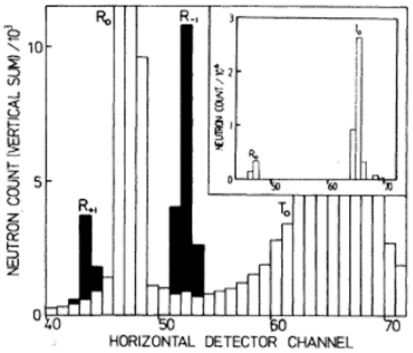
Off Specular Scattering: What It Can Tell You & (some of) What You Need to Know

Bill Hamilton

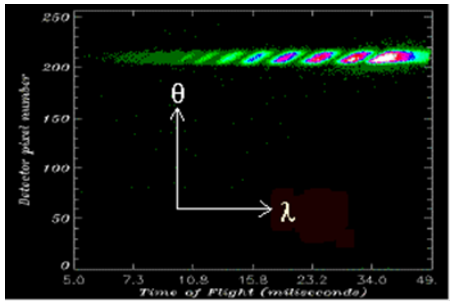
Formerly
1982-87 Particles and Fields Group, School of Physics, University of Melbourne
1987-90 LANSCE/Lujan Center, Los Alamos National Laboratory
1991-2006 Neutron Scattering Section, Oak Ridge National Laboratory
2006-2010 Bragg Institute, ANSTO, Lucas Heights, Australia
2011-2016 Instrument Development Group, Oak Ridge National Laboratory
Currently
2019-2020 PIFI Fellow, Chinese Spallation Neutron Source (now virtually …)

LUND INSTITUTE OF ADVANCED NEUTRON AND X-RAY SCIENCE LINXS GISANS Workshop **25 September 2020**

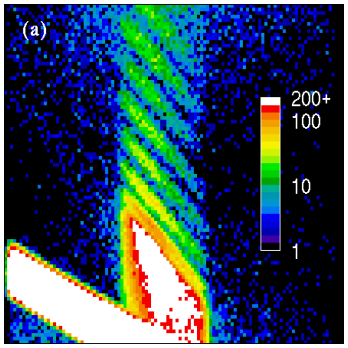
Some prehistory …



1982-1986 ***Neutron Diffraction by Surface Acoustic Waves***
with Tony Klein & Geoff Opat University of Melbourne
& Peter Timmins, ILL
Doppler shifted grating diffraction ↔ surface phonon scattering
on D17 when it was a SANS …



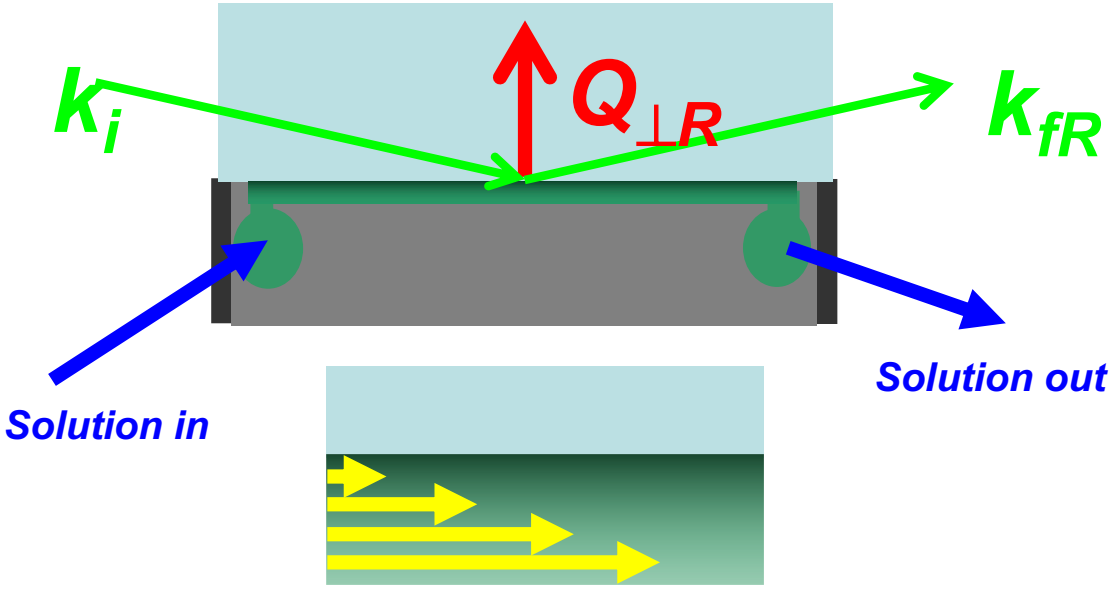
1987-1990 ***SPEAR Reflectometer*** *LANSCE, LANL*
with Greg Smith & Roger Pynn
&
1991-1993 ***MIRROR Reflectometer*** *HFIR, ORNL*
with John Hayter

