Uses of USANS

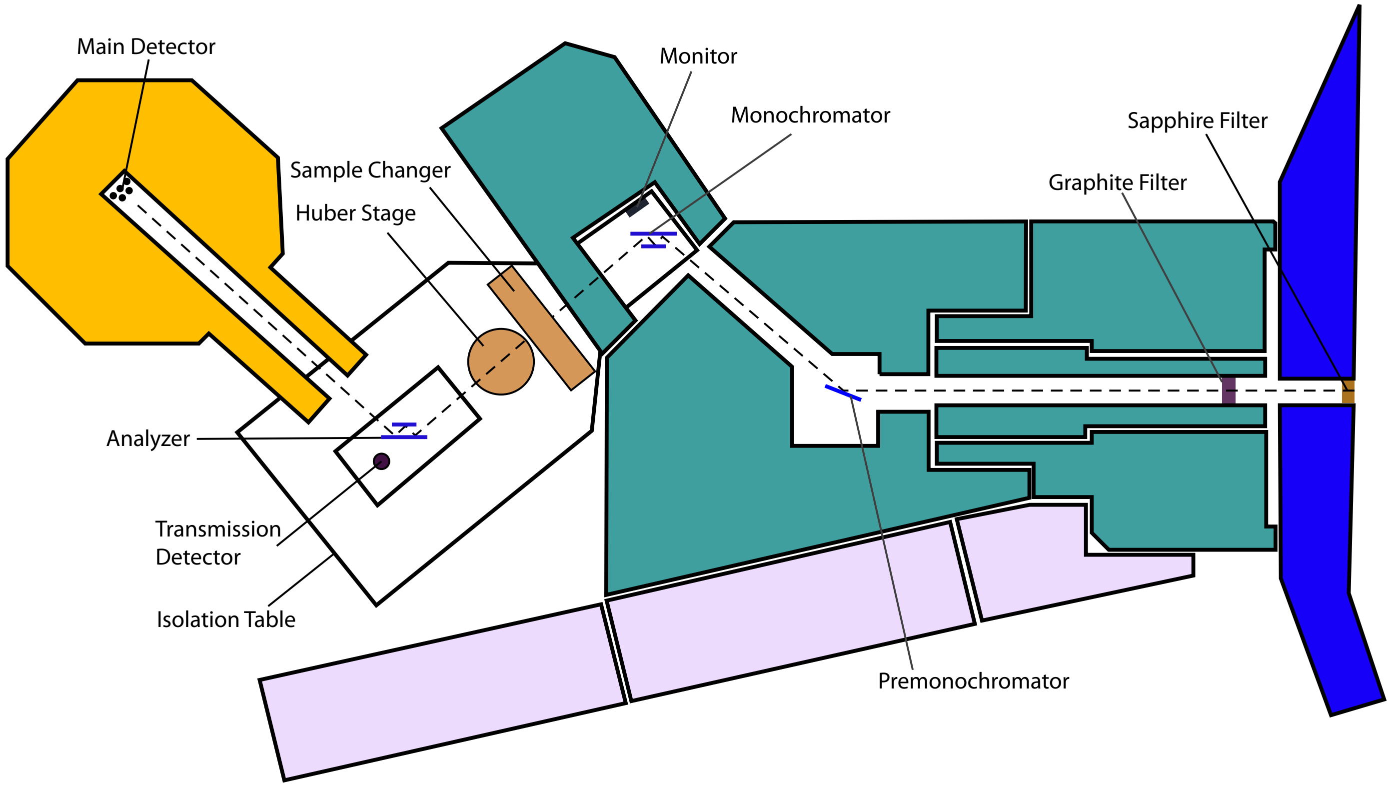
NCNR Summer School, June 2012

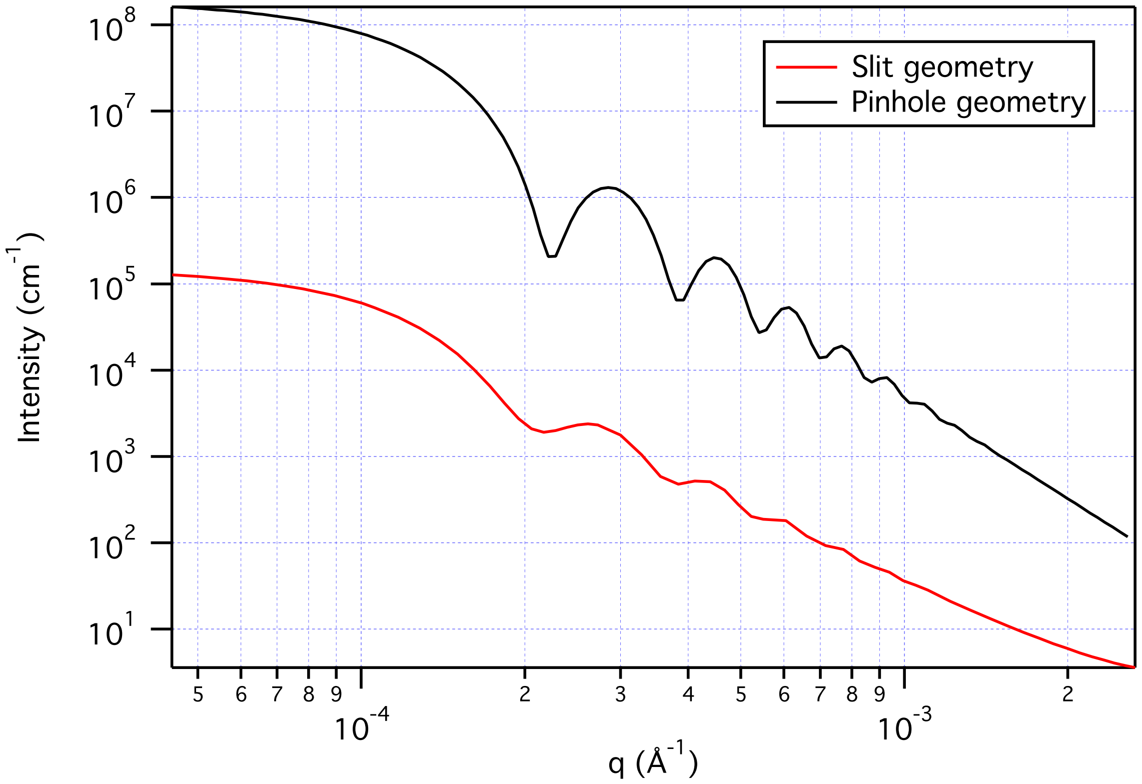
EUROPEAN
SPALLATION
SOURCE

Andrew Jackson
Instrument Scientist
ESS

USANS in a slide

- Q range: ~3×10^{-5} Å^{-1} to ~3×10^{-3} Å^{-1}
- Size range: ~0.5 to ~10 um
- Slit geometry
- Same sample environments as SANS





$$\frac{d\Sigma_s}{d\Omega}(q) = \frac{1}{\Delta q_v}\int_0^{\Delta q_v} \frac{d\Sigma}{d\Omega}\left(\sqrt{q^2+u^2}\right)du$$

Effects of High Pressure on Casein Micelle Structure

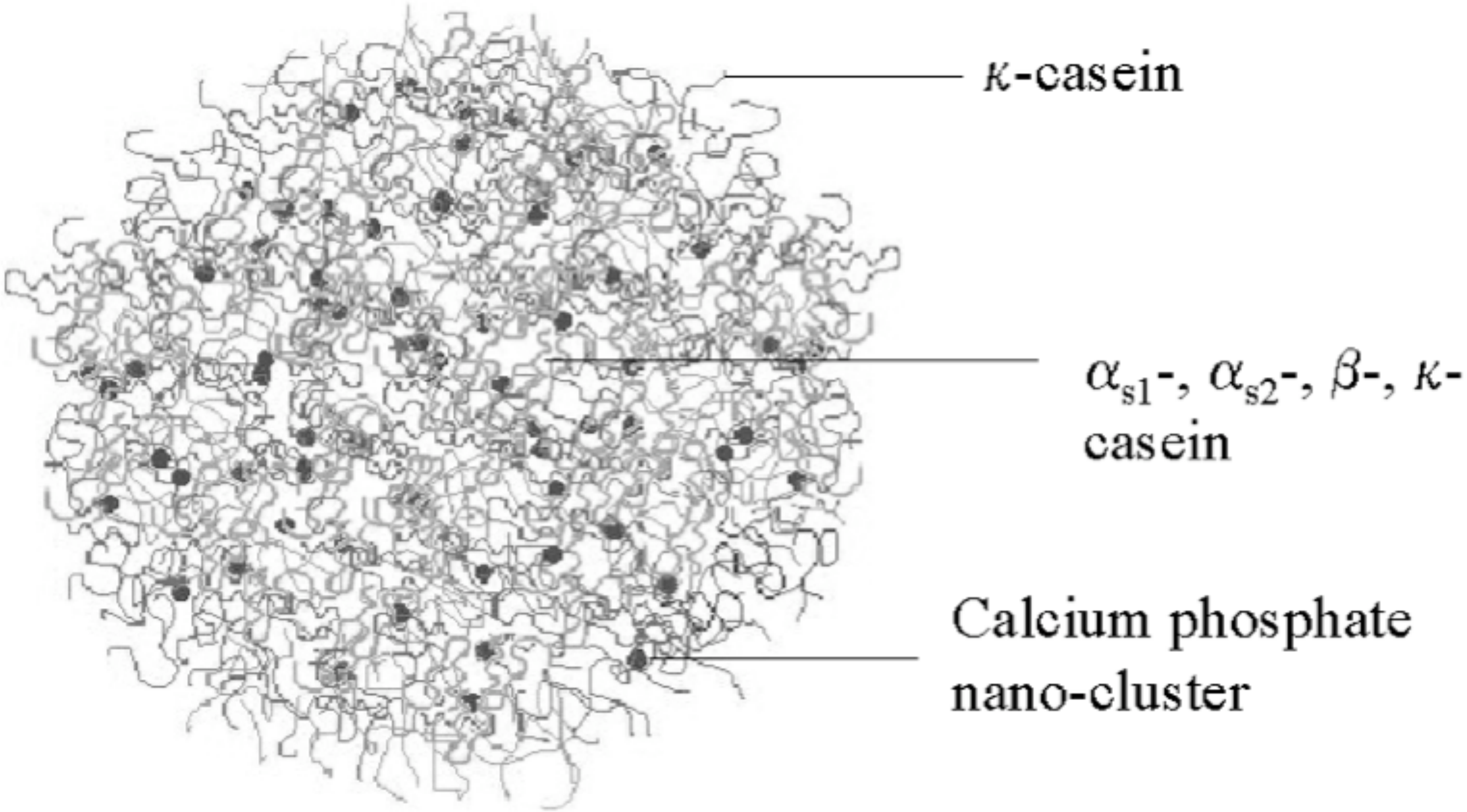
UNIVERSITY OF DELAWARE

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

THE UNIVERSITY OF AUCKLAND
NEW ZEALAND
Te Whare Wānanga o Tāmaki Makaurau

UNIVERSITY OF MARYLAND

Casein Micelles



Holt, *Yearbook Hannah Research,* (1994)

