}H_{62}$:$C_{36}D_{74}$ - aged for ca. 2.5 years!



	Mixing transition, T_{mix}			Orthorhombic-to-rotator transition, T_{rot}			Rotator-to-melt transition, T_m		
	Onset/°C	Peak/°C	Integral J g^{-1}	Onset/°C	Peak/°C	Integral J g^{-1}	Onset/°C	Peak/°C	Integral J g^{-1}
Heating	47.62	52.02	17.48	57.93	61.97	47.69	66.65	70.67	140.69
Cooling	–	–	–	60.45	57.13	36.17	66.72	62.78	125.40
Re-heating	–	–	–	58.17	61.93	37.26	66.29	70.25	120.81

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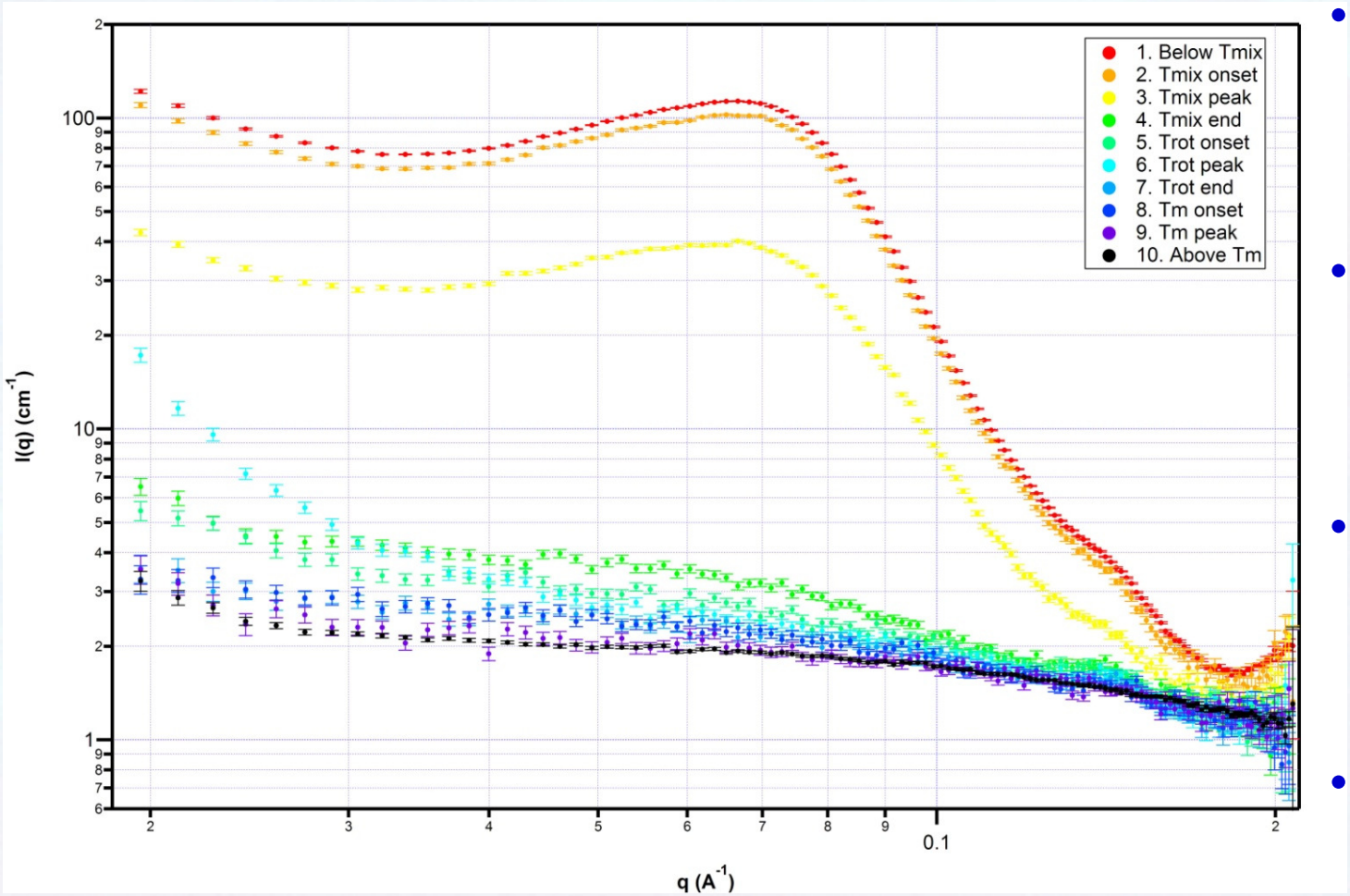
FIRST SIMULTANEOUS DATA