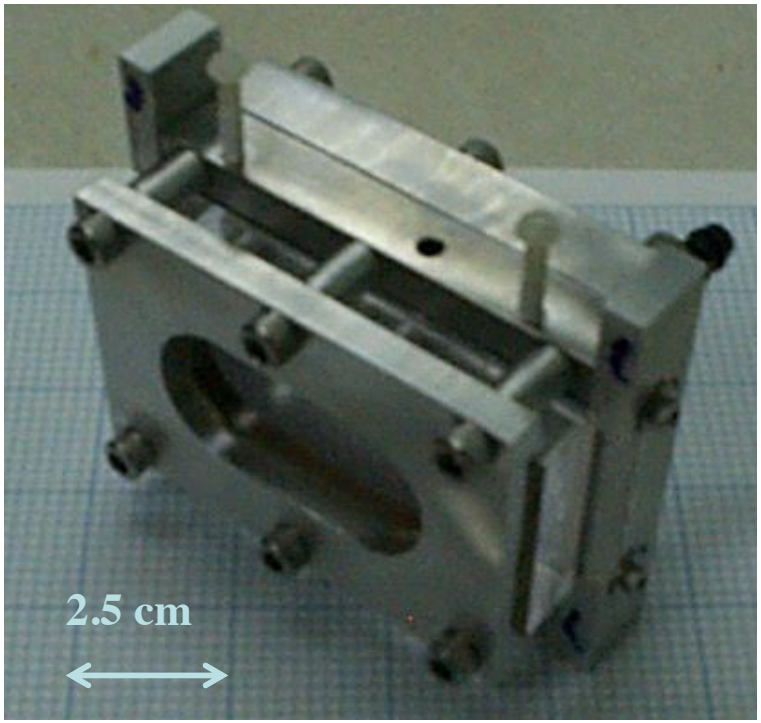


… then 1993 ***"Neutron Reflectometry studies of micellar systems under Poiseuille (surface) Shear"***
ORNL collaboration with Lee Magid & Paul Butler, University of Tennessee
And Greg Smith, Shenda Baker & Roger Pynn, LANSCE/LANL

What our cells looked like:

Reflection geometry Quartz-Solution Poiseuille shear cell





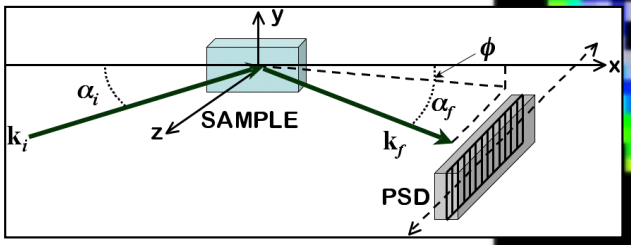
1 mm deep flow trough beneath polished Quartz slab

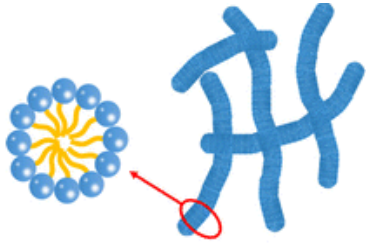
Original idea to simply to use Specular NR to study surface adsorption and constraint effects on complex fluids under Poiseuille shear as sample flowed past quartz surface extend to surface organization work John and others had begun on systems under bulk Couette shear at ILL in the mid 80's