Effects of Pressure

Micelle begins disintegration

100 MPa

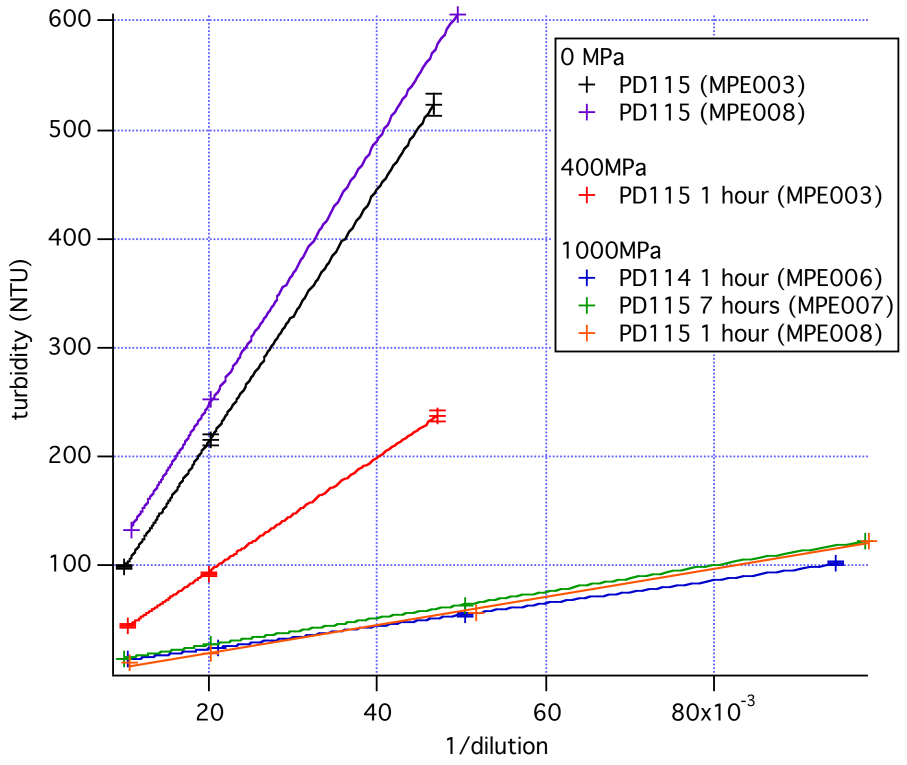
β-lactoglobulin denatures

250 MPa

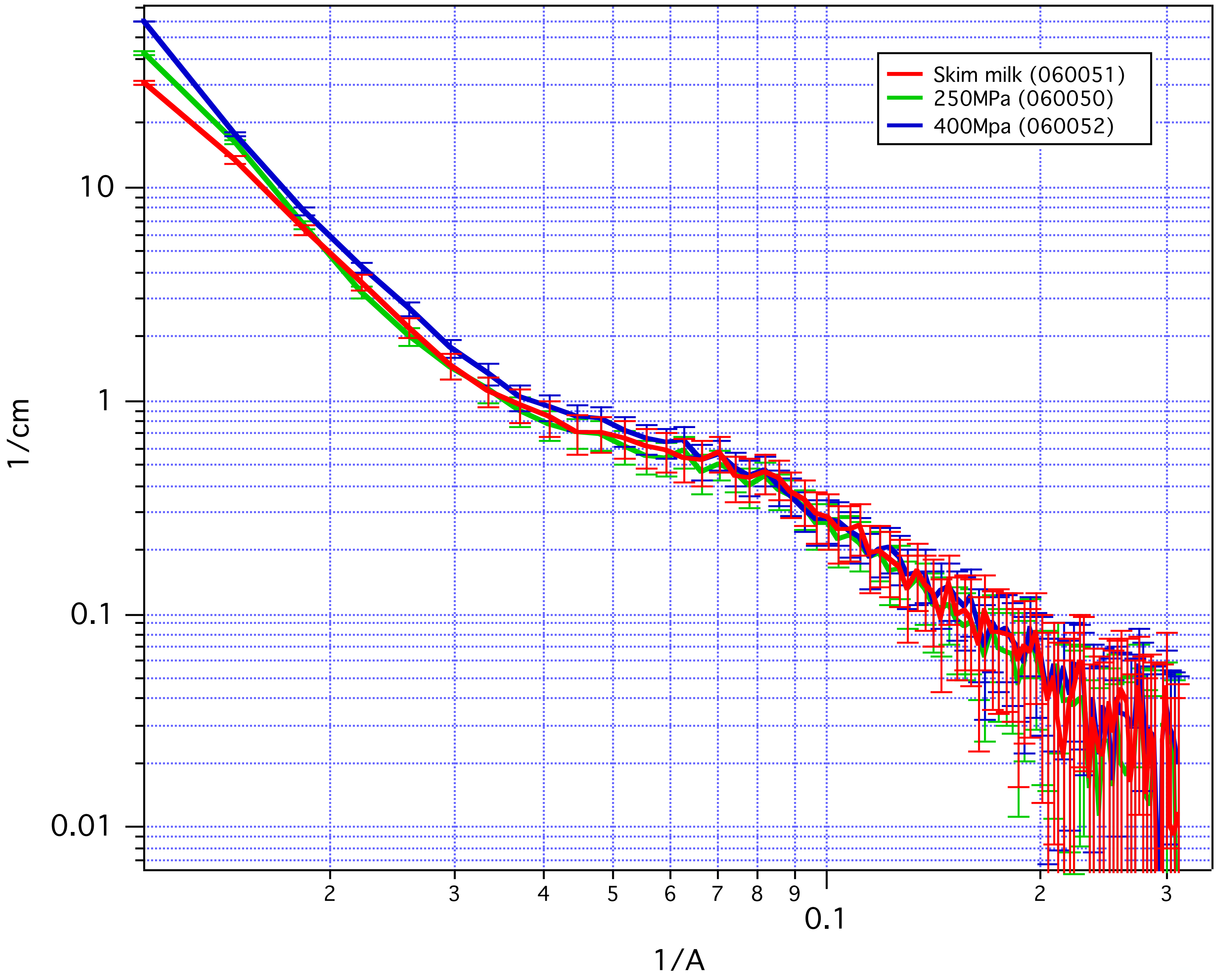
Irreversible micelle breakdown

400 MPa

α-lactalbumin and bovine serum albumin denature

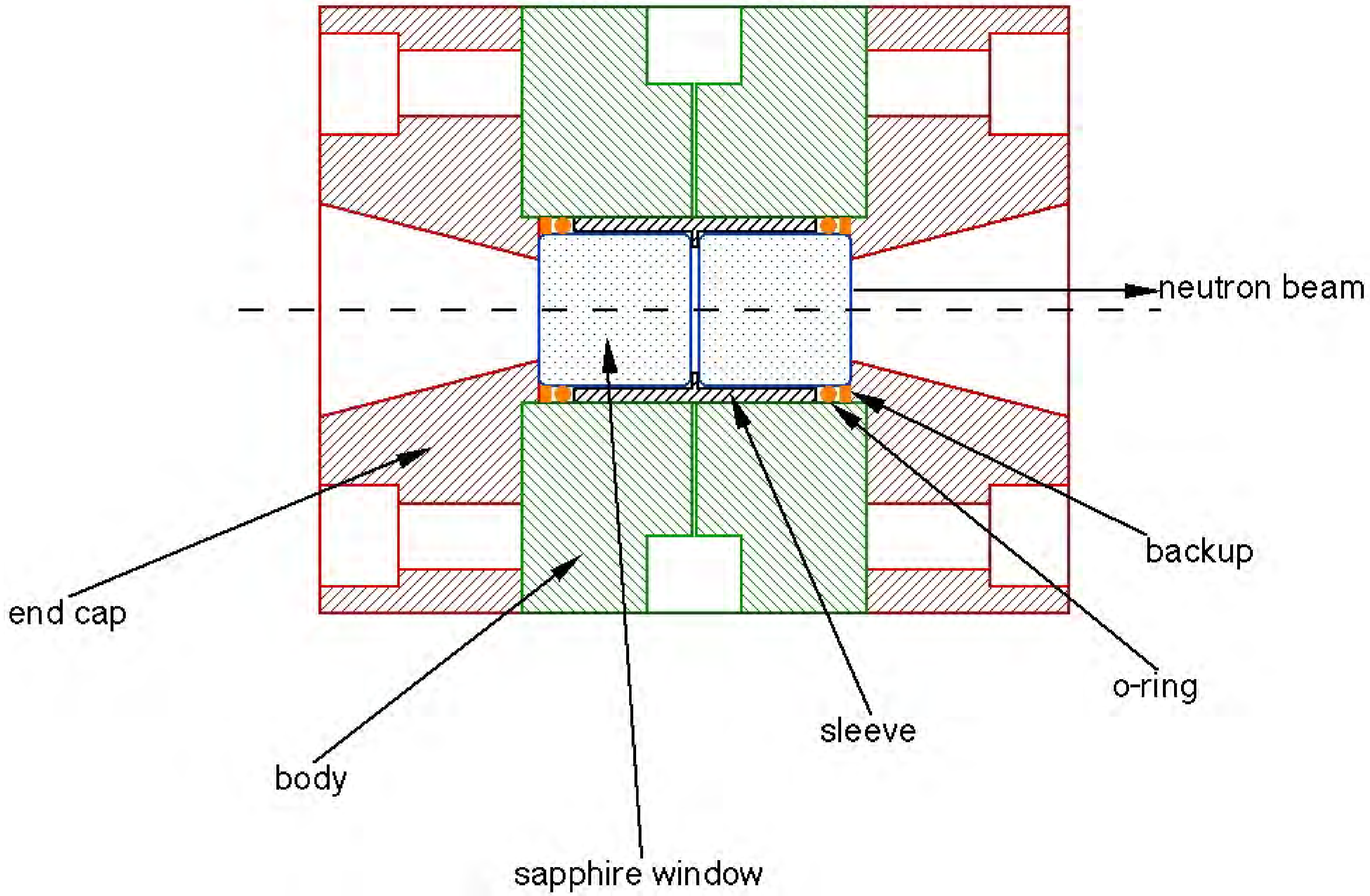


SAXS

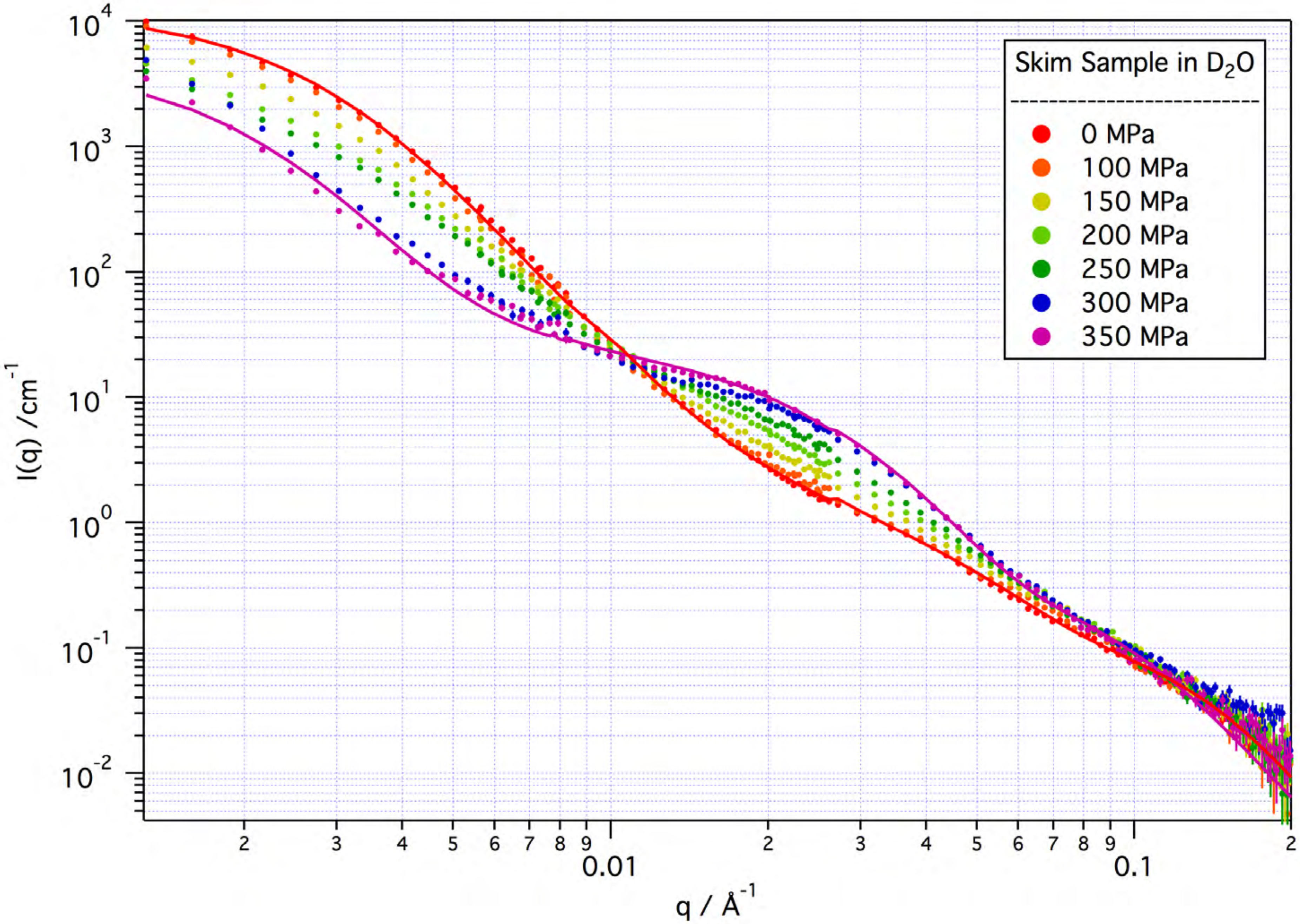


- Pressure ***not*** affecting SAXS lengthscale
- Calcium phosphate clusters ***not*** broken down

In-Situ Pressure Measurements

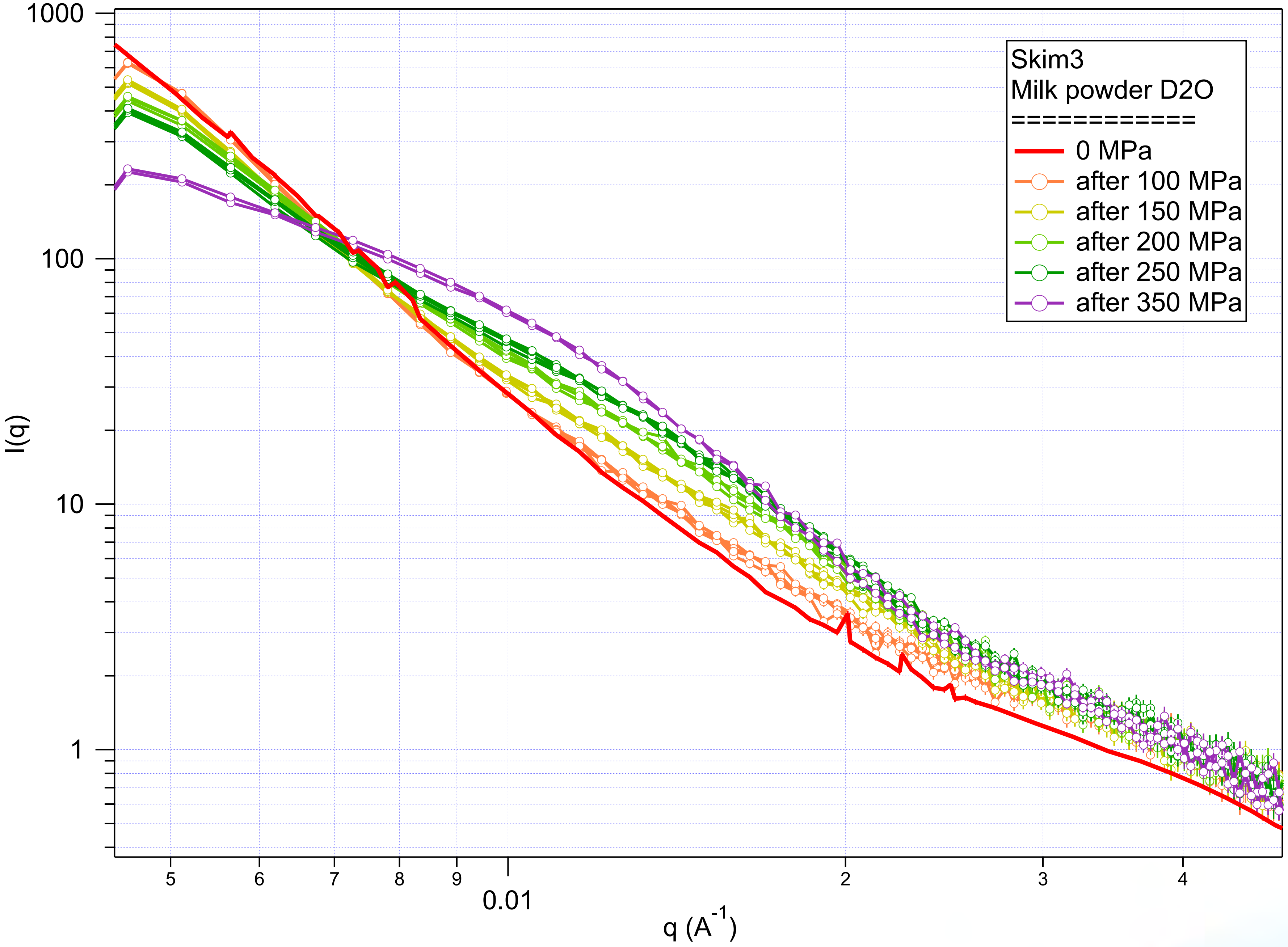


Changes with Pressure



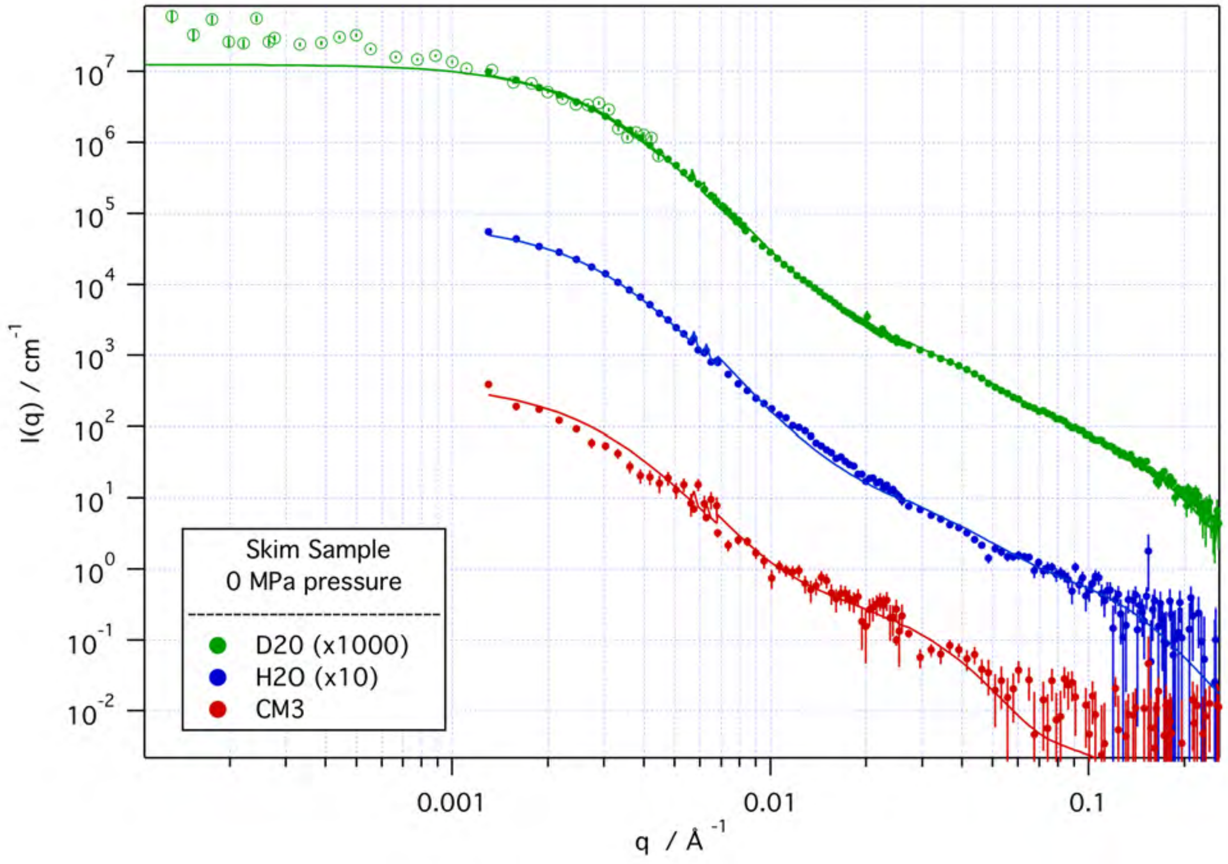
A. J. Jackson, and D. J. McGillivray *Chem. Comm.* (2011) **47** (1) 487-489