- Times associated with transitions used for time binning
- SANS peak q = 0.07 $Å^{-1}$, decreases at onset and by > 50% at endotherm peak
- SANS peak does not return on cooling; first endotherm does not re-appear
- Feature unambiguously associated with previously demixed / modulated superstructure

CONCLUSIONS AND FURTHER WORK

- SAXS / DSC useful but SAXS yields ‘average’ information
- First demonstration of simultaneous SANS and DSC
- No compromise on quality of DSC data
- Opportunity to contribute to new insights where contrast insufficient for SAXS or where SANS essential or inherently desirable (e.g. isotope effects)

- Improvements:
  - Modification to N_2 supply to polymer box improved baseline significantly
  - Triggering and data collection to simplify data reduction process.

- Investigations underway to extend the T range to 700 C of the DSC
  - replacing outer Al wall with higher T neutron transparent material
  - replacing Al crucibles with quartz crucibles of modified design
  - quartz cell will also extend use to weaker scatterers

- Measurement Science Technology 25 (2014) 055606

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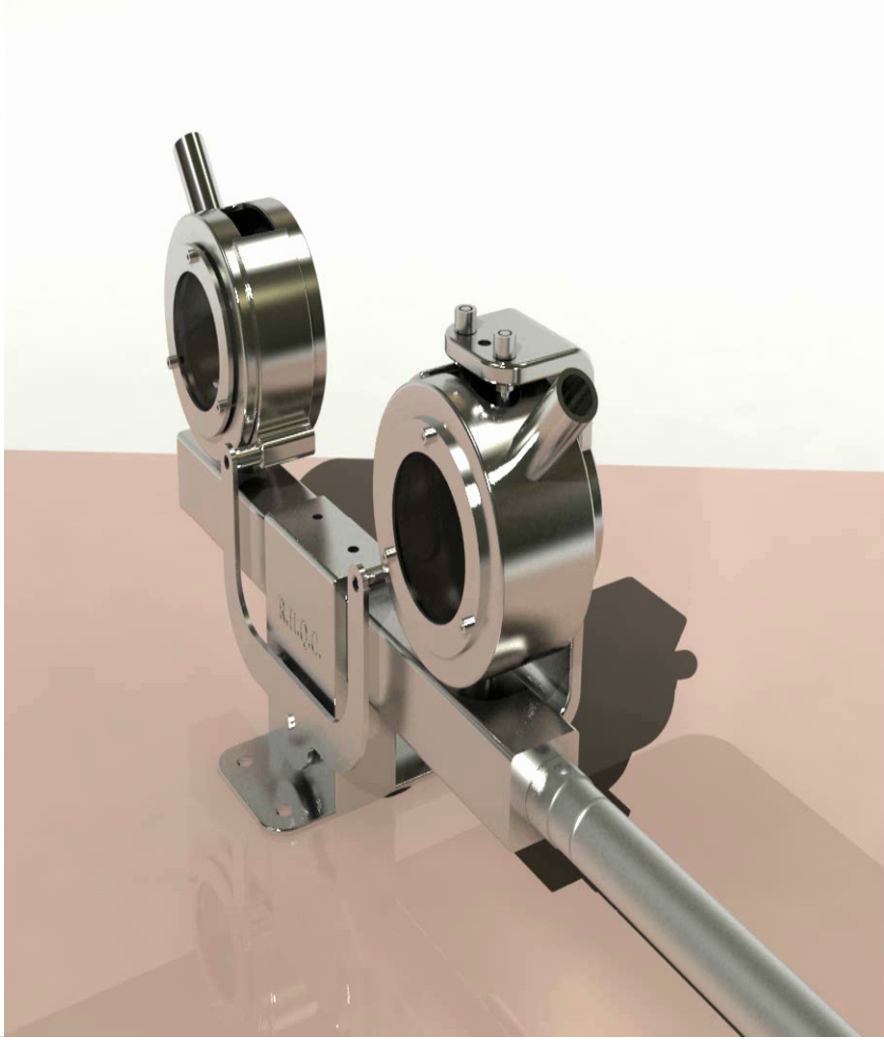
SAMPLE ENVIRONMENTS FOR SAS