Original cell design: S.Baker, G.S. Smith, P.D. Butler, J.B. Hayter, W.A. Hamilton, R. Pynn and L.J. Magid, *Rev. Sci. Inst.* **65**, 412 (1994)

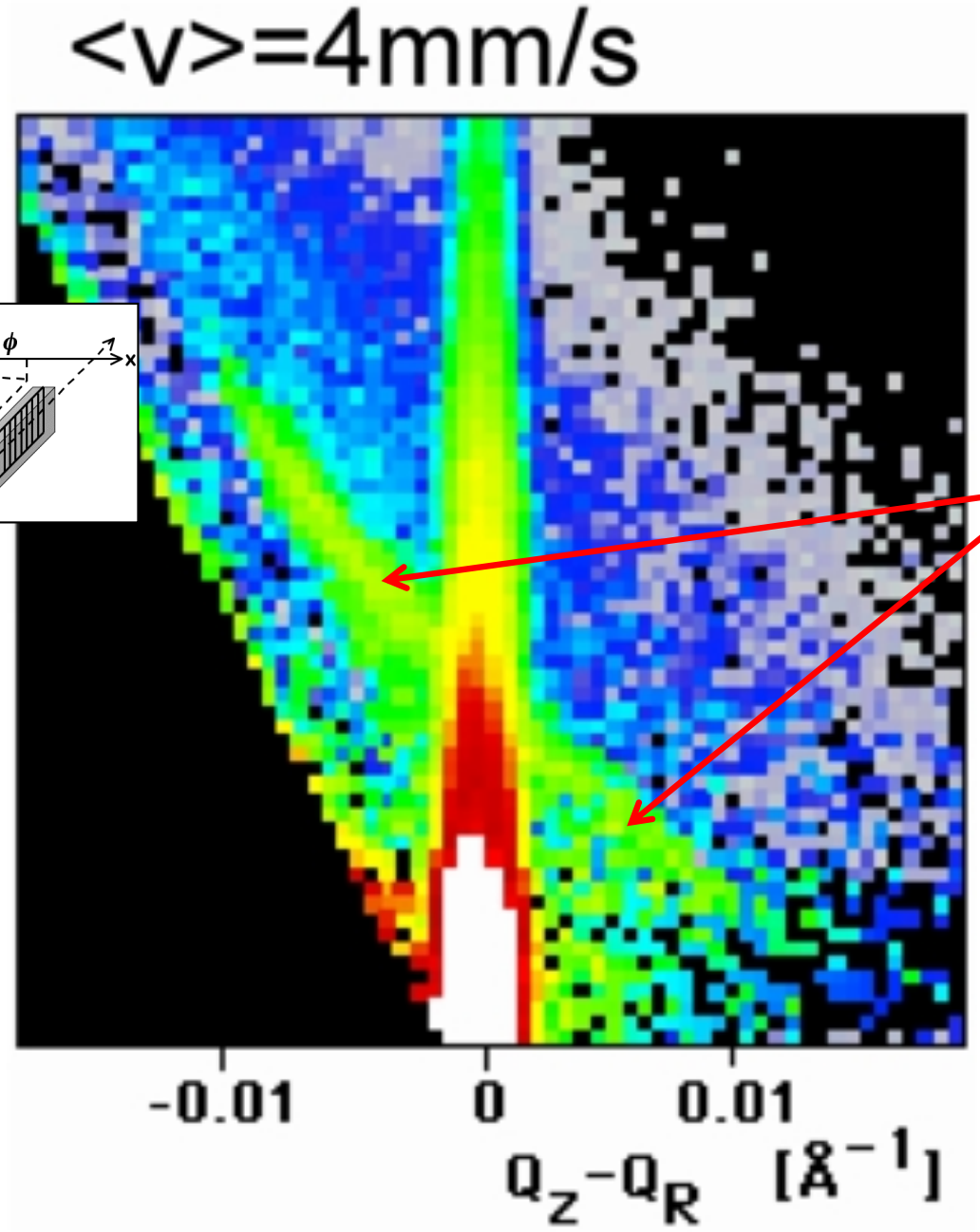
When Off Specular Scattering Happens - 1