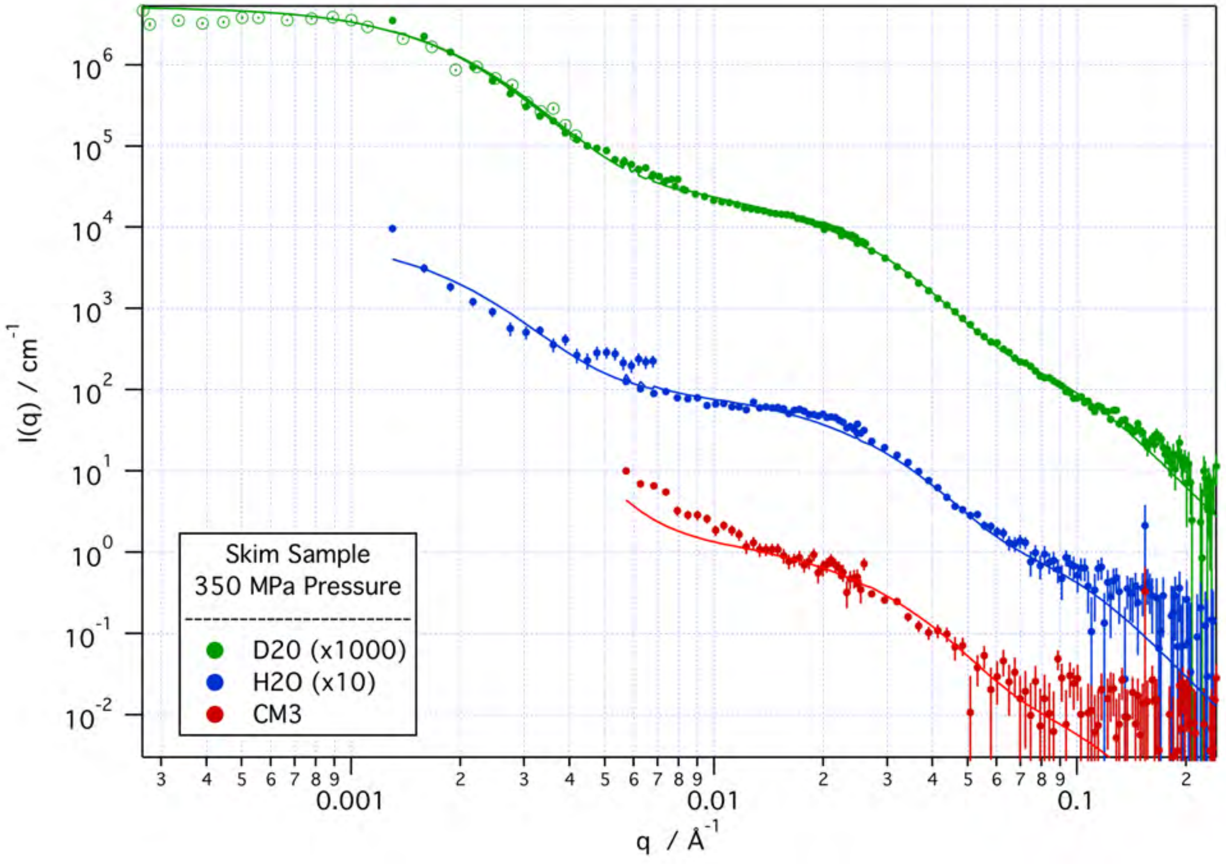
Stability and Reversibility



A. J. Jackson, and D. J. McGillivray *Chem. Comm.* (2011) **47** (1) 487-489

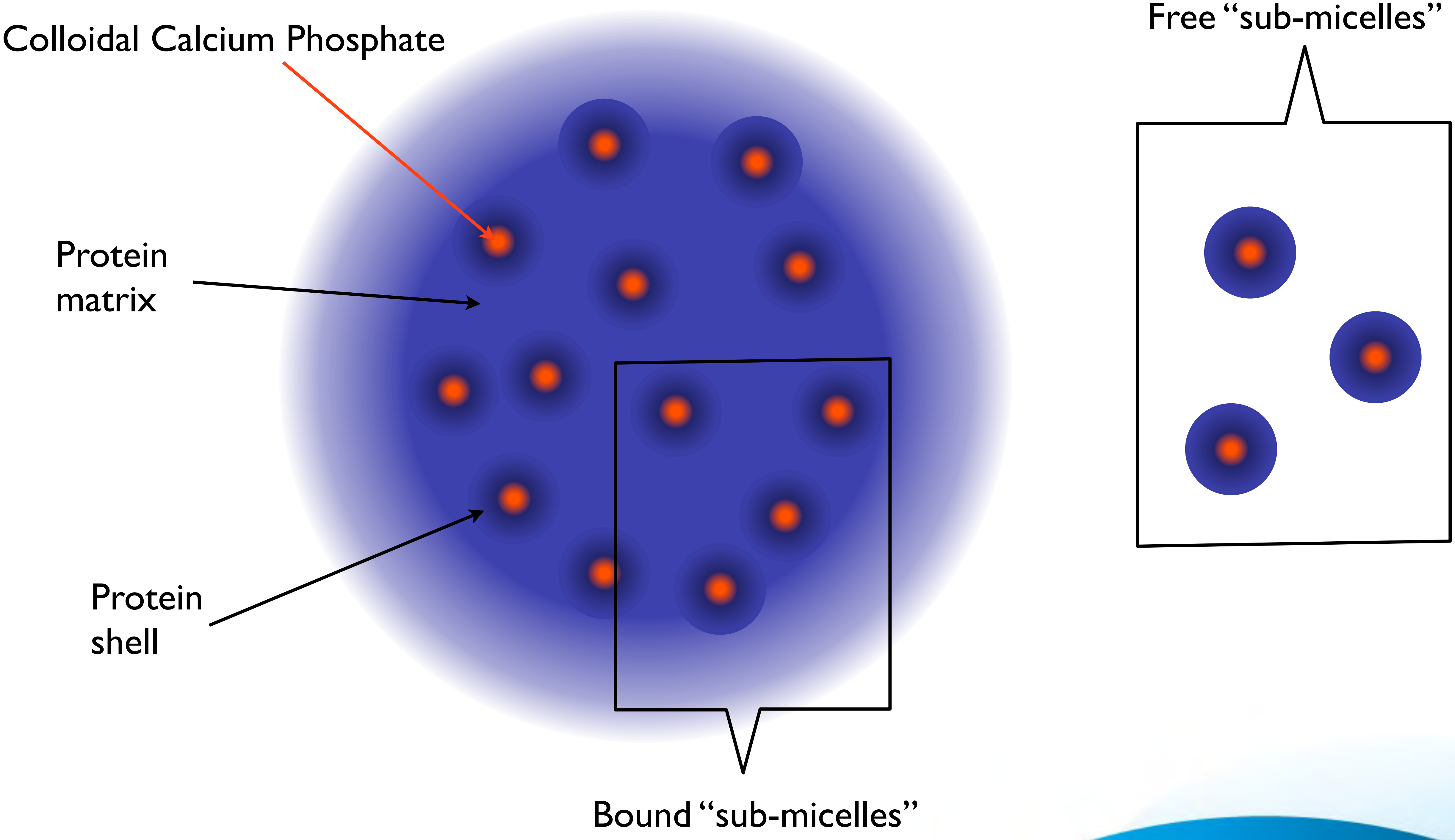
Skim Milk at Multiple Contrasts





A. J. Jackson, and D. J. McGillivray *Chem. Comm.* (2011) **47** (1) 487-489

Model of Casein Micelle



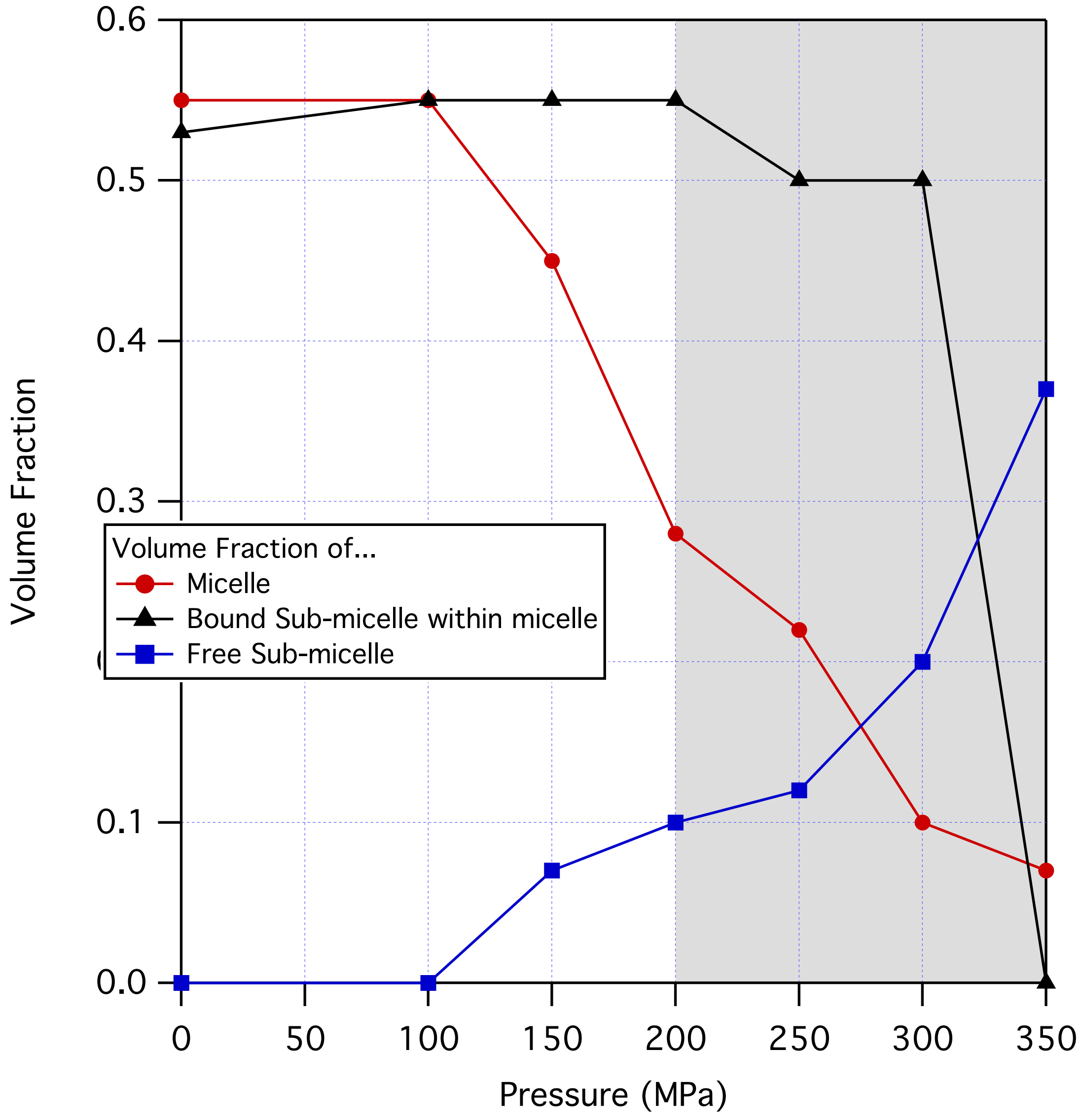
Colloidal Calcium Phosphate

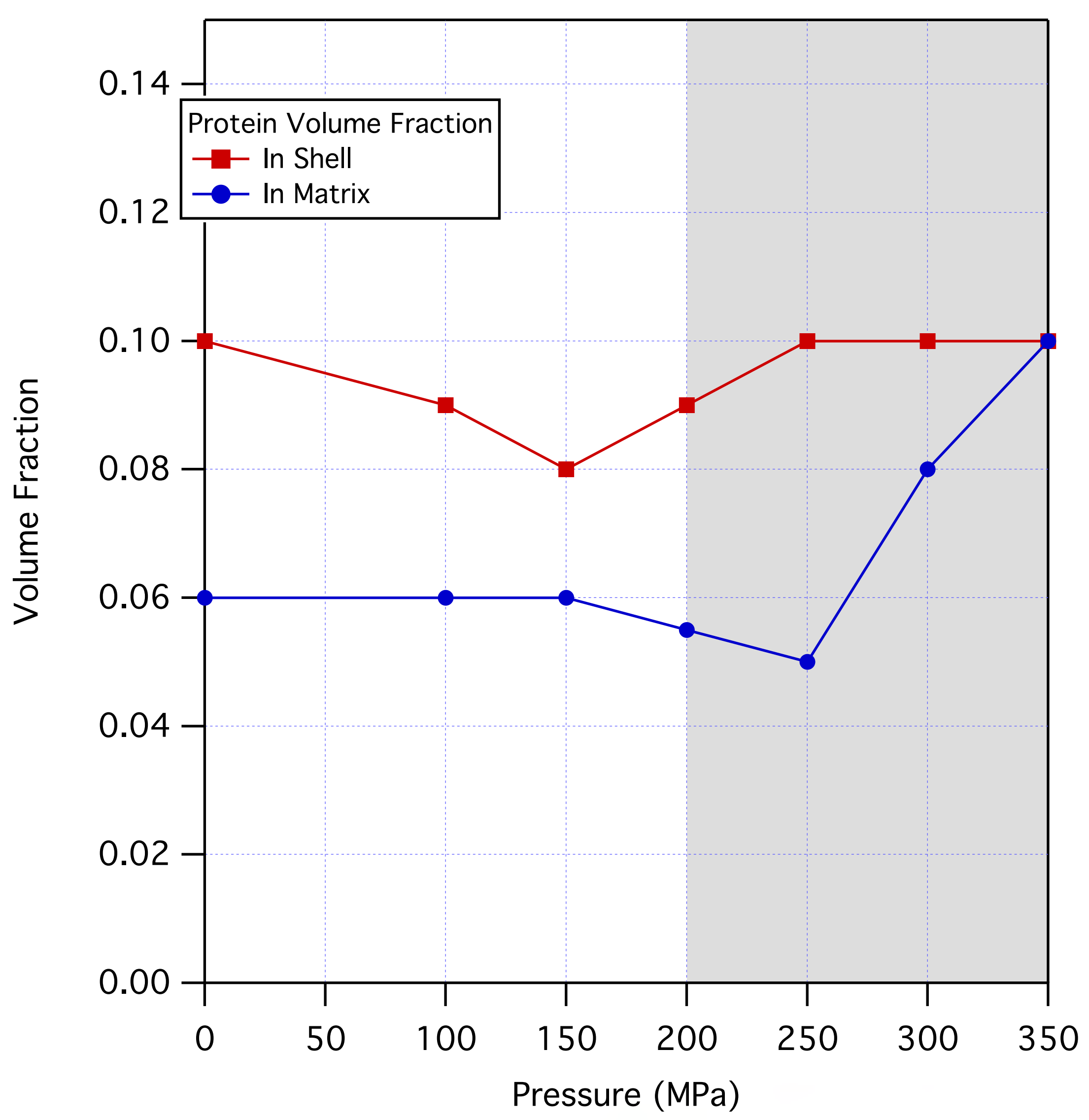
Protein matrix

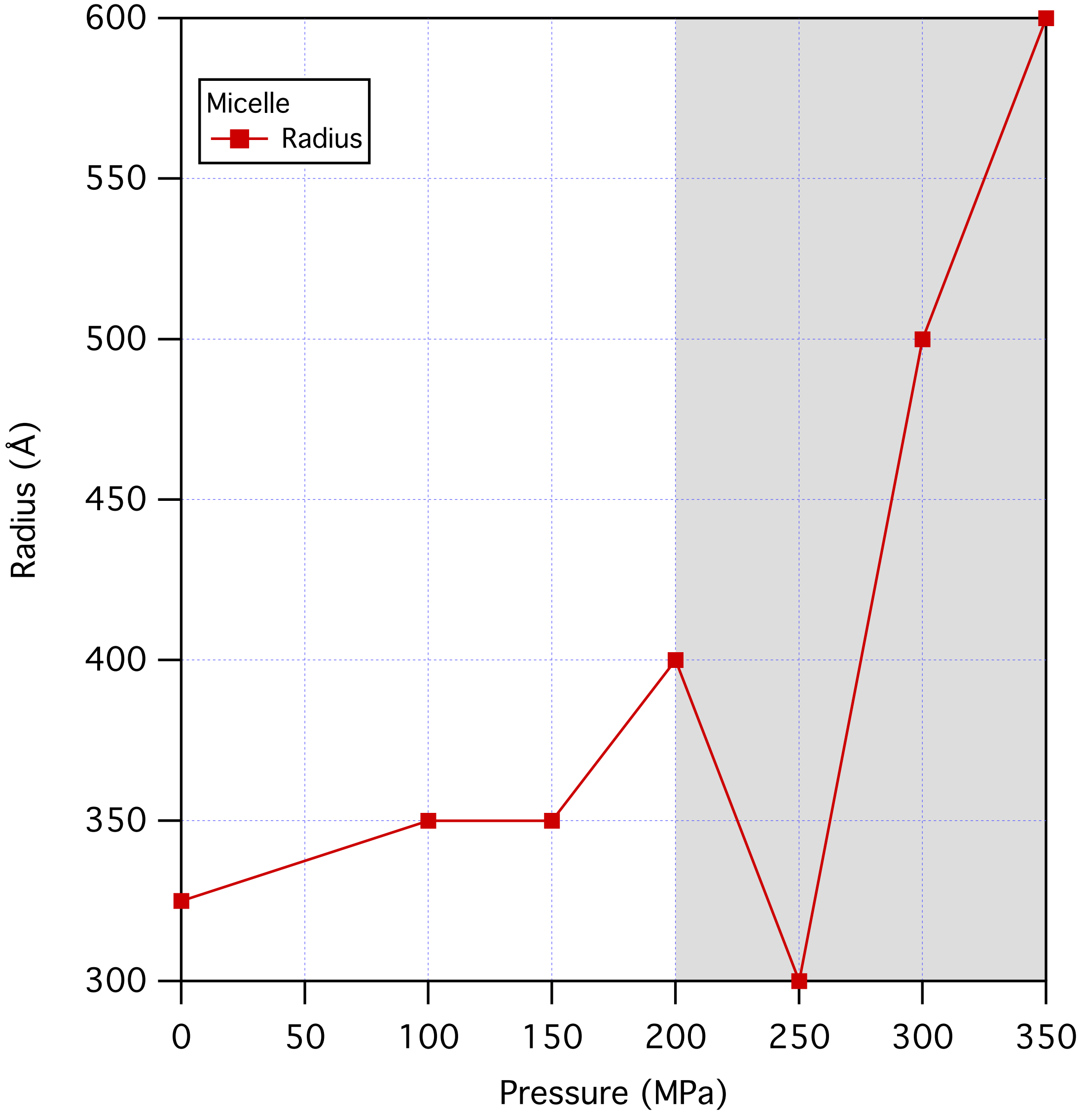
Protein shell

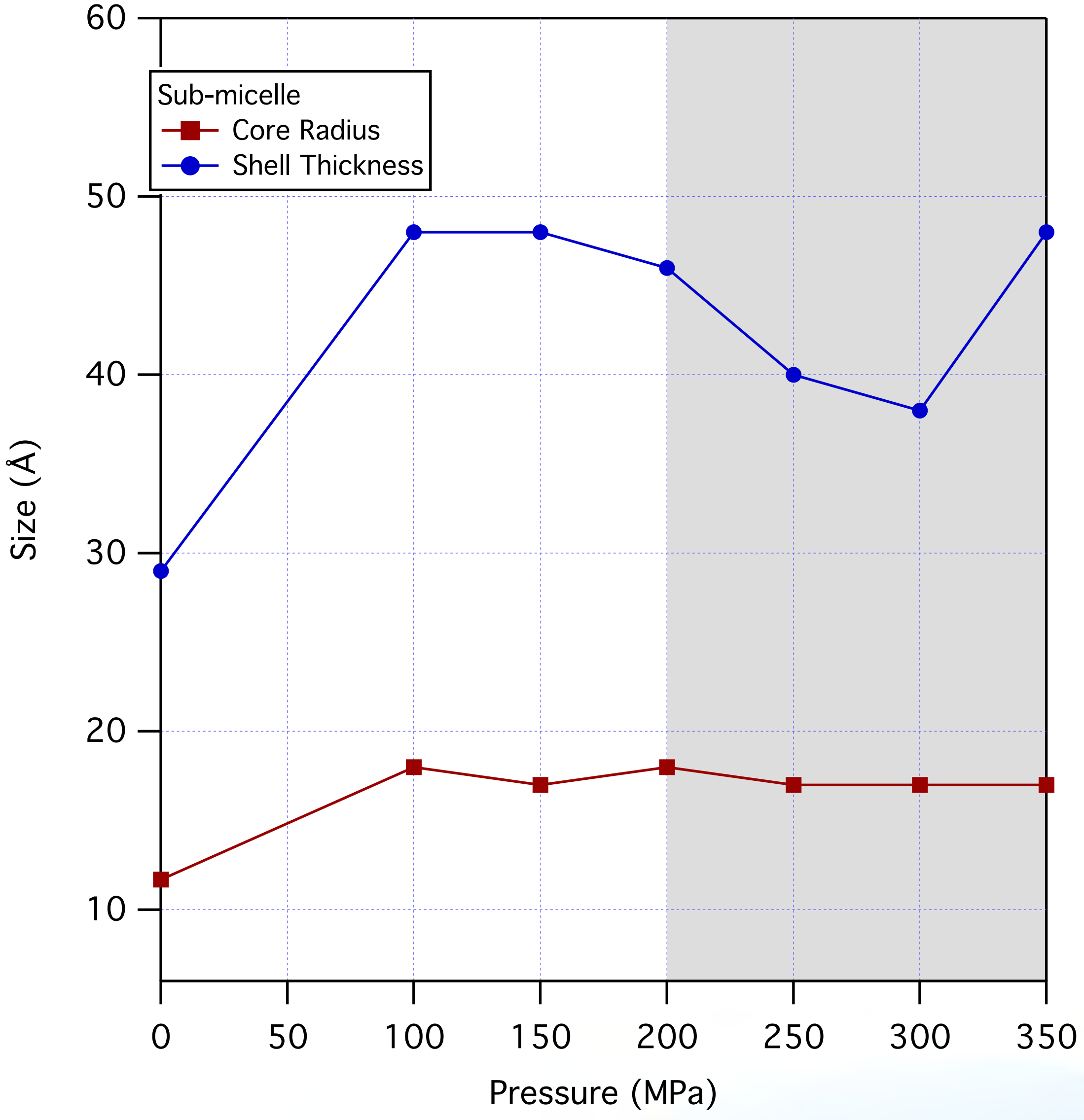
Bound "sub-micelles"

Free "sub-micelles"


Volume Fraction of...
Micelle
Bound Sub-micelle within micelle
Free Sub-micelle
Volume Fraction
0.6
0.5
0.4
0.3
0.1
0.0
0
50
100
150
200
250
300
350
Pressure (MPa)


Protein Volume Fraction
In Shell
In Matrix
Volume Fraction
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
50
100
150
200
250
300
350
Pressure (MPa)


Micelle
Radius
Radius (Å)
600
550
500
450
400
350
300
0
50
100
150
200
250
300
350
Pressure (MPa)


Sub-micelle
Core Radius
Shell Thickness
Size (Å)
60
50
40
30
20
10
0
50
100
150
200
250
300
350
Pressure (MPa)

Summary

Neutrons enable in-situ measurement of structure under pressure

Multiple contrasts and co-refinement reduce the number of free parameters in modelling complex systems

Casein micelles appear to break down into subunits consistent with protein decorated calcium phosphate clusters when subjected to high pressures.

High Internal Phase Emulsions and Sphere Packing

NIST
National Institute of Standards and Technology
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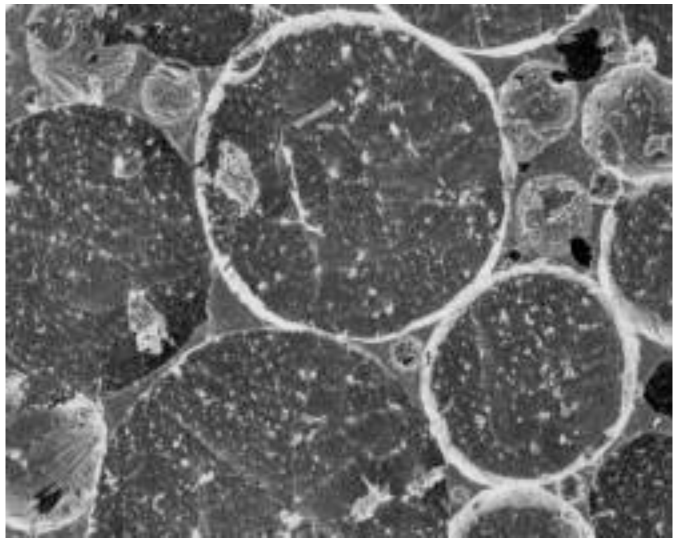
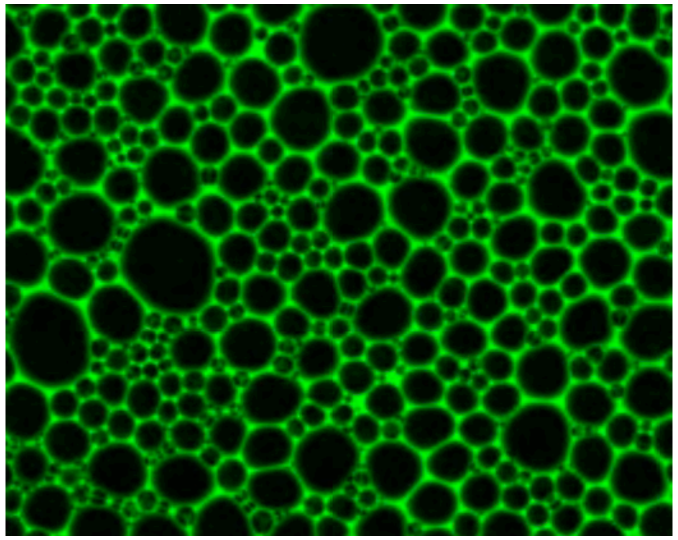
UNIVERSITY OF MARYLAND

High Internal Phase Emulsions

On-site manufactured.
Pumped ANFO for mining applications



Water-in-oil type emulsion
with internal phase volume
fraction > 90%

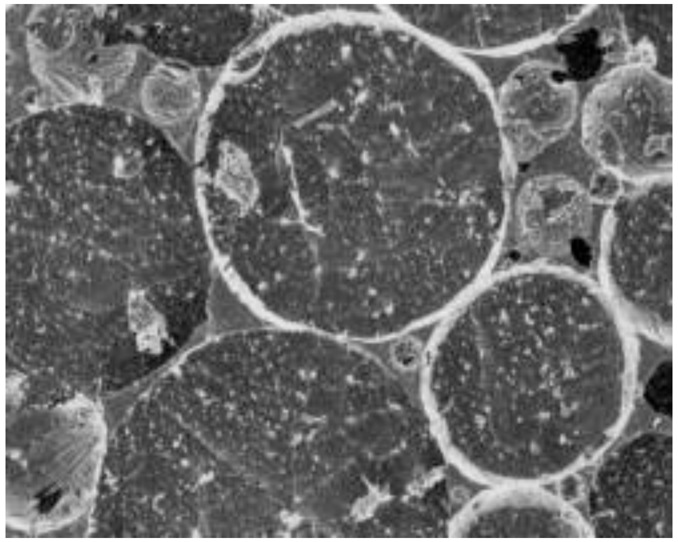


Deformation

Polydispersity

High Internal Phase Emulsions

On-site manufactured.
Pumped ANFO for mining applications



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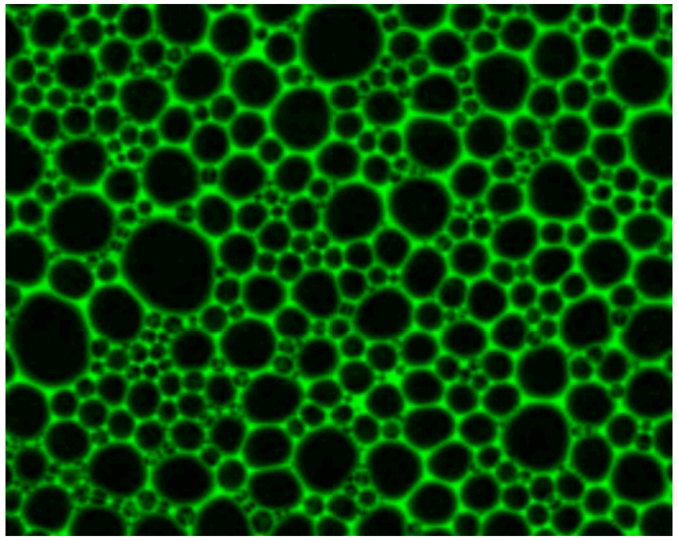
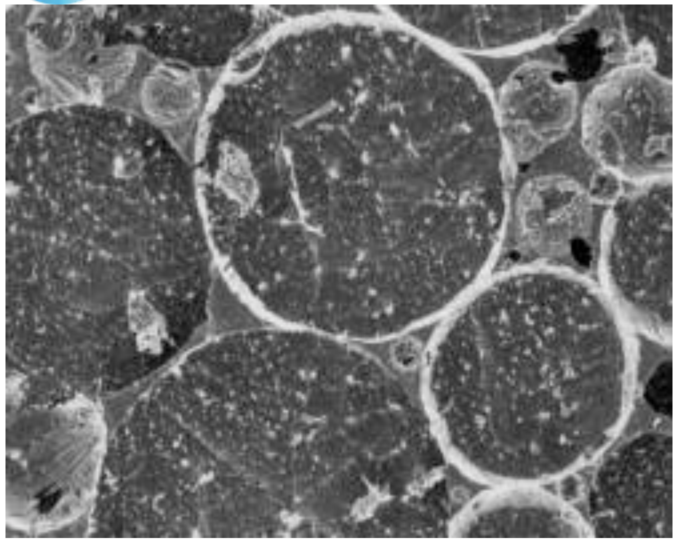


~~Deformation~~

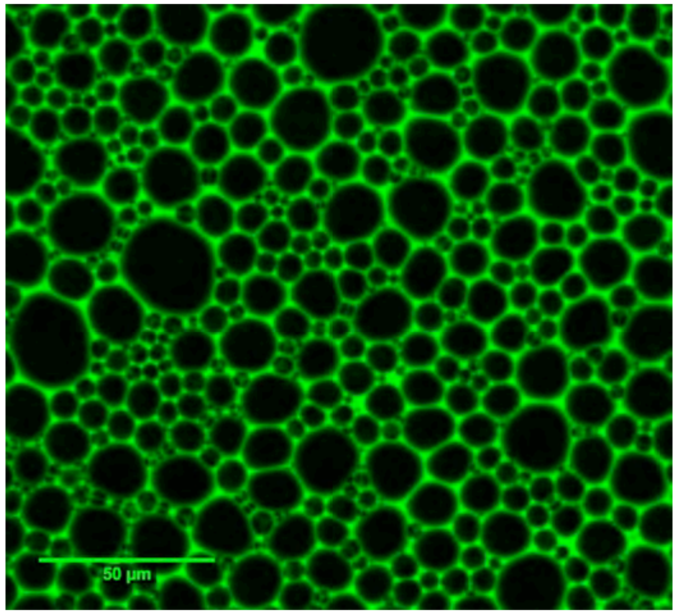
Polydispersity

Microscopy



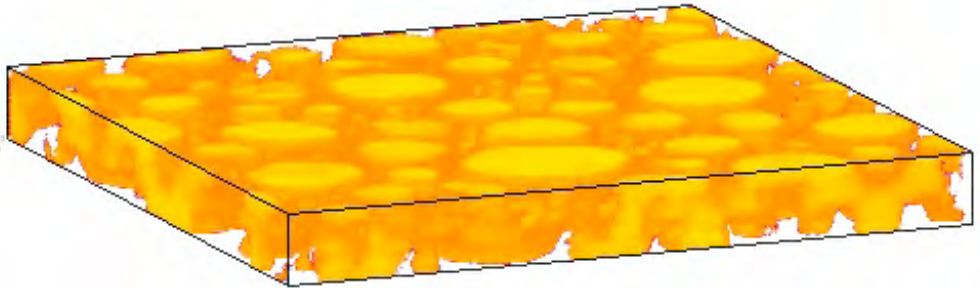
Cryo-EM

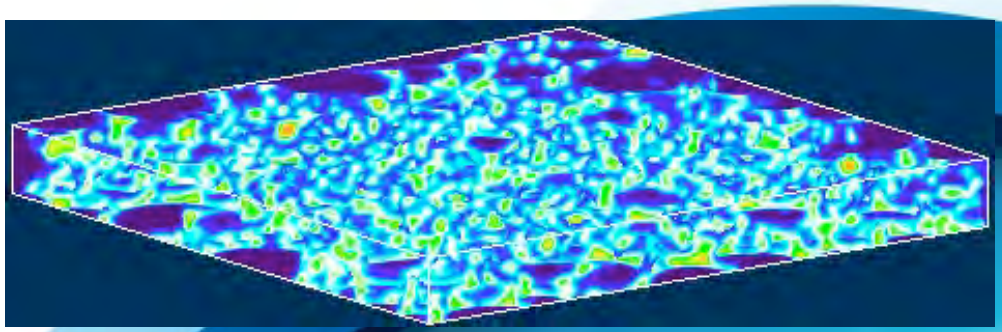
- Direct imaging of emulsion
- Freeze-fracture process may damage structure