Code	Name	Description	Capability
CF-1	CF-1: Cryofurnace, bottom loader, 8K - 300K or 20K - 750K	Standard bottom loader for TAIPAN and SIKA can reach 750K with high T insert; Can be used with EF-1.	Temp Range: 8K - 300K Temp Range: 20K - 750K
CF-4	CF-4: Cryocooler, bottom loader, 5K - 300K	Bottom loader can be used with EF-1 or with VM-1 magnet	Temp Range: 5K - 300K
CF-6	CF-6: Cryocooler for Reflectometry/SANS, 5K - 300K	Bottom loader designed to fit into the electromagnet HM-3, can be used with EF-1; it has a manual sample rotation stage	Temp Range: 5K - 300K
DSC-1	DSC-1: Differential Scanning Calorimeter, -50°C +350°C	DSC for in-situ SANS experiments	Temp Range: -50° C - 350°C
EC-1	EC-1: C shaped Eulerian Cradle	C shaped eulerian cradle; can accommodate CF-5	
EF-1	EF-1: Electric Field, 10 kV	10kV DC variable power supply system	Voltage: up to 10kV
GD-1	GD-1: Gas Delivery and Sorption/Desorption System, max 200 bar	Hiden Isochema IMI-HTP volumetric/manometric system for in-situ sorption/desorption measurements	Pressure: max 200 bar
GS-1	GS-1: Dynamic Sampling Gas Spectrometer, 1-200 AMU	Hiden Gas Spectrometer HPR-20 100 mbar - 2 bar	Pressure Range: 100 mbar - 2 bar
HM-1	HM-1: 5T dry horizontal field cryomagnet, B < 5T	5 Tesla, closed cycle, 80 mm warm bore, used with CF-3 cryofurnace	
HM-2	HM-2: 10T horizontal field wet magnet, 1.5K – 300K; B<10T	10 Tesla horizontal field magnet can reach 11 T with lambda plate	
HM-3	HM-3: 1 T Electromagnet, B < 1T	1 Tesla Bruker Electromagnet can be used with CF-6	
RH-1	RH-1: Shear cell / rheometer, -40°C - 80°C	Rheometer for SANS experiments based on Anton_Paar MCR 500 model	Temp Range: -40° C - 80°C
RQ-1	RQ-1: Rapid Heat and Quench Cell, 150K - 700K	Rapid thermal system for SANS, it allows rapid quenching/heating of samples	Temp Range: 150K - 700K
RT-1	Rapid Heat and Quench Cell RT-1	Rapid Thermal system for SANS from -150C to 500C.	
RV-1	RV-1: Rapid Viscosity Analyser	Rapid Viscosity Analyser	
SC-2	SC-2: 20 position SANS sample changer, -40 °C - 120 °C	Thermally controlled sample changer for 20 samples	Temp Range: -40 ° C - 120 °C
SF-1	SF-1: Stopped Flow mixing cell, 0.01ml	Able to rapidly mix fluids as small as 0.01ml	
SPC-1	SPC-1: SANS 350MPa pressure cell, 0°C - 50°C	Pressure cell for SANS experiments	Temp Range: 0°C - 50°C
TB-1	Temperature bath (TB-1) Julabo LH 45 -50C to 200C	-50C - 250C	
TB-3	Temperature bath (TB-3) Julabo FP40 -20C to 120C	-50C-250C	
TB-4	Temperature Bath (TB-4) Julabo FP50ME 5C-90C		
TB-5	Temperature Bath (TB-5) Julabo FP50HE 5C-90C		
VD-1	VD-1: Vapour Delivery System static/dynamic, RT-50 °C	Hiden Isochema XCS environmental system for in-situ static/dynamic vapour delivery	Temp Range: RT-50 °C



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