ORNL
"MIRROR" NR
λ=2.59Å
1D Detector





Threadlike
Micellar solution
in Poiseuille
flow cell
20mM
70:30
CTA-3,5ClBz/CTAB
c. June 1993



Initially weak
SANS background,
became
much stronger

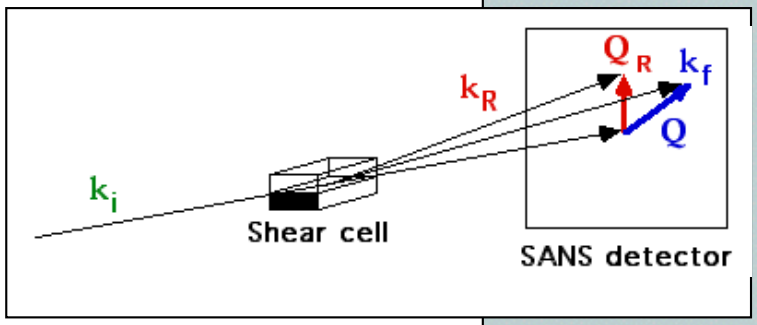
With one
Very SHARP
Flow dependent
Peak in
Off specular
SANS
signal

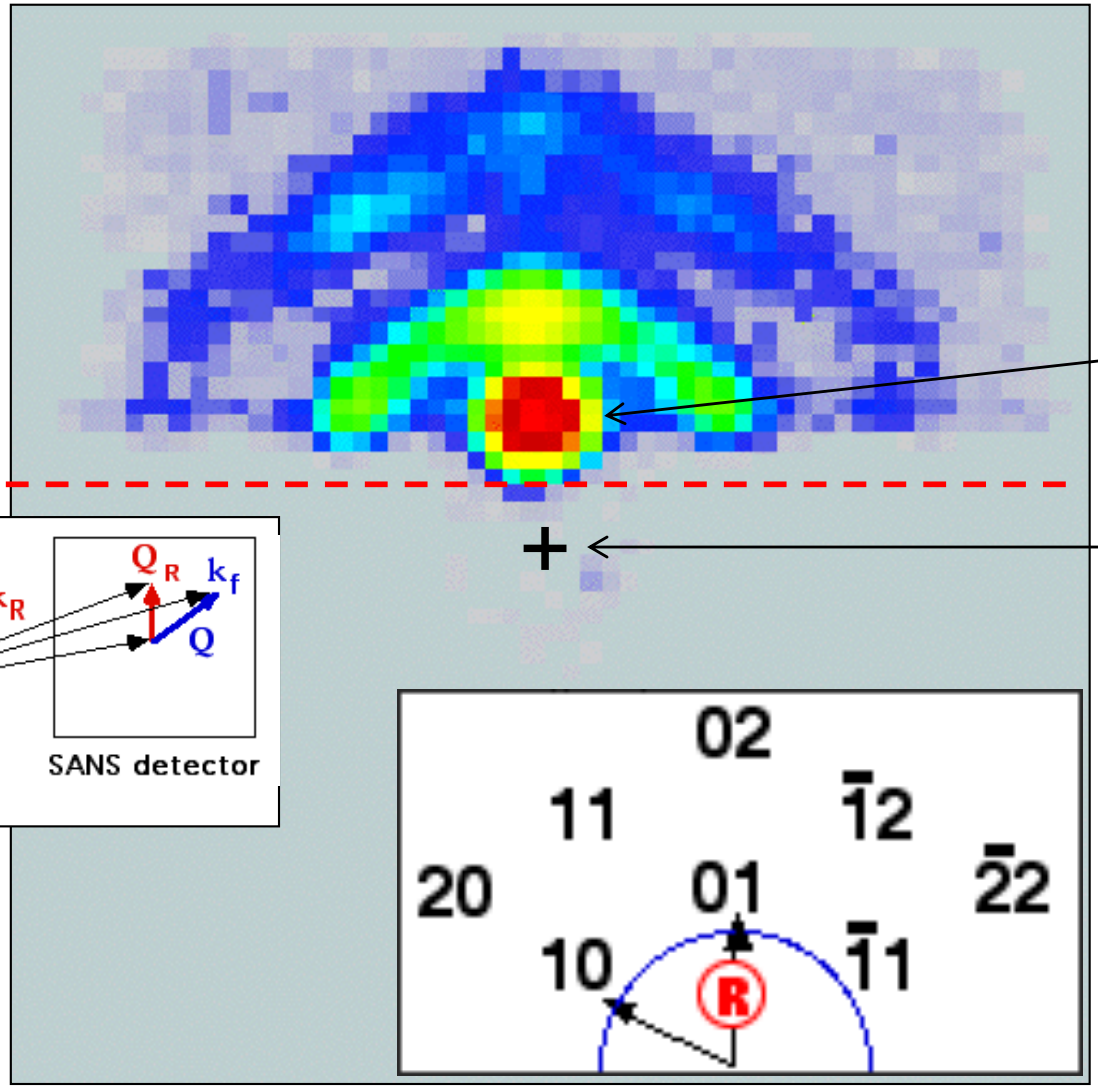
Q_{peak} ~ 0.023Å^{-1}

Also kinda
persistent when