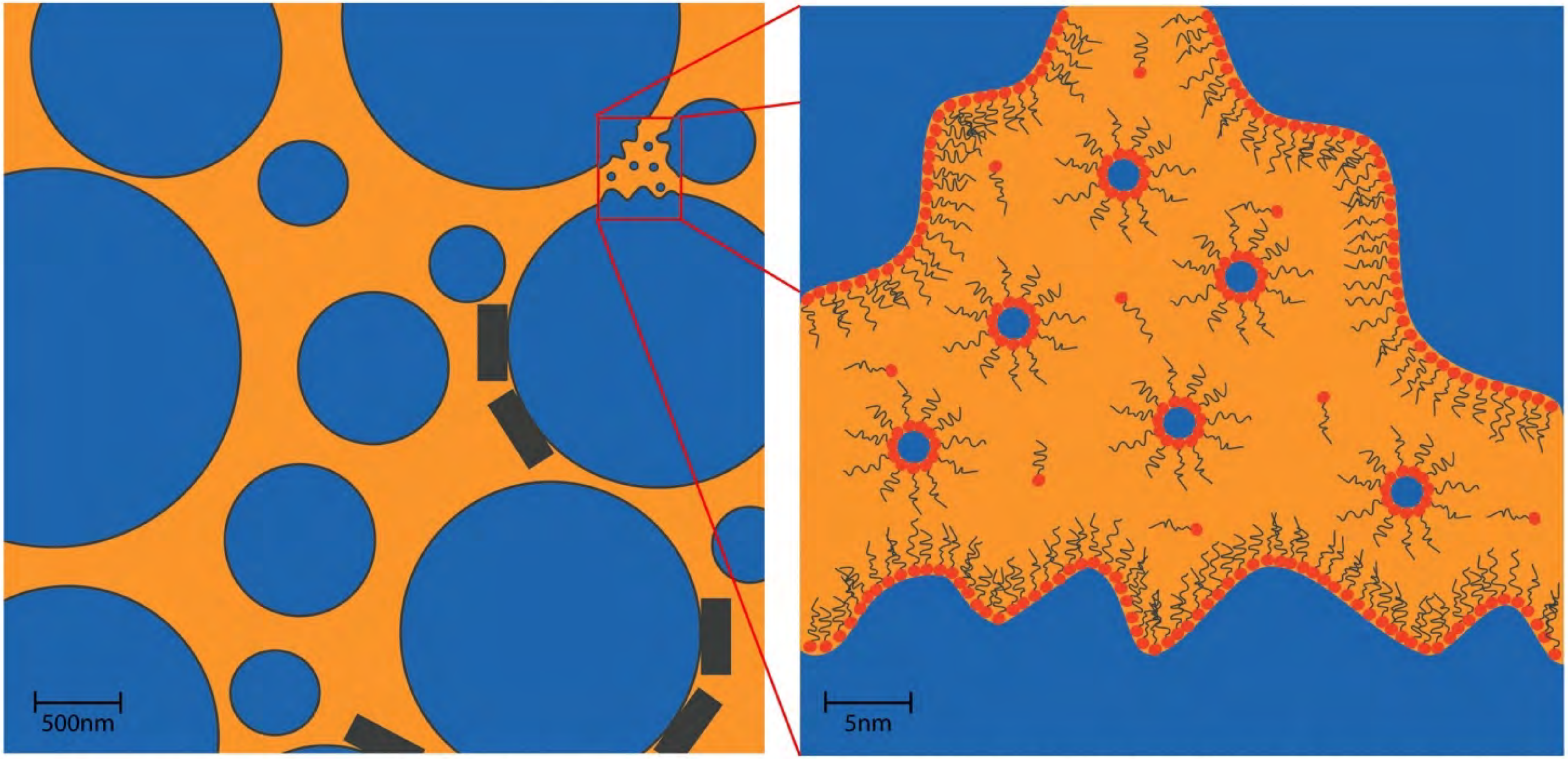
Confocal Fluorescence

- Direct imaging of "unperturbed" emulsion
- Depth scanning for volume reconstruction
- Local probe only
  - Theoretical treatment needs statistical sample
- Edge effects probably important in thin samples
  - Present up to 10 particle diameters from surface
  - Surface induced crystallization





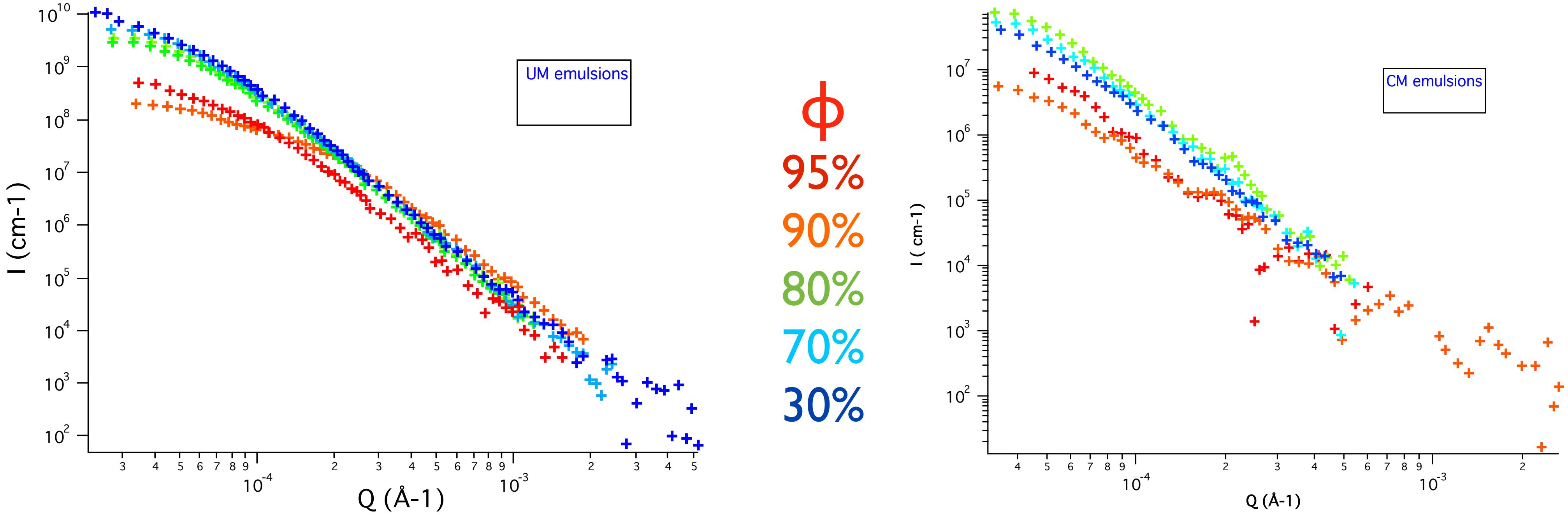
Emulsions



Mesoscale Structure of High Internal Phase Emulsion

Nanoscale Structure of High Internal Phase Emulsion

Emulsions



Oil phase SLD from Invariant

S/V from Porod

- Polydispersity varies with aqueous volume fraction
- At highest values, we cannot generate ever smaller minimum sizes (< 0.5 micron), so maximum size increases to achieve required polydispersity thus decreasing surface areas
- At ϕ of about 0.7 spheres lose contact and creaming results due to lack of long range forces (cf. Emulsion dilution in hexadecane)

Our Tasks

Construct model systems of mixed spheres on relevant length scales

Determine packing density

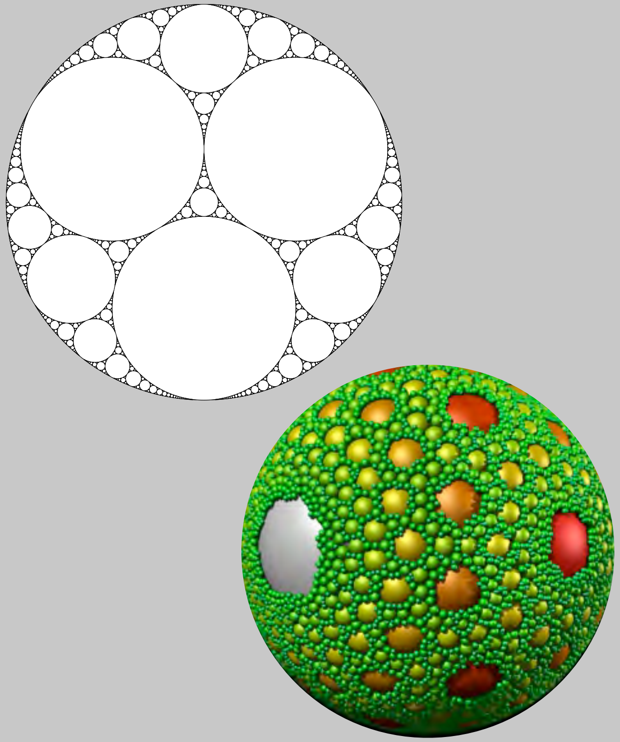
Determine pair correlations

Goal

To correlate polydispersity with packing arrangement and density and then with physical properties of the system.

The Ancient Quest

Apollonius of Perga
ca. 262 - 190 BC



Johannes Kepler
1571 - 1630

Carl Freidrich Gauss
1777 - 1855

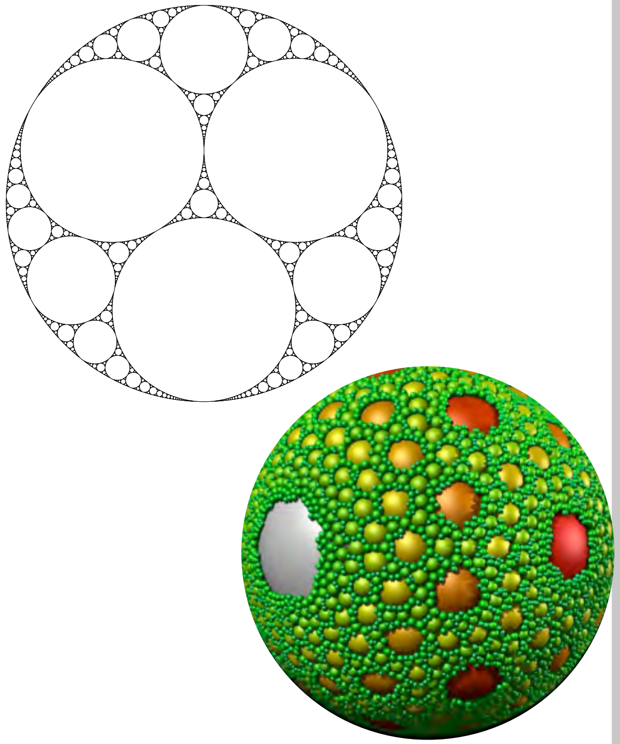
FCC is
densest lattice

Thomas C. Hales

1998
Proof of Kepler
Conjecture

The Ancient Quest

Apollonius of Perga
ca. 262 - 190 BC



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1571 - 1630

$$\frac{\pi}{\sqrt{18}}$$

Carl Freidrich Gauss
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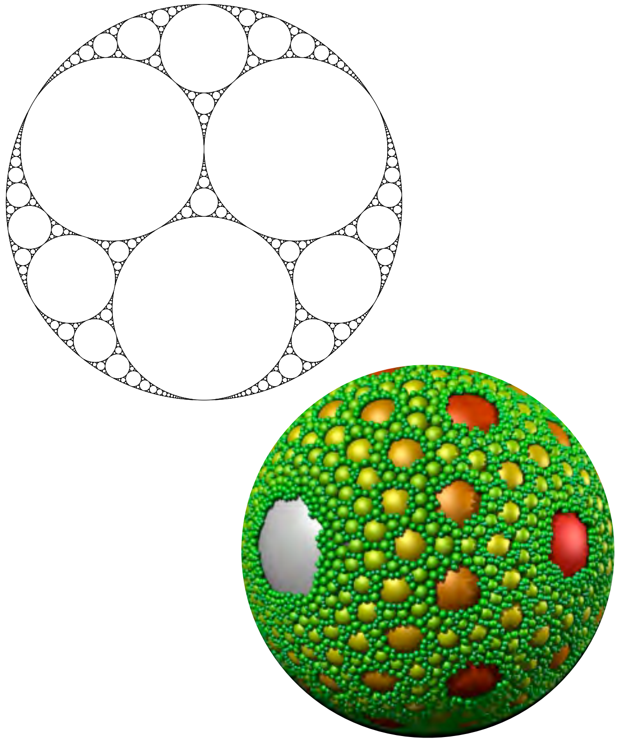

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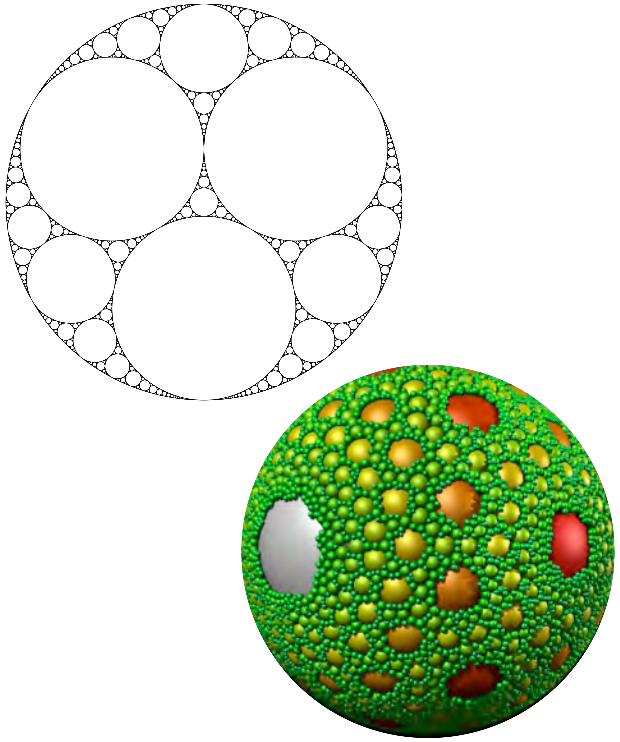

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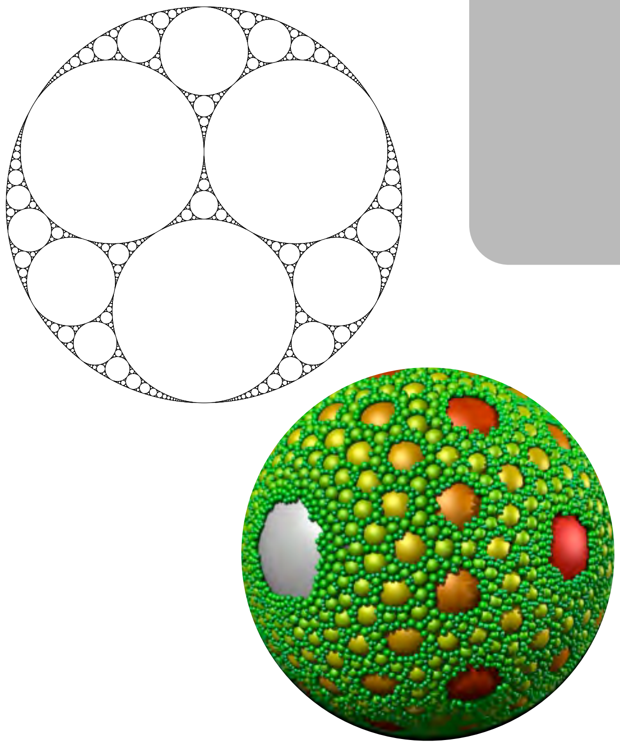

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1998
Proof of Kepler
Conjecture

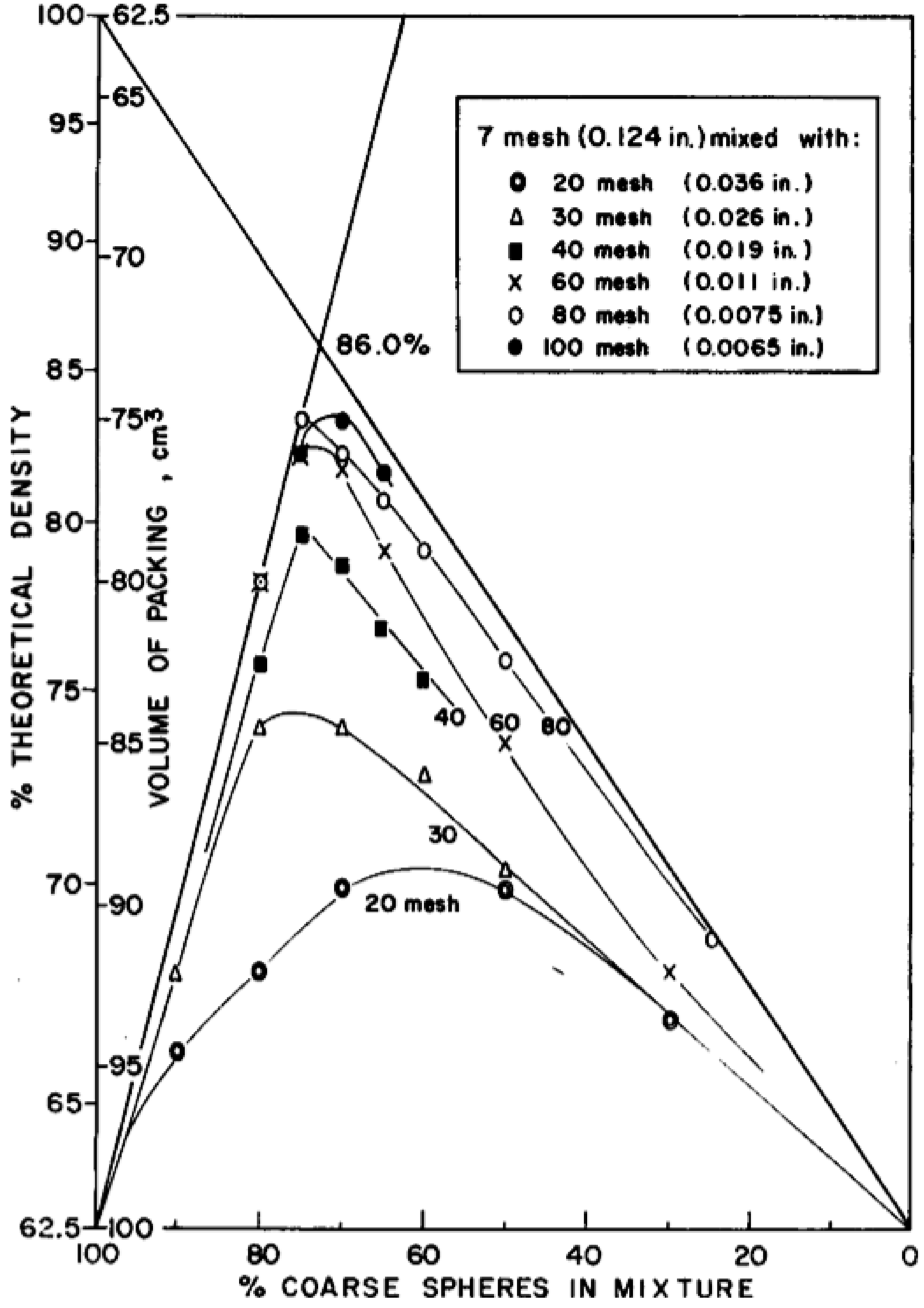
Random / Loose Packing?

Polydispersity?