flow stopped …

When Off Specular Scattering Happens - 2

ORNL
30m SANS
λ=4.75Å
2D Detector





Specular reflection

Interface "Horizon"

Direct beam (Q=0)

Threadlike
Micellar solution
- Poiseuille
flow cell

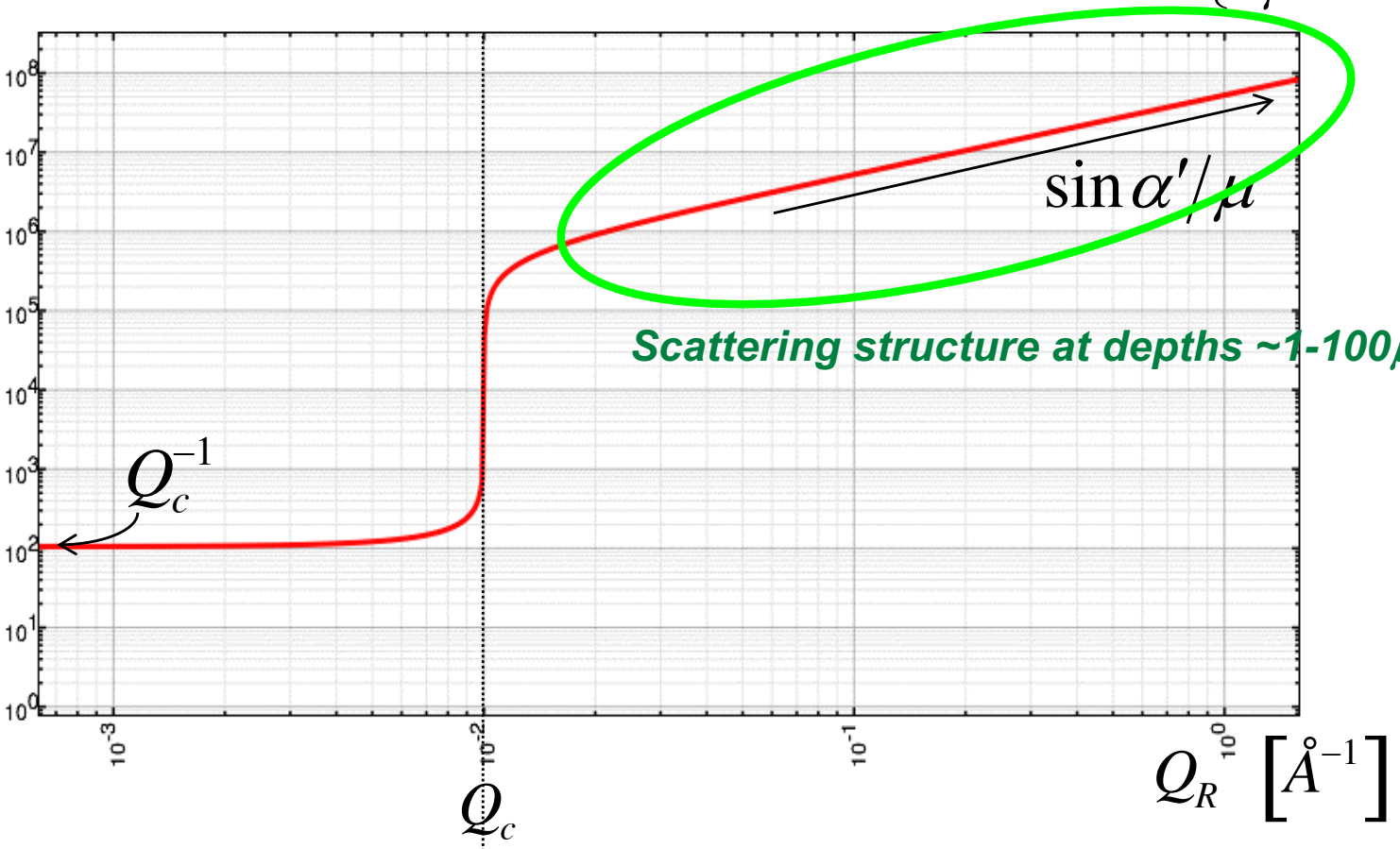
W.A. Hamilton, P.D. Butler, S.M. Baker, G.S. Smith, J.B. Hayter, L.J. Magid and R. Pynn,
Physical Review Letters **72**, 2219 (1994)