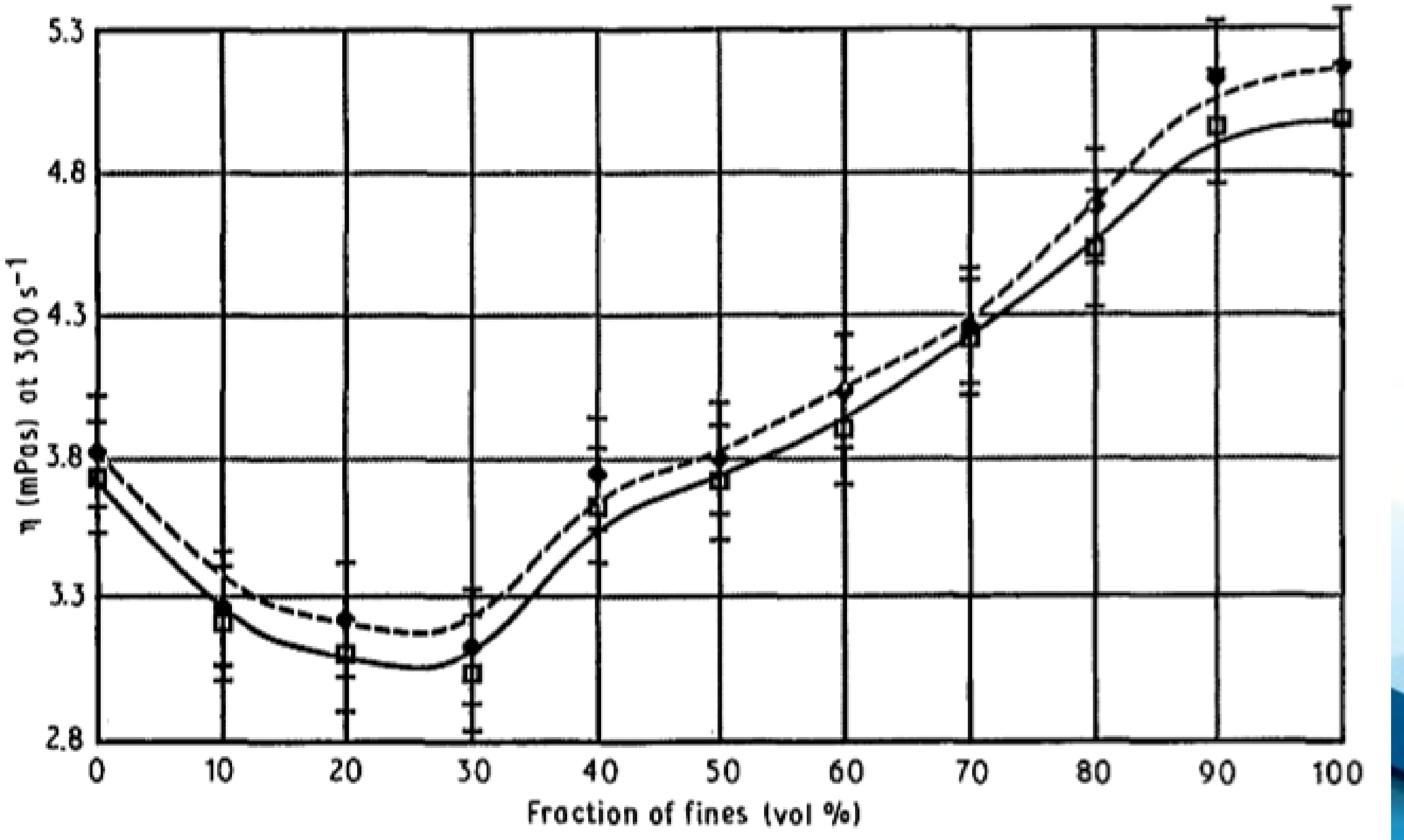
Previous Studies

Mixtures of metal balls

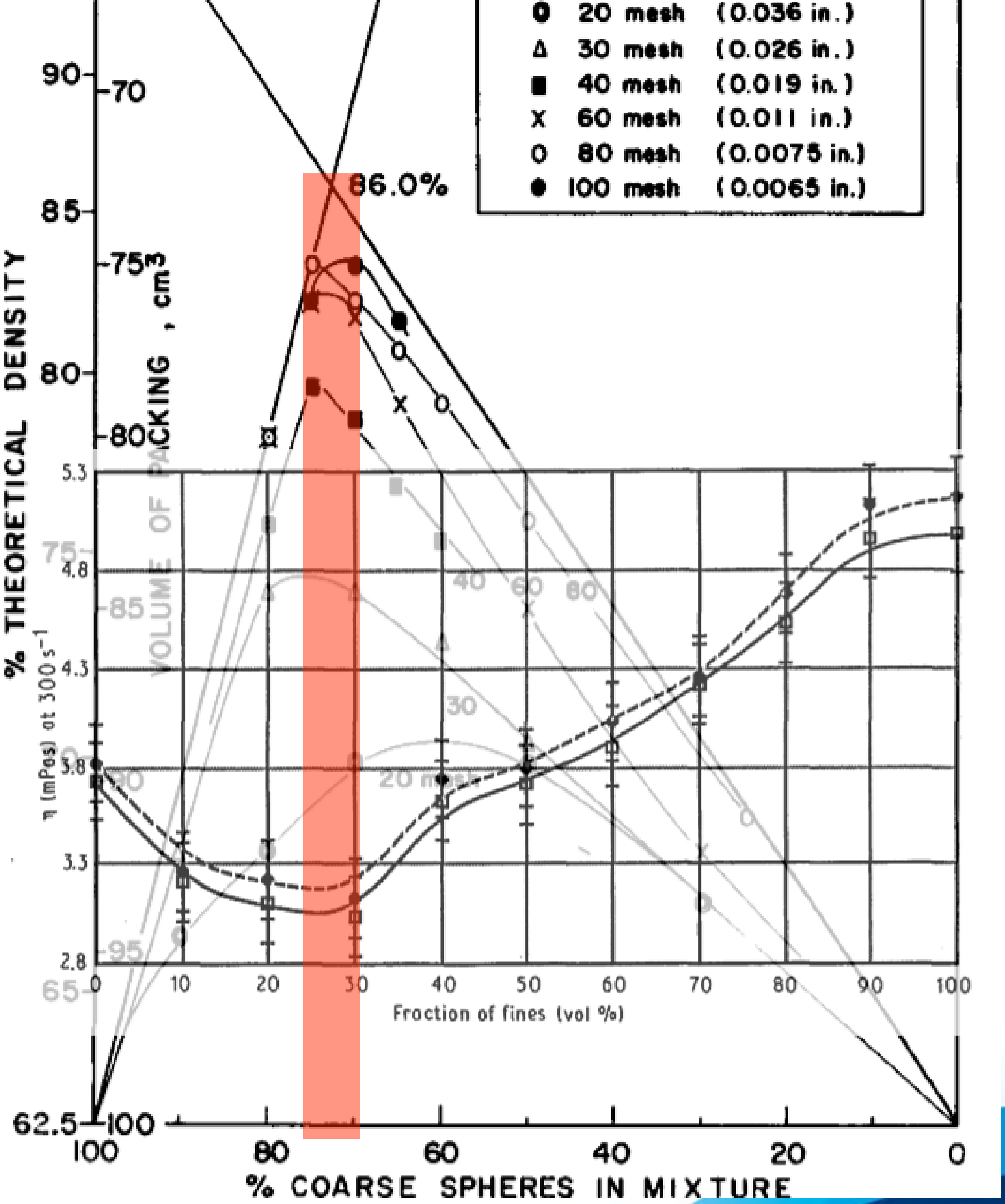
- Sizes must be different enough
- Too-large a difference leads to phase separation
- Max. packing fraction at 20-30% small spheres
- Sphere correlations not known



McGeary, R. K. (1961)
J. Amer. Ceramic Soc. **44,** 513.



Gauthier, F. G. R. & Danforth, S. C. (1991)
J. Mater. Sci. **26,** 6035



Maximum Packing Density = Minimum Viscosity

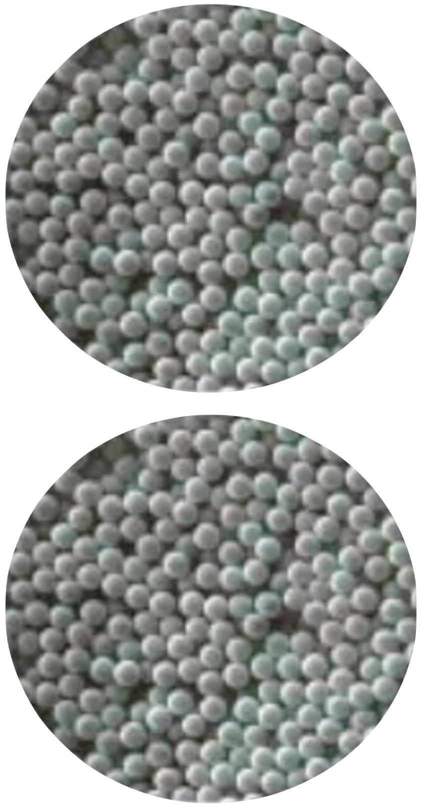
Materials

Emulsions - PIBSA:hexadecane:saturated Ammonium Nitrate

Glass spheres - polydisperse ‘3-10’ micron range

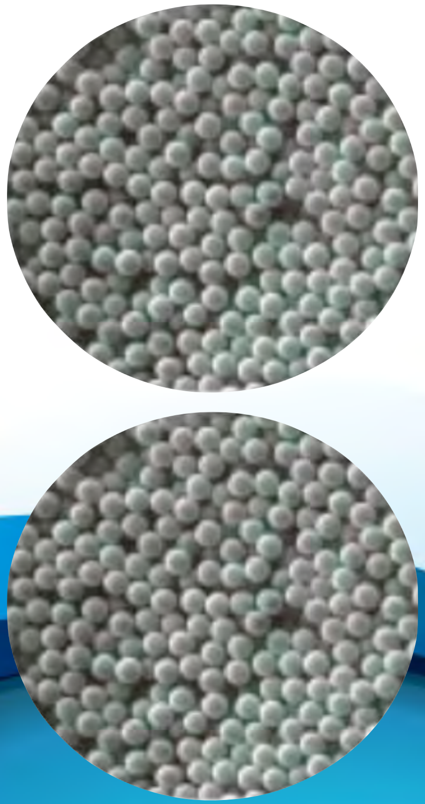
PMMA spheres- monodisperse ‘1.5’ and ‘10’ microns

Silica spheres - monodisperse ‘1’ and ‘5’ micron diameter

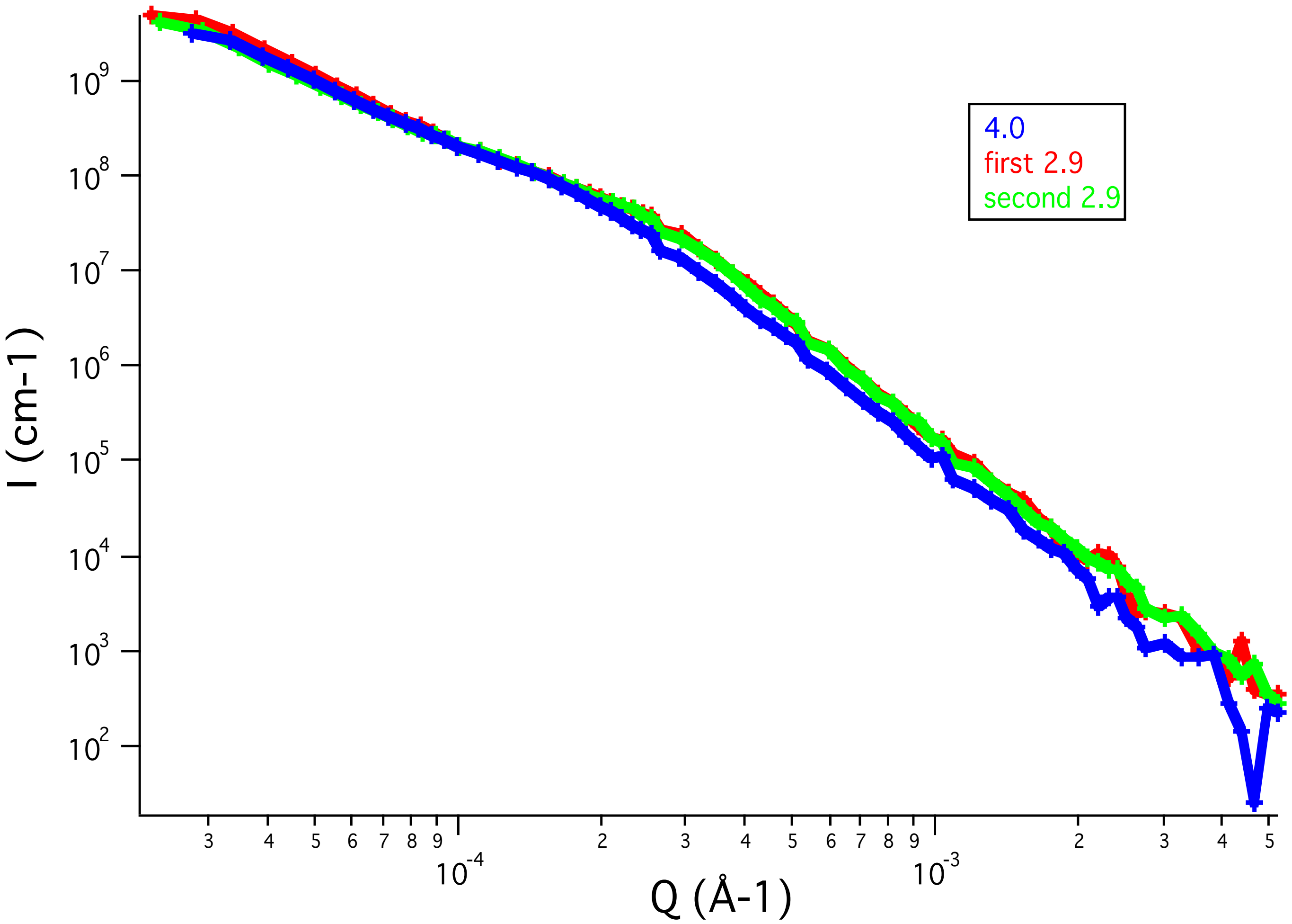


Why PMMA/Silica/Glass?

- Chemically inert
- Useful scattering length density
- Available in suitable sizes



Polydisperse Glass Spheres



Obvious polydispersity (as expected)

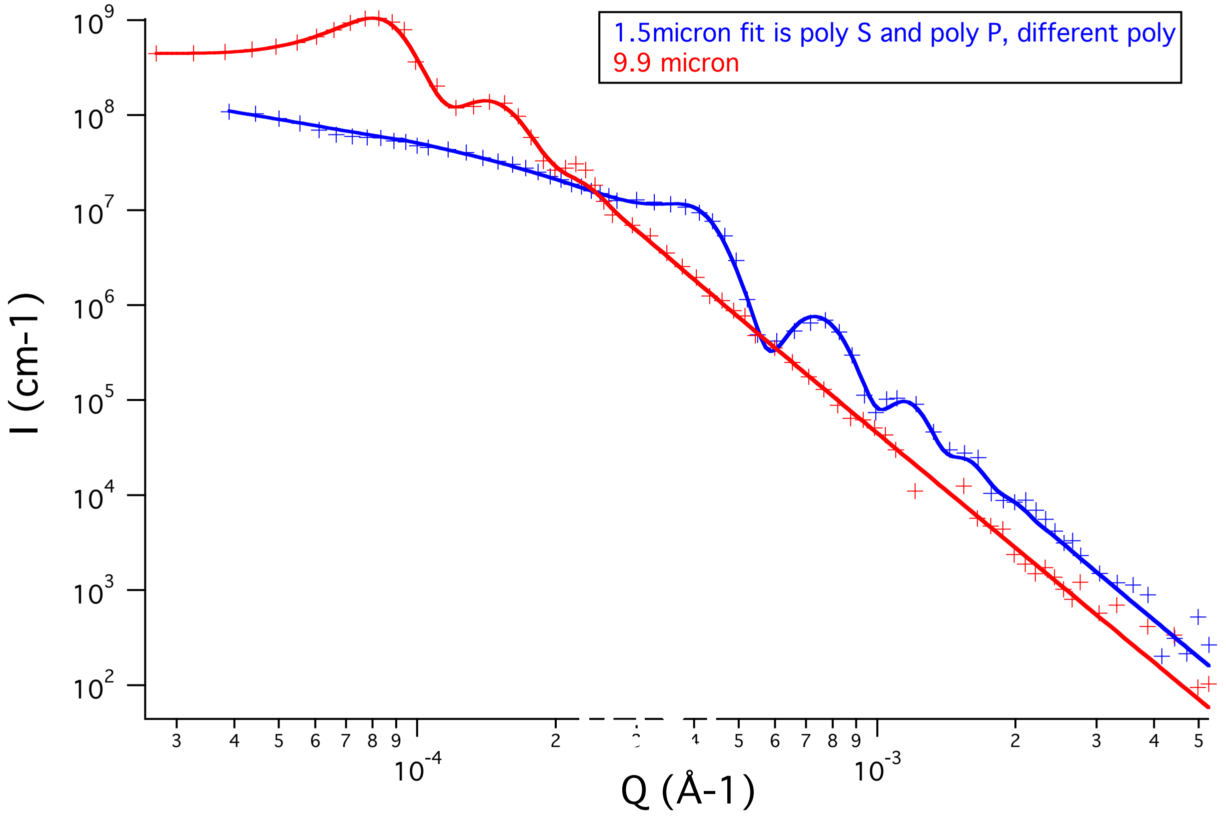
Two "knees" in the data give lower and upper size bounds of 2 µm and 20 µm. Compare with nominal 3 - 10 µm

Porod/Invariant suggest incomplete wetting

Unmixed PMMA Spheres

Porod/Invariant
$\phi = 0.45$

Gravimetric
$\phi = 0.33$



Porod/Invariant
$\phi = 0.61$

Gravimetric
$\phi = 0.53$

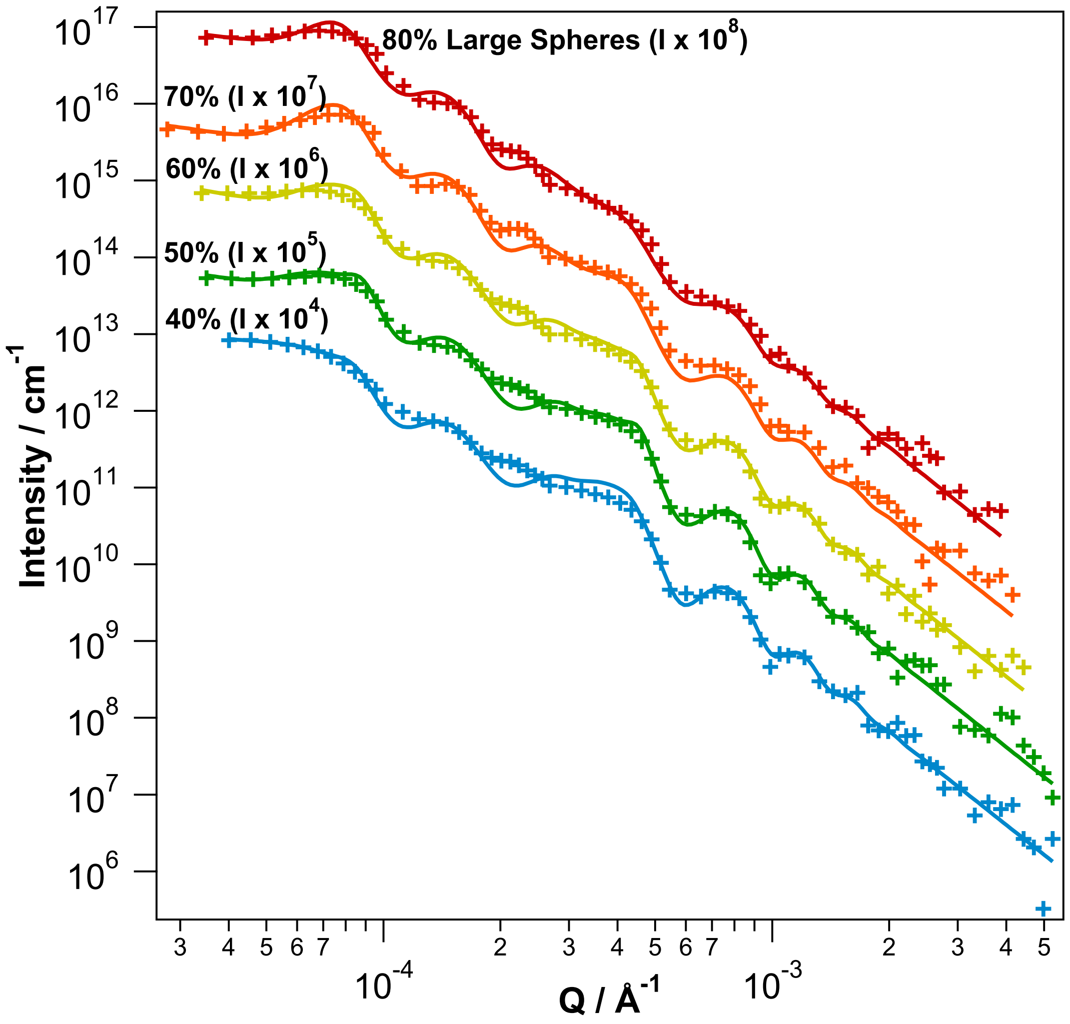
Loose packing at 1.5 μm - electrostatic forces more important than gravity.