Penetration depth vs Q_R - the "source" term

$$k'_{//} = k_{//} = k\cos\alpha_i \quad \& \quad k'_{\perp} = \sqrt{(k\sin\alpha_i)^2 - 4\pi nb} = \sqrt{(Q_R^2 - Q_c^2)/4 + ik\mu}$$

$$\begin{cases} Q_c = 0.01\ \text{Å}^{-1} \\ \mu \sim 1\ cm^{-1} \end{cases}$$

$$z_{1/e} = 2\,\mathrm{Im}\{k'_{\perp}\}\ [\text{Å}]$$



Scattering structure at depths ~1-100μm

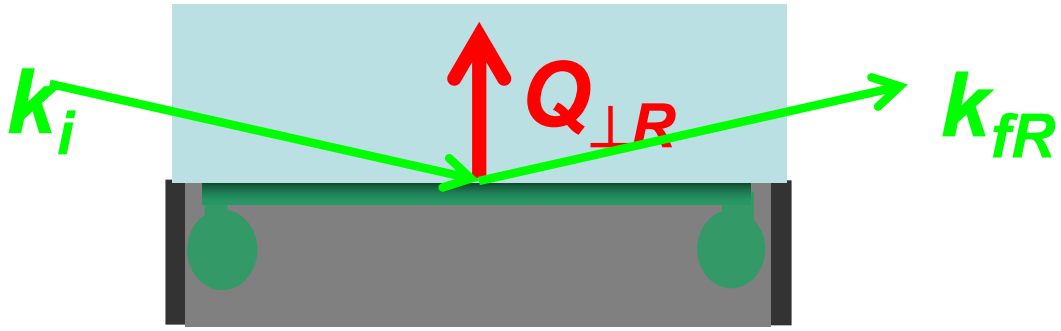
Q_c

Evanescent | *Transmitted*

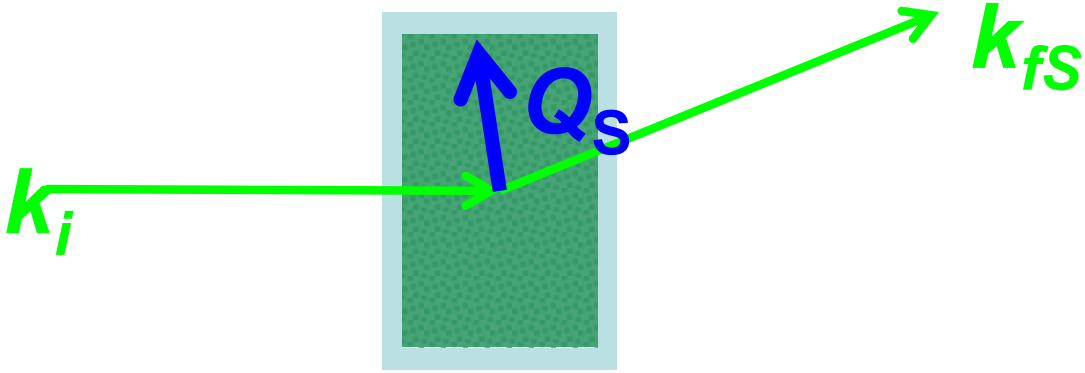
Surface correlated scattering | *and ?* | *uncorrelated - aligned ?*