Use Percus-Yevick Fluid model with Schulz size distribution

Two corrections
A Debye-Buche term for voids - packing not exactly like a fluid
Allow structure factor to have different polydispersity from form factor

P. A. Reynolds, D. J. McGillivray, A. J. Jackson, and J. W. White, *Physical Review E* (2009) **80** (1) 011301

Mixed PMMA Spheres



$$I(Q) = I_{SS} + I_{LL} + I_{SL} + I_{DB}$$

I_{SS} and I_{LL} are calculated as for unmixed spheres

I_{DB} accounts for voids in the packing

I_{12} is calculated using Ashcroft-Langreth S(Q) for bimodal spheres

Two "empirical" factors:

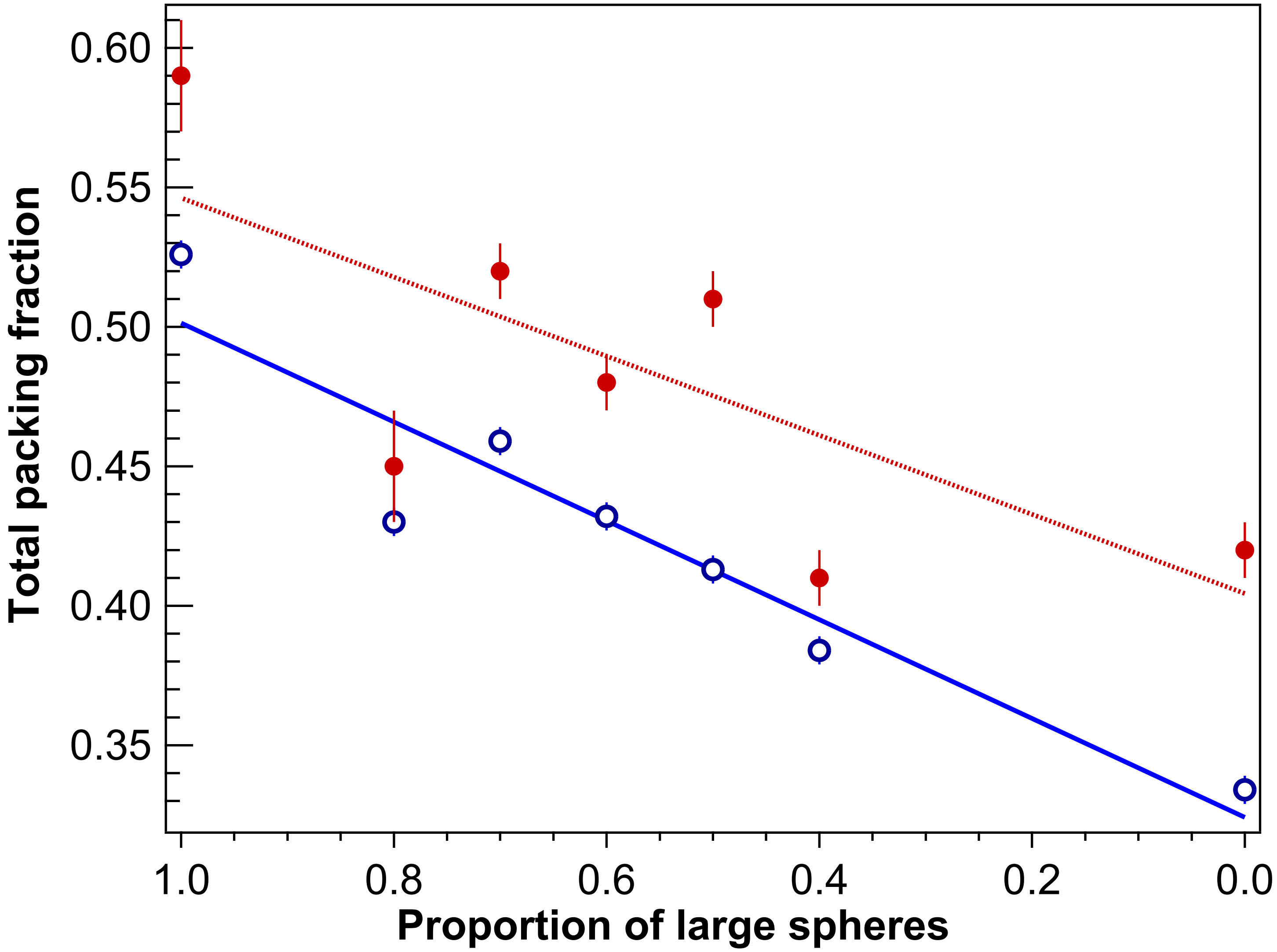
- Allow Small-Large interactions to vary independently of Small-Small and Large-Large
- Take account of size segregation

Mixed phases are partially self-segregated

S_{12} is less than for perfectly mixed spheres

P. A. Reynolds, D. J. McGillivray, A. J. Jackson, and J. W. White, *Physical Review E* (2009) **80** (1) 011301

Mixed PMMA Spheres



Linear relationship

No peak in packing fraction

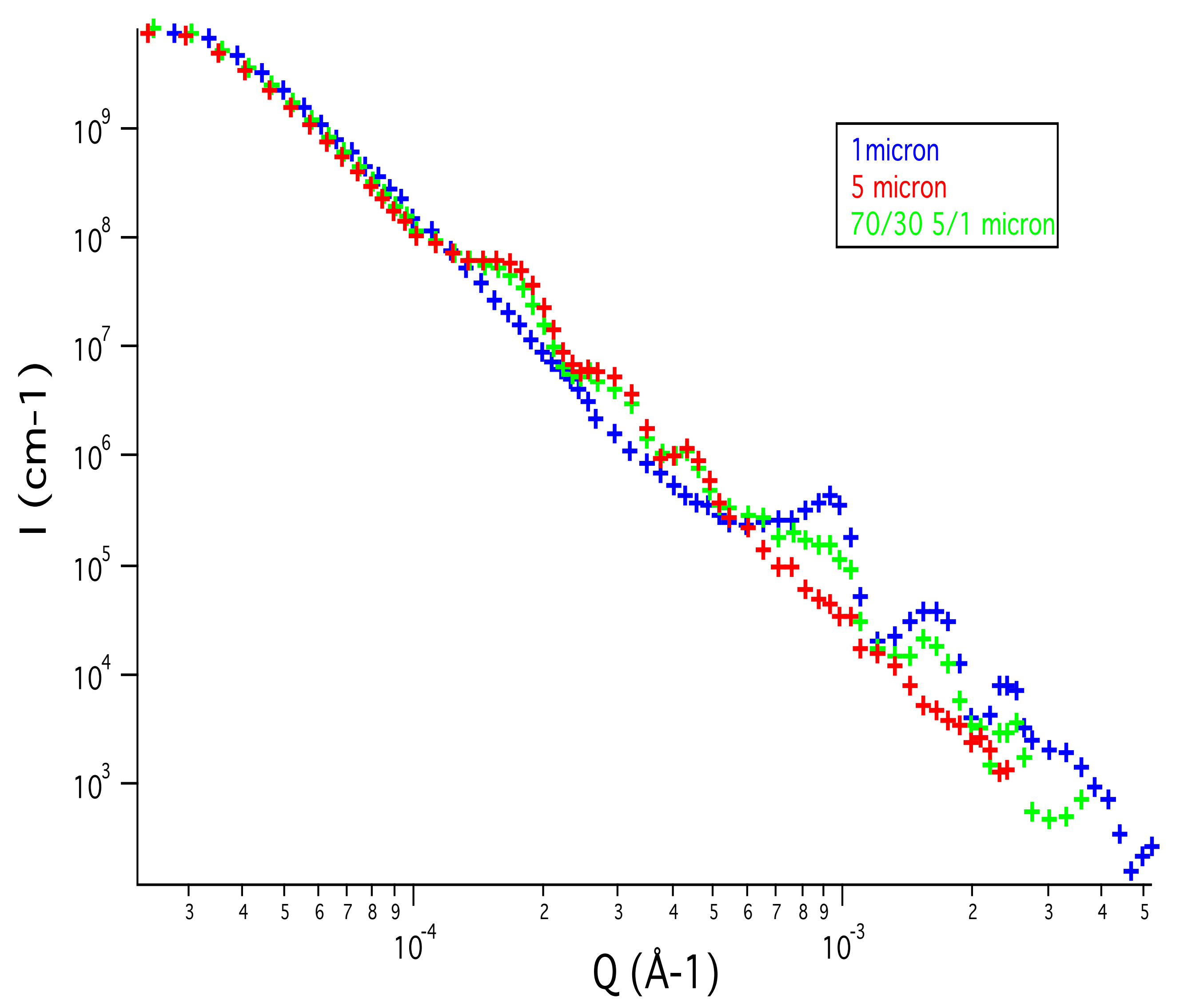
P. A. Reynolds, D. J. McGillivray, A. J. Jackson, and J. W. White, *Physical Review E* (2009) **80** (1) 011301

Conclusions

- PMMA systems display low total packing fractions indicating that non-gravitational forces are indeed important at this length scale.
- Around 50% of a mixed size PMMA sample is demixed
- The mixed volumes are not a random distribution of small and large spheres - the large spheres tend to self avoid and are coated with small particles
- USANS can provide rich data on mixed powders on the micron length scale which contains non-trivial information

Monodisperse Silica

- Loaded into quartz cuvettes
- Tamped by tapping on desk
- Measure mass of silica to estimate packing density
- Wetted with H2O/D2O mixture to reduce scattering contrast



Fitting and Porod/ Invariant give contrast that is too large.

Guinier region not present.

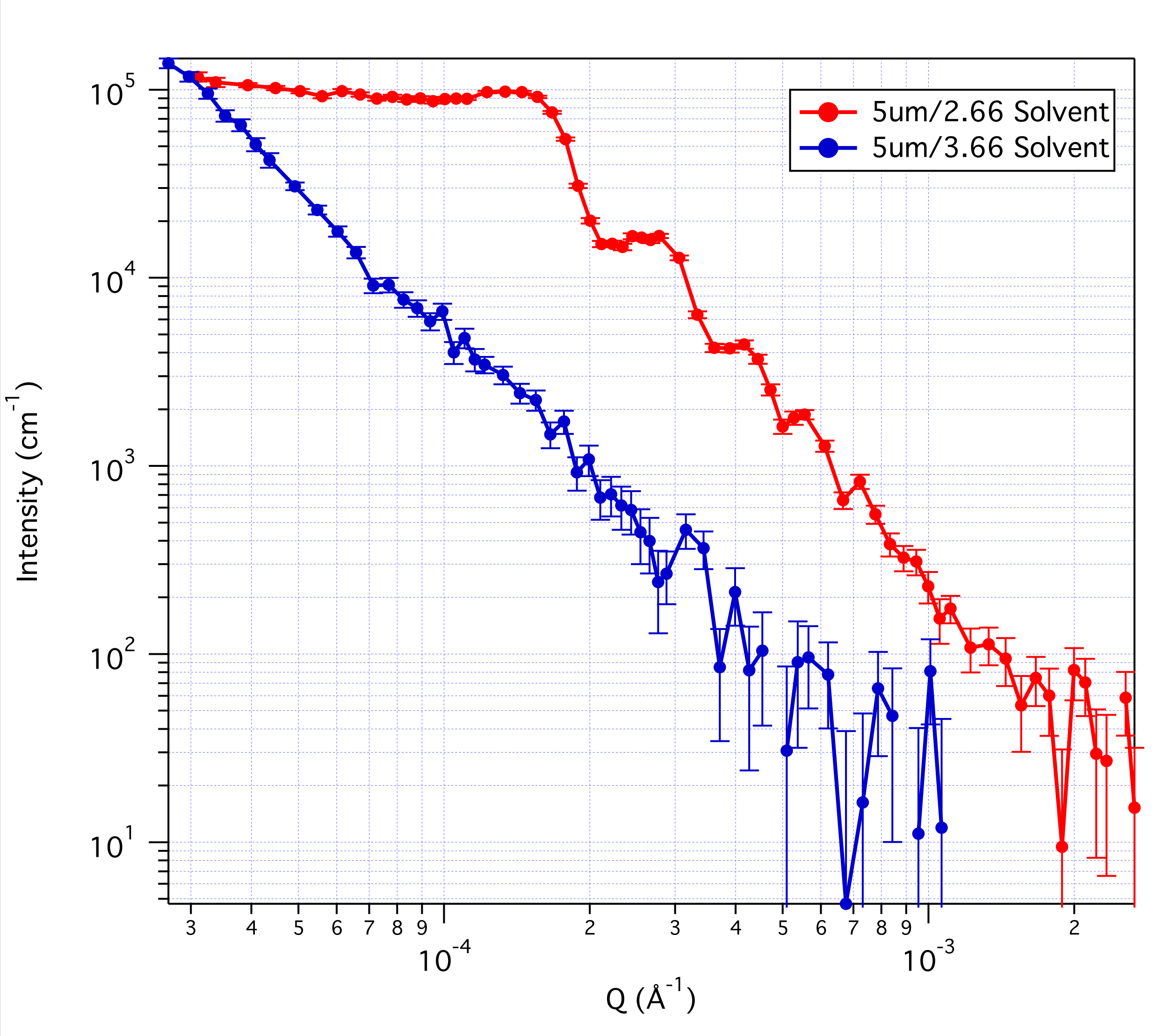
Turnover at too low Q

Incomplete Wetting
Air Bubbles

Monodisperse Silica

Repeat method as before but:

- Put sample under vaccum to remove air
- Load water into cell whilst sample is under vacuum

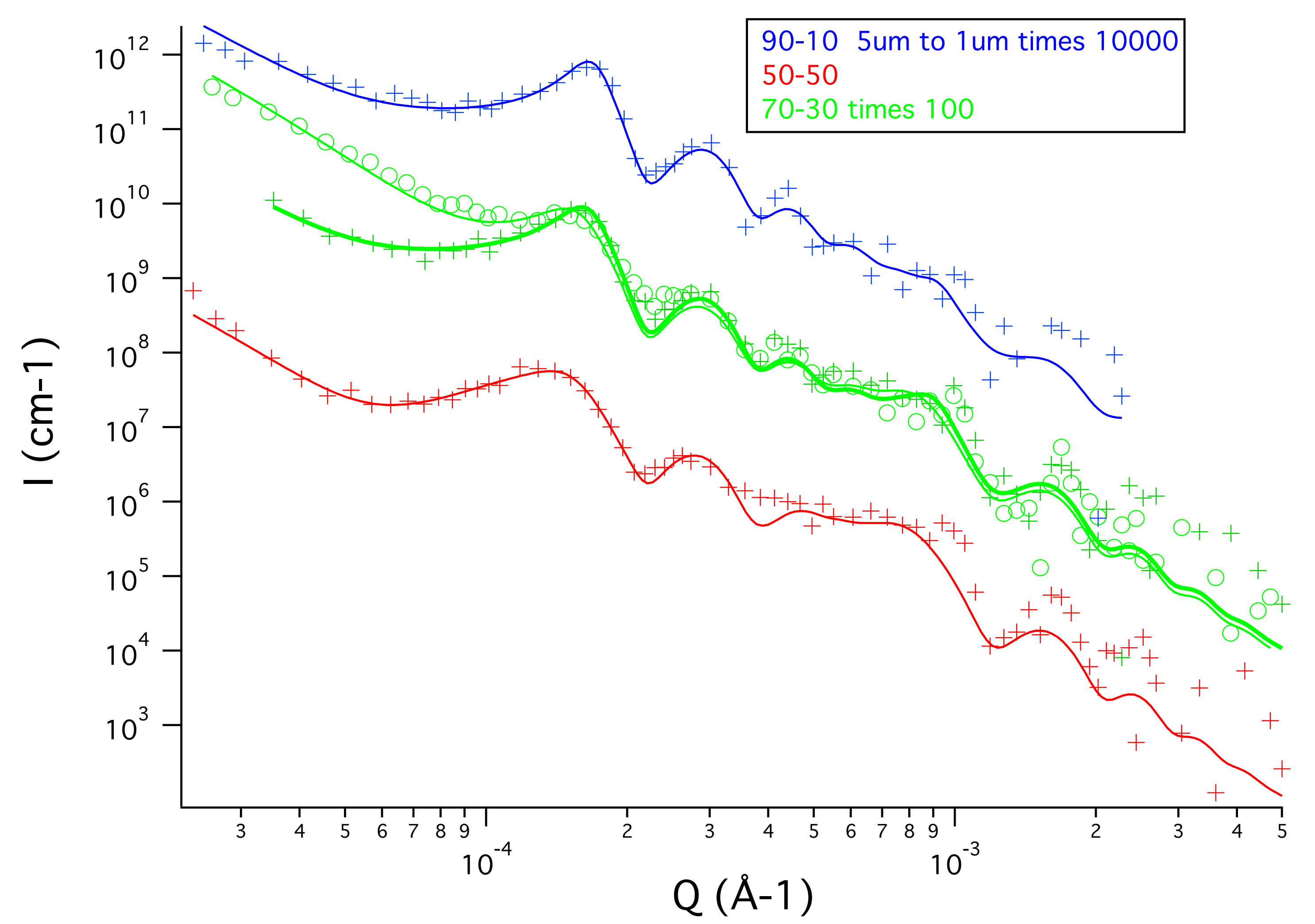


Guinier region now present.

Silica contrast matched sample shows residual scattering from remaining air bubbles.

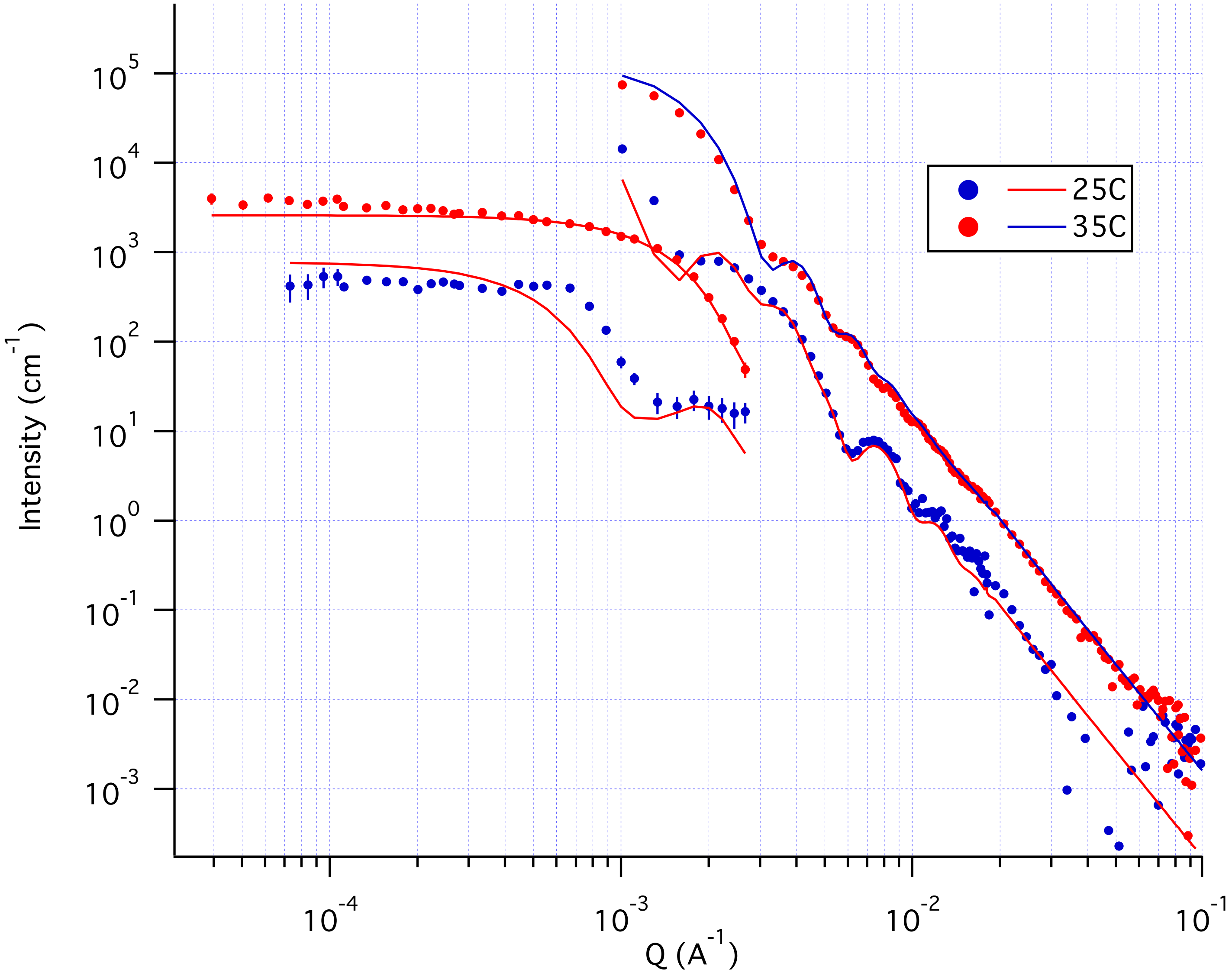
Much better wetting
Air bubbles not causing a significant perturbation

Monodisperse Silica



Initial fits to wetted silica data using model

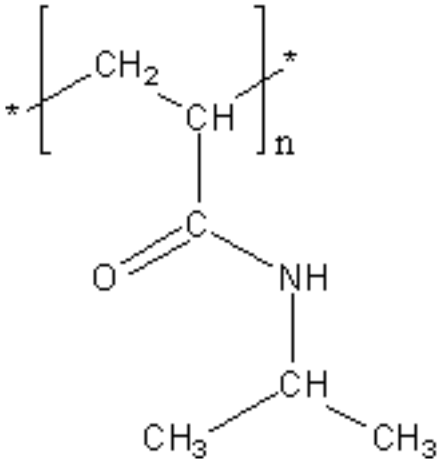
Soft Spheres

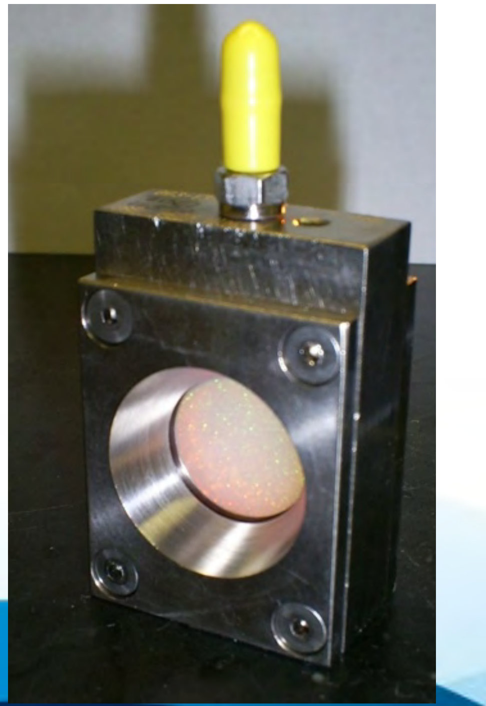


Poly-NIPAM

Thermo-responsive

"Easy" to synthesize





Varying size difficult

- Change chemistry (co-acrylic acid / co-acrylamide)
- Core-Shell (polystyrene core)

Ongoing Work

- Continuing analysis of wetted silica data
- Contrast matching studies to extract partial structure factors directly:
  - Silica/PMMA mixtures ~~(experiment next week)~~
  - Make deuterated PMMA.
- Computer simulations of packing to compare with our model and data - will hopefully provide basis for "empirical" factors or a replacement.
- Ternary/Quaternary/... mixtures
- Viscosity
  - Would like to understand viscosity - polydispersity relationship

Ongoing Work

Started with emulsions but ...

Important theoretical problem with applications beyond emulsions

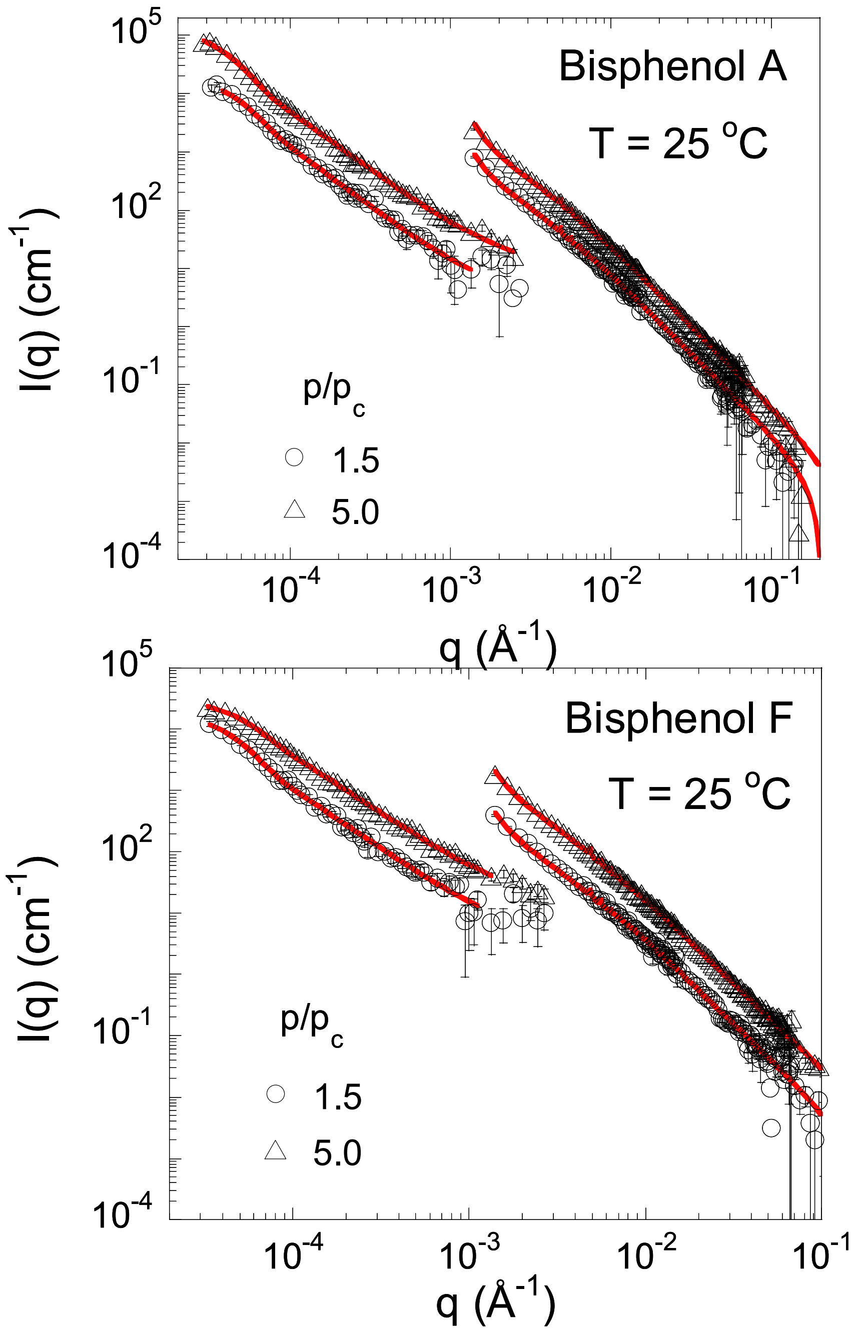
“What distribution of sizes do I need to get this volume fraction or that physical property”

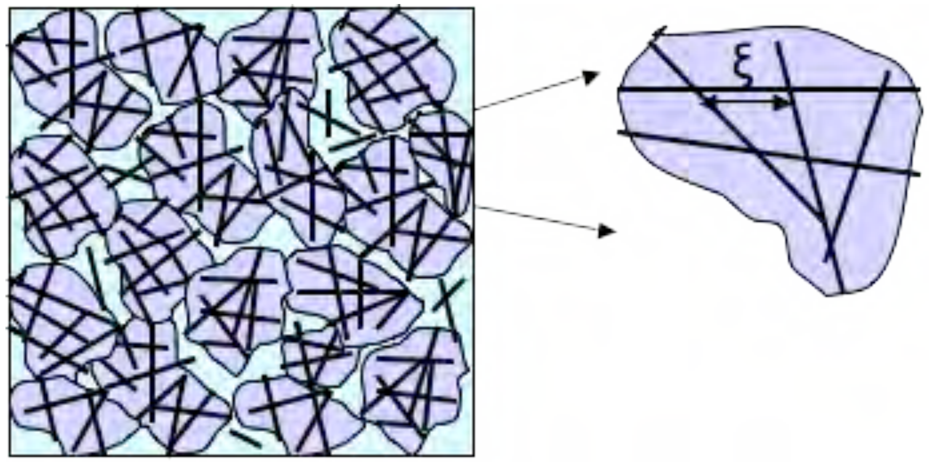
Foams
Powder Processing
Composite Filler Aggregation
Pumped Slurries
Geology and Carbon Capture

NCNR USANS Highlights

SWNT/Epoxy

T. Chatterjee and R. Krishnamoorti, U. Houston, and A. Jackson



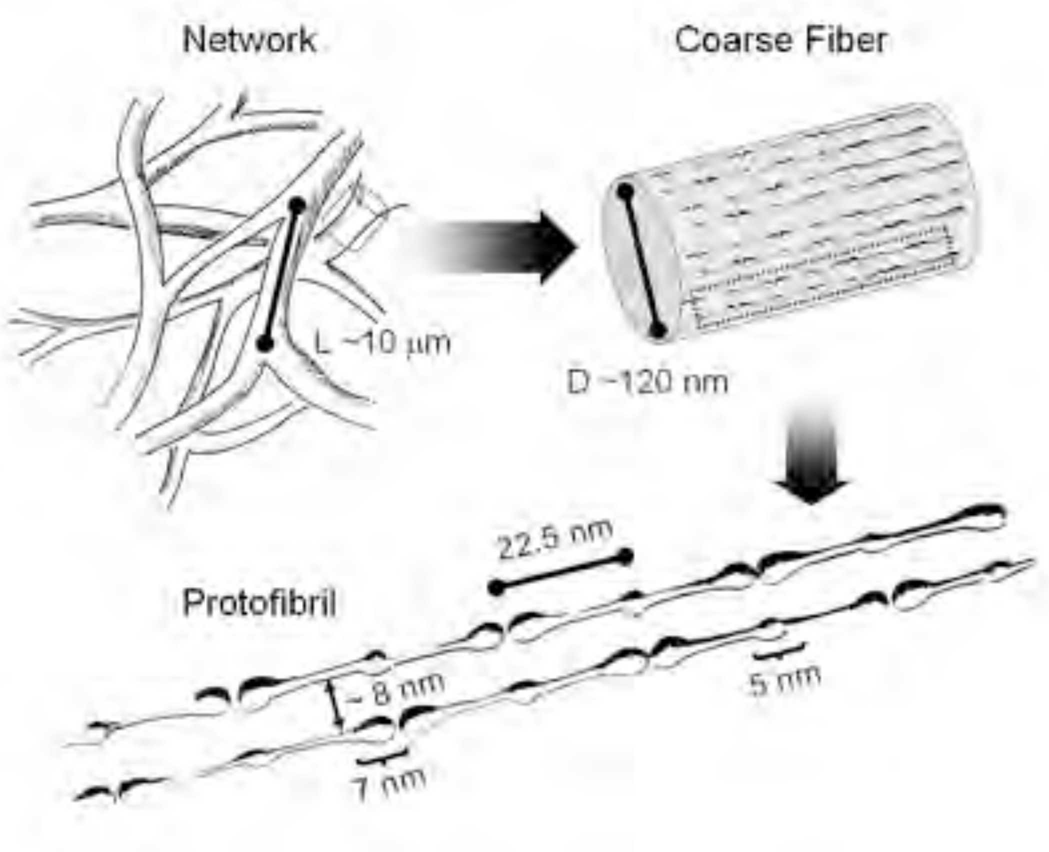


Floc size is invariant under different concentration conditions. This suggests that it is floc-floc interactions that are determining elastic network strength.

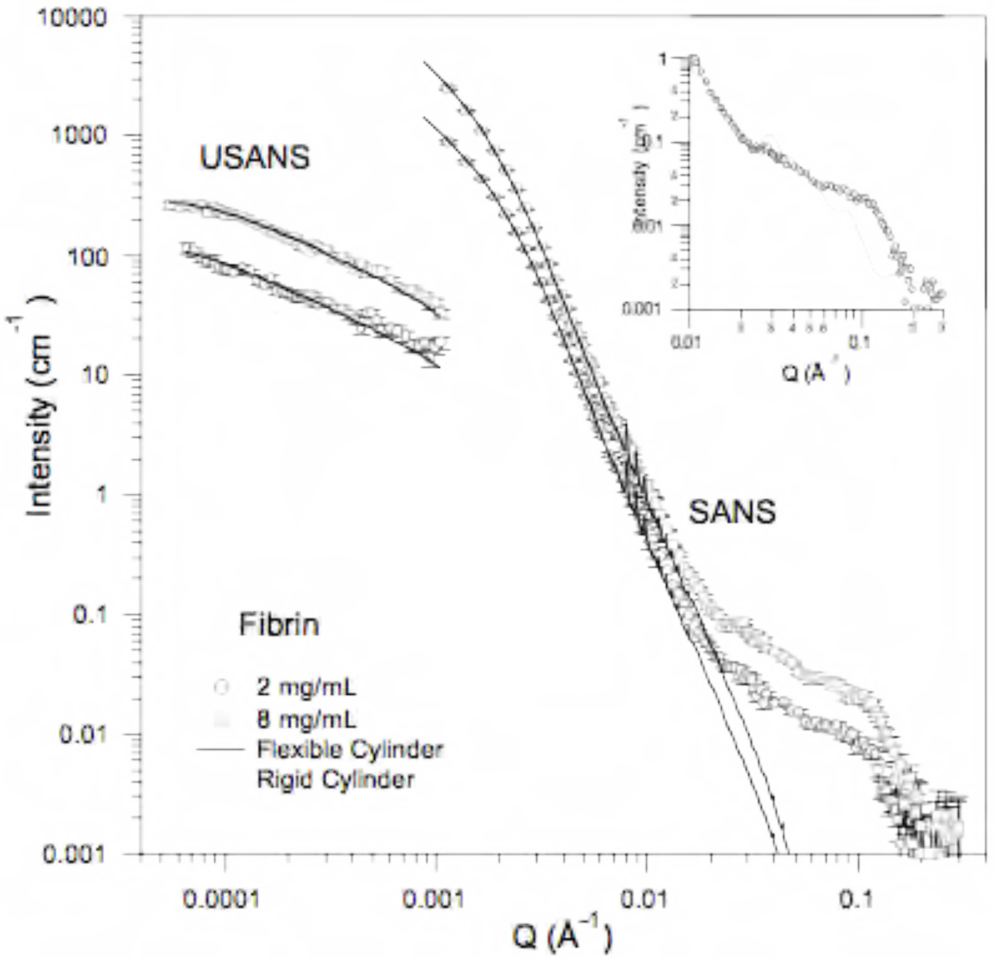
T. Chatterjee, R. Krishnamoorti, *Phys. Rev. E.*, **75** (5), 050403, 2008
T. Chatterjee, A. Jackson, R. Krishnamoorti, *J. Am. Chem. Soc*, **130** (22), 6934, 2008

Fibrinogen Clots

D. Pozzo, U. Washington, L. Porcar, ILL/NCNR and P. Butler, NCNR



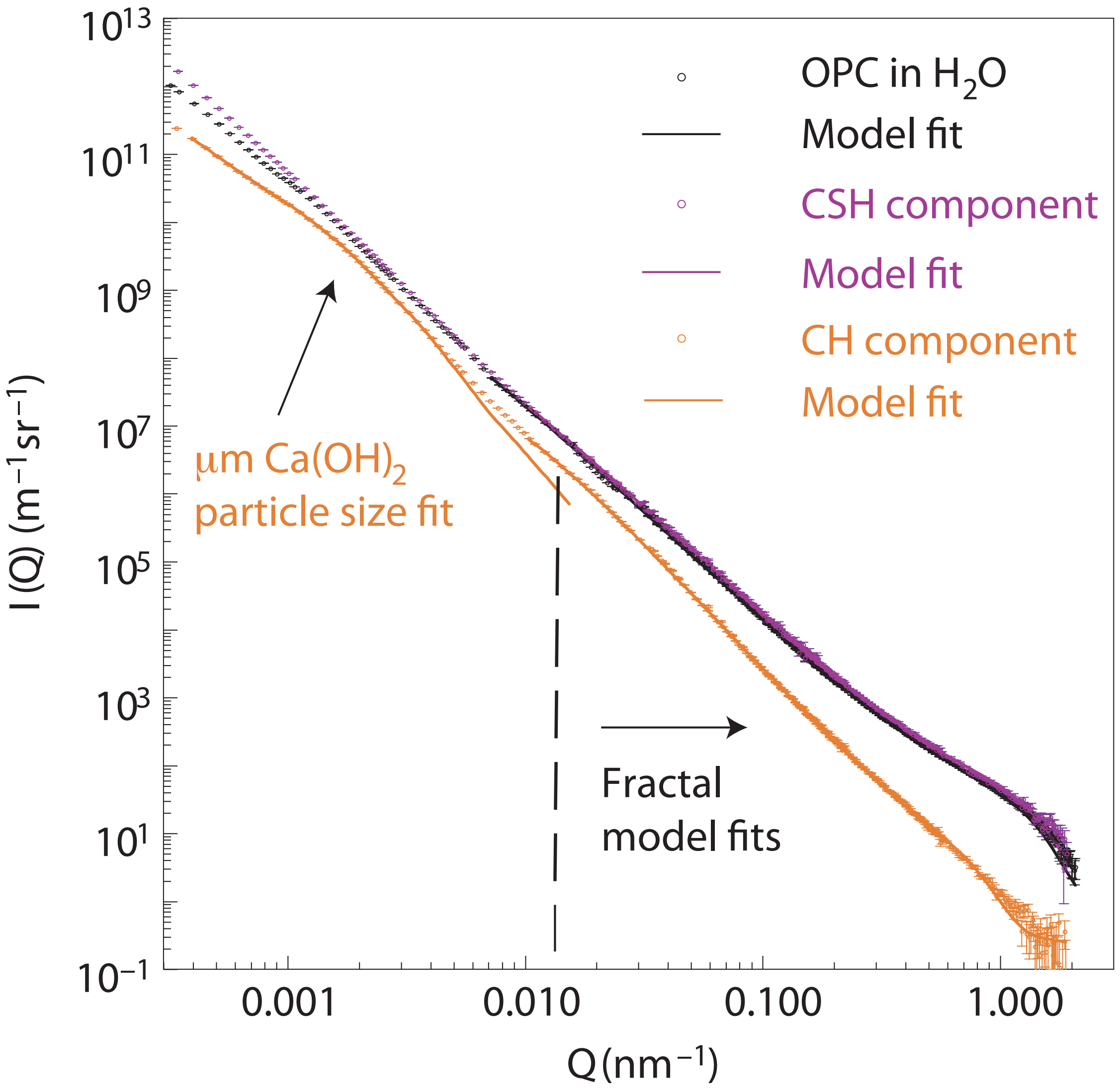
Combined SANS/USANS provides structural information over 4 orders of magnitude.

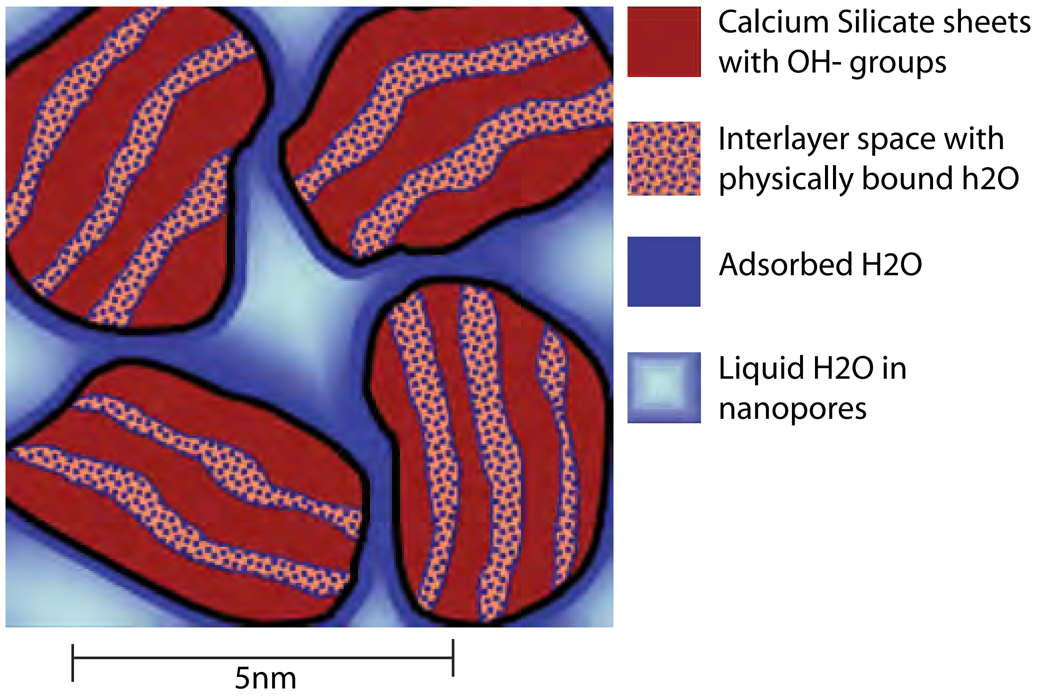


Neutrons allow us to study the system under shear and under biologically relevant conditions

Cement

A. Allen, NIST Ceramics Division and J. Thomas and H. Jennings, Northwestern University





Combination of SANS/USANS and SAXS/USAXS gives detailed information about the mean formula and mass density of calcium-silicate-hydrate without drying - the first such measurement.

Allen AJ, Thomas JJ, Jennings HM. Nature Materials, **6**(4), 311 (2007)

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- Johann Zank (ANU, now Orica) (Emulsions)

- Mara Levine (Hood College) (Soft Spheres)

- Access to Major Research Facilities Program (AMRFP) fund (Australian Government)

- NIST Center for Neutron Research

- NSF - Center for High Resolution Neutron Scattering

- Orica

Questions?

andrew.jackson@esss.se

Unmixed

$$I_{SS}(Q) = \phi_S \ll V_S \gg \ll P_S(Q) \gg S^M_{SS}(Q)$$

$$S_{DB}(Q) = \frac{A_0}{(1+Q^2\zeta^2)^2}$$

$$I_{SS}(Q) = \phi_S \ll V_S \gg < P_S(Q) > (S^M_{SS}(Q) + S_{DB}(Q))$$

Mixed

$$I(Q,\phi_L,\phi_S) = I_{SS}(Q,\phi_L,\phi_S) + 2I_{SL}(Q,\phi_L,\phi_S) + I_{LL}(Q,\phi_L,\phi_S) + I_{DB}(Q,\phi_L,\phi_S)$$

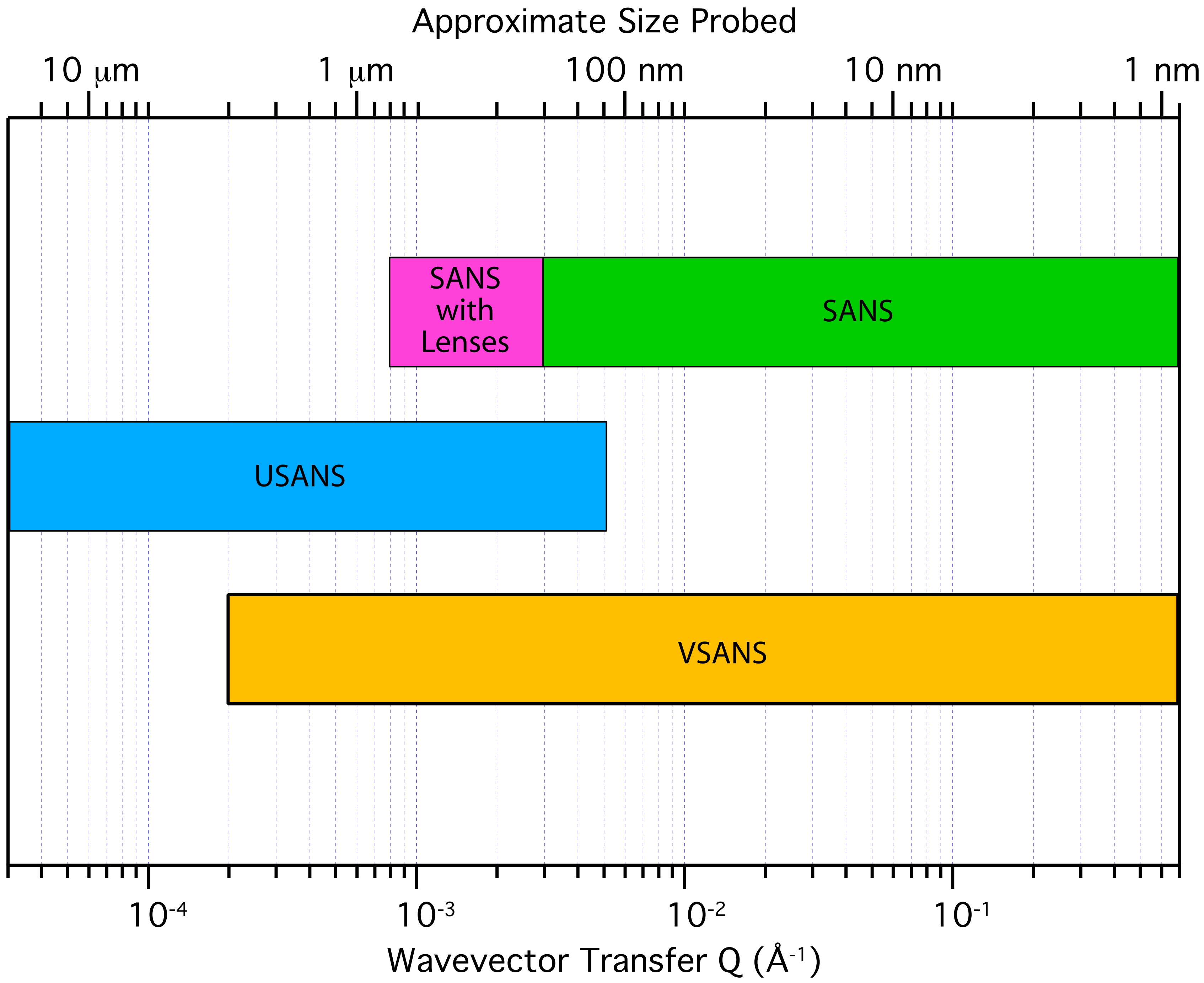
$$I_{DB}(Q,\phi_L,\phi_S) = \frac{\phi_S < P_S(Q) > +\phi_L < P_L(Q) >}{(\phi_S + \phi_L)} \frac{A_0}{(1+Q^2\zeta^2)^2}$$

$$I_{SS}(Q,\phi_L,\phi_S) = \phi_S \ll V_S \gg < P_S(Q) > S^M_{SS}(Q)$$

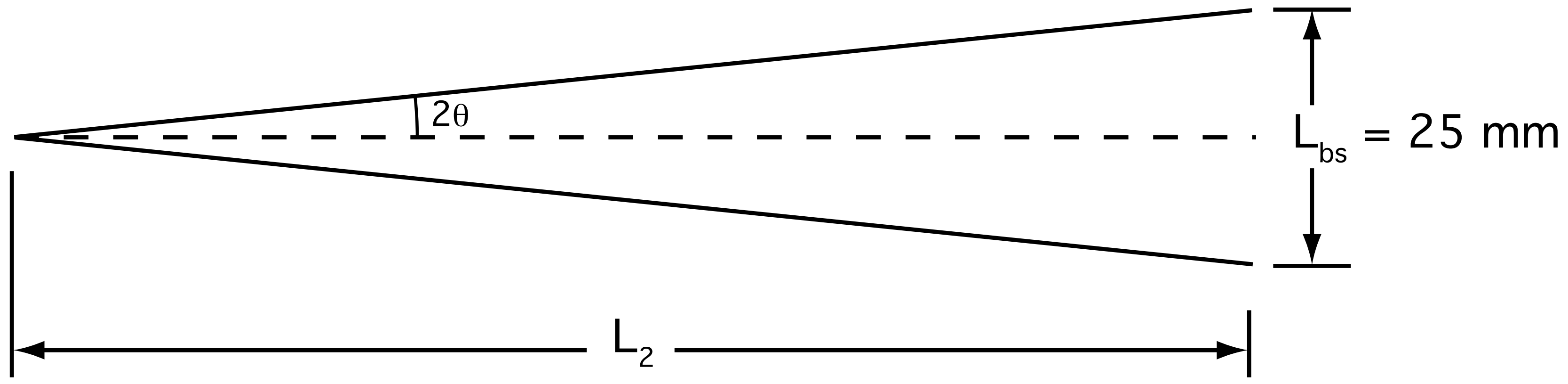
$$I_{SL}(Q,\phi_L,\phi_S) = M \times (\phi_S \ll V_S \gg < P_S(Q) > \phi_L \ll V_L \gg < P_L(Q) >)^{1/2} < S_{SL}(Q) >$$

$$I = F \times I(mixed) + (1-F) \times I(unmixed).$$

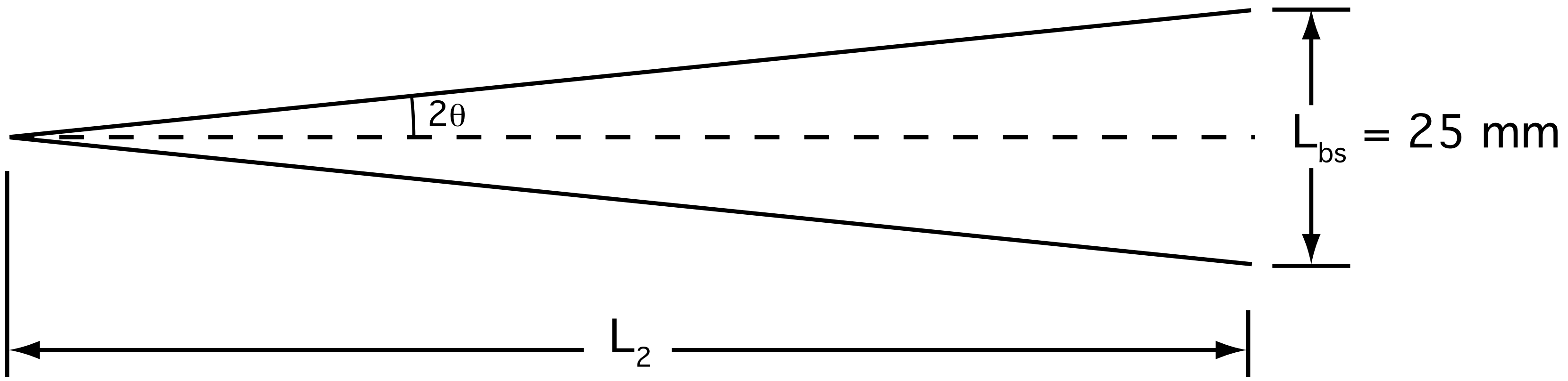
USANS - What and Why?



USANS - What and Why?

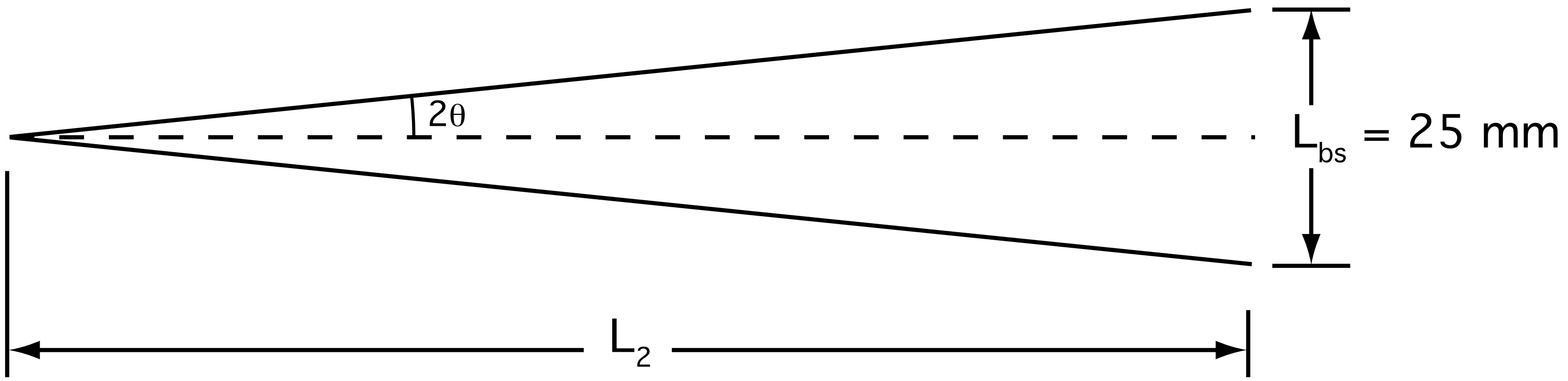


USANS - What and Why?



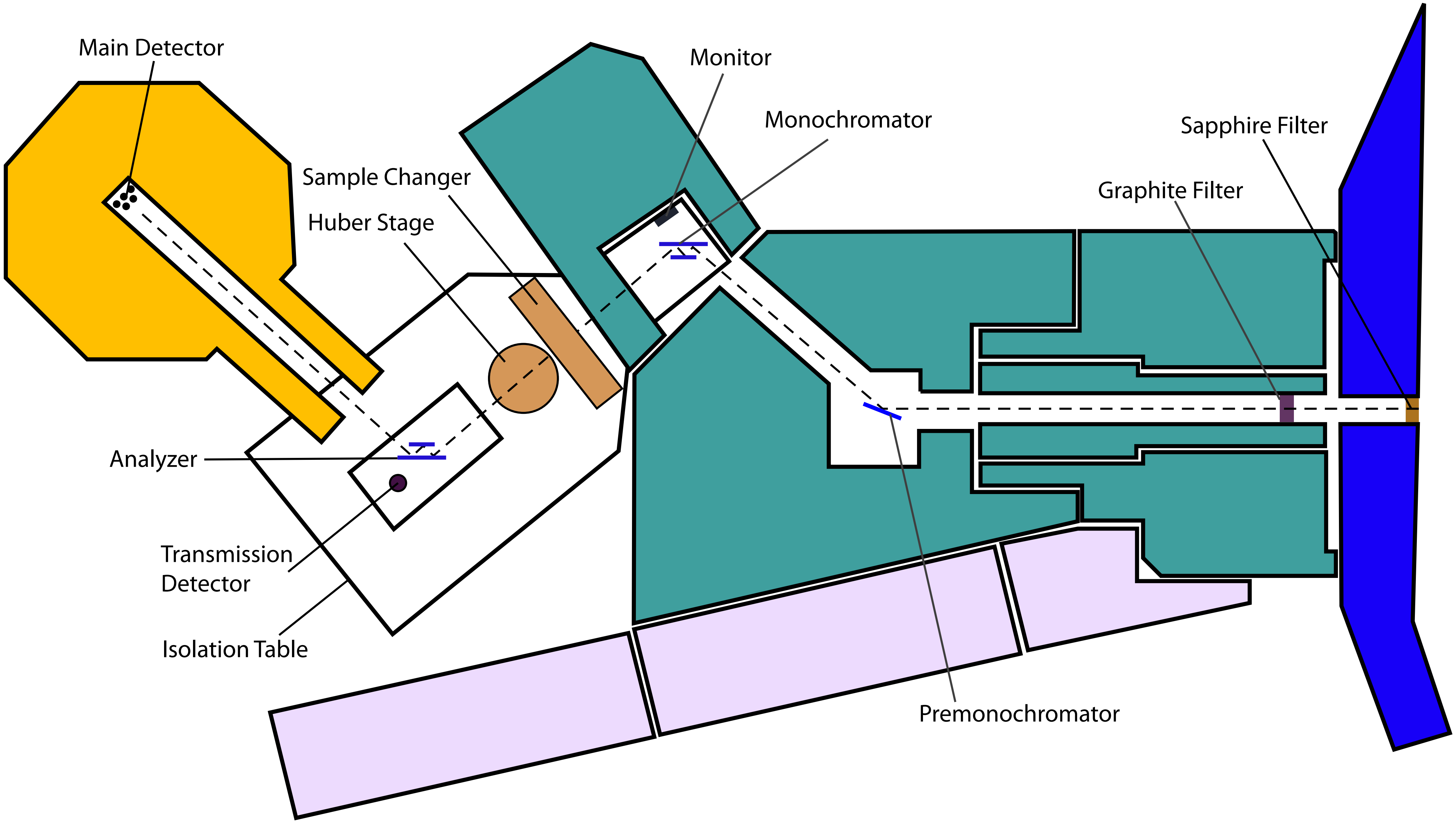
$Q = 3\times10^{-5}$ Å^{-1}, $\lambda = 6$ Å

USANS - What and Why?



$Q = 3\times10^{-5}$ Å^{-1}, $\lambda = 6$ Å → $L_2 = 443$ m !

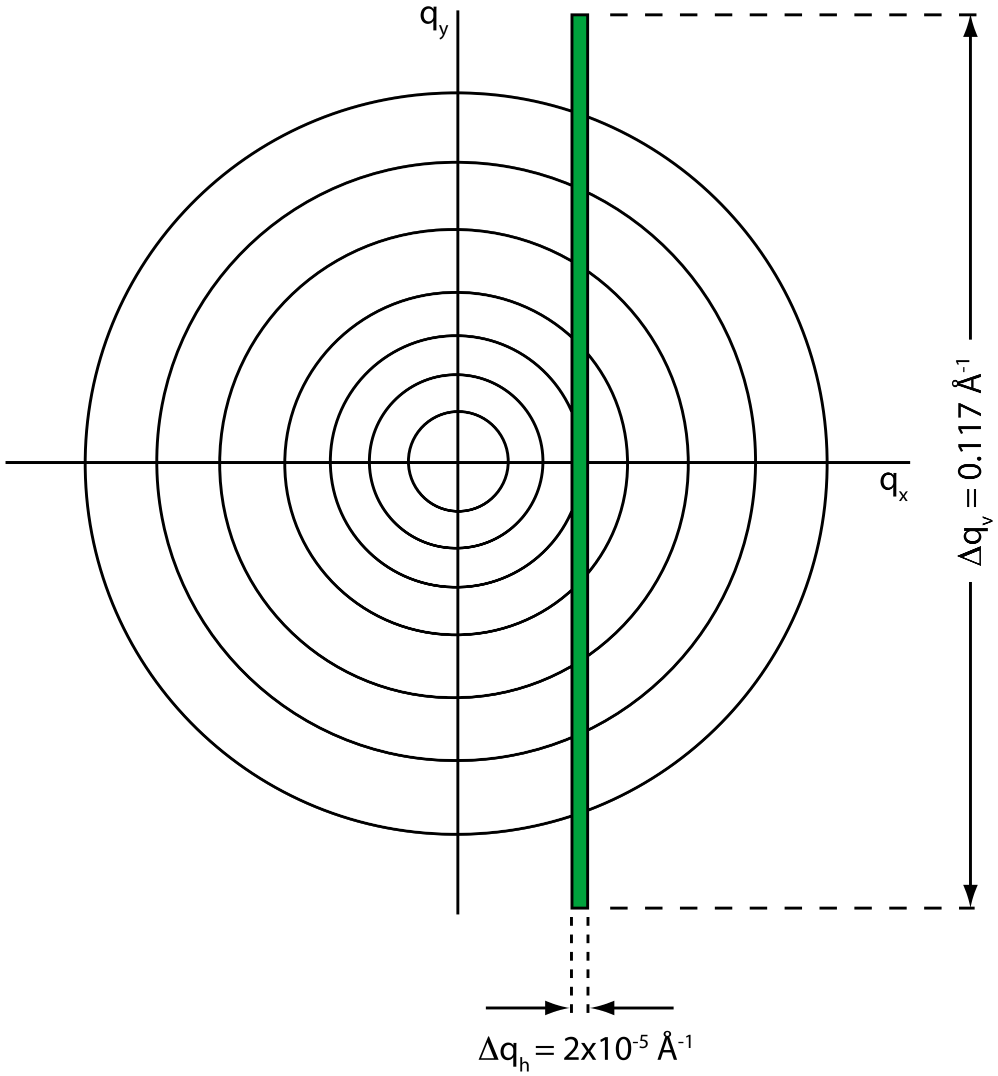
Instrument Details

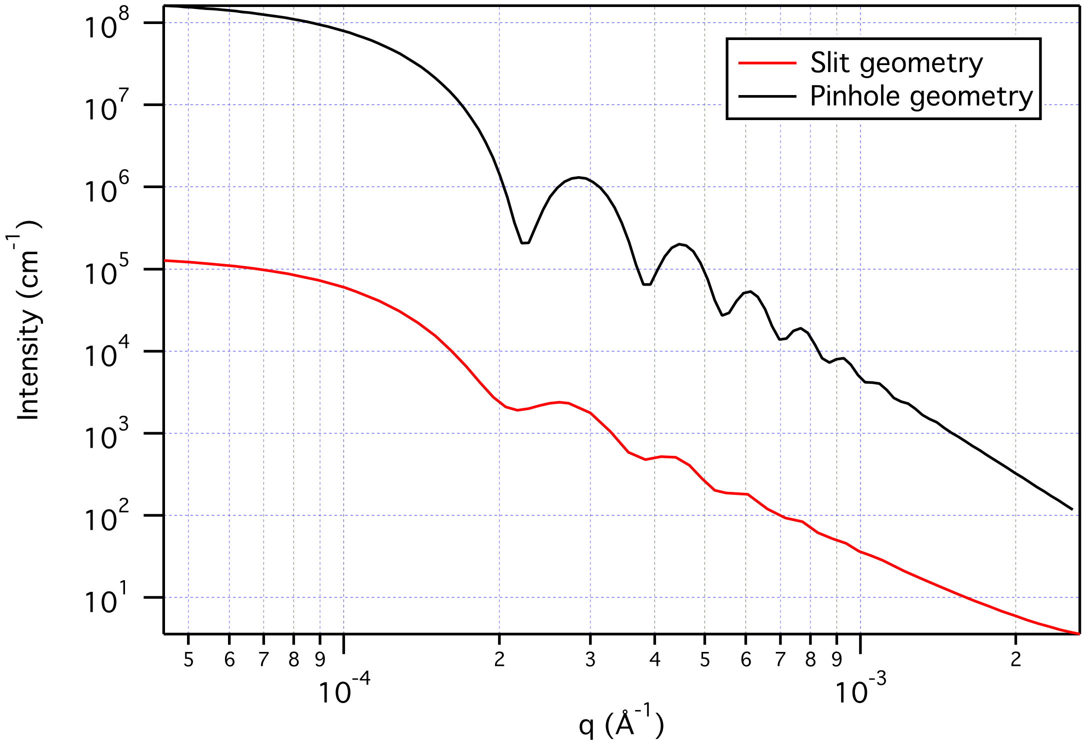


EUROPEAN
SPALLATION
SOURCE

Differences from SANS

Slit vs Pinhole Geometry





$$\frac{d\Sigma_s}{d\Omega}(q) = \frac{1}{\Delta q_v}\int_0^{\Delta q_v}\frac{d\Sigma}{d\Omega}(\sqrt{q^2+u^2})du$$

Differences from SANS

0D vs 2D detector

SANS

- 2D detector
- Collect wide Q range simultaneously
- Non-azimuthally symmetric data easily analyzed

USANS

- 0D detector
- Point-by-point data collection
- Non-azimuthally symmetric data hard to analyze

EUROPEAN
SPALLATION
SOURCE

Differences from SANS

Data Collection

SANS	USANS
Multiple sample-detector distances to cover whole Q-range	Multiple sets of analyzer angle scans to cover whole Q-range
Transmission and blocked beam measurements	Transmission measurement is part of scan, blocked beam is constant
Counting time per sample < 1 hour	Counting time per sample 1 to 12 hours (6 hours usual)