NS-SANS: $z_{1/e} \approx \sin\alpha'/\mu$

"Near-Surface" or Reflection Geometry SANS



In an NR measurement mostly R<<1, so ...
what happens to the beam transmitted into a sample ?



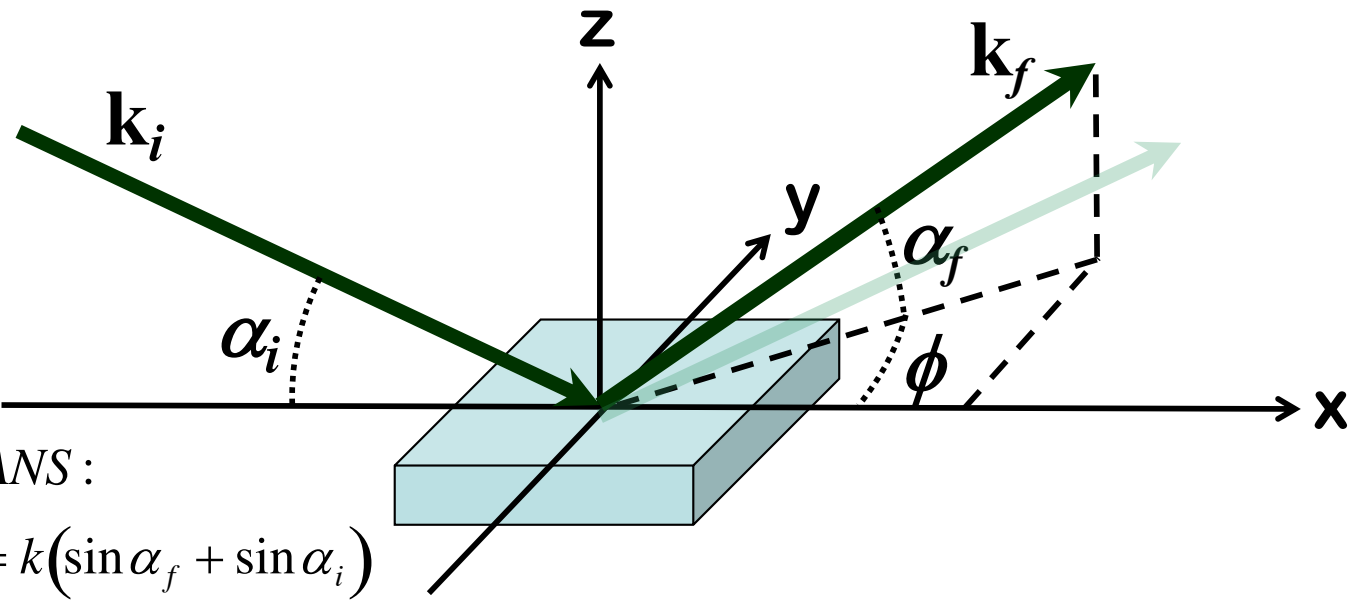
mostly Small Angle Neutron Scattering (SANS) happens

(NB in <u>both</u> cases: μ must be mostly absorption & incoherent otherwise multiple scattering can be a problem …)

Geometry: Scattering vector components

$$\boldsymbol{Q} = \boldsymbol{k}_f - \boldsymbol{k}_i \qquad k = 2\pi/\lambda$$

$$Specular\ (\alpha_f = \alpha_i, \phi = 0): \qquad Q_z = Q_R = 2k\sin\alpha_i \quad Q_x = Q_y = 0$$



GSANS:

$$Q_z = k\left(\sin\alpha_f + \sin\alpha_i\right)$$

$$Q_y = k\cos\alpha_f \sin\phi$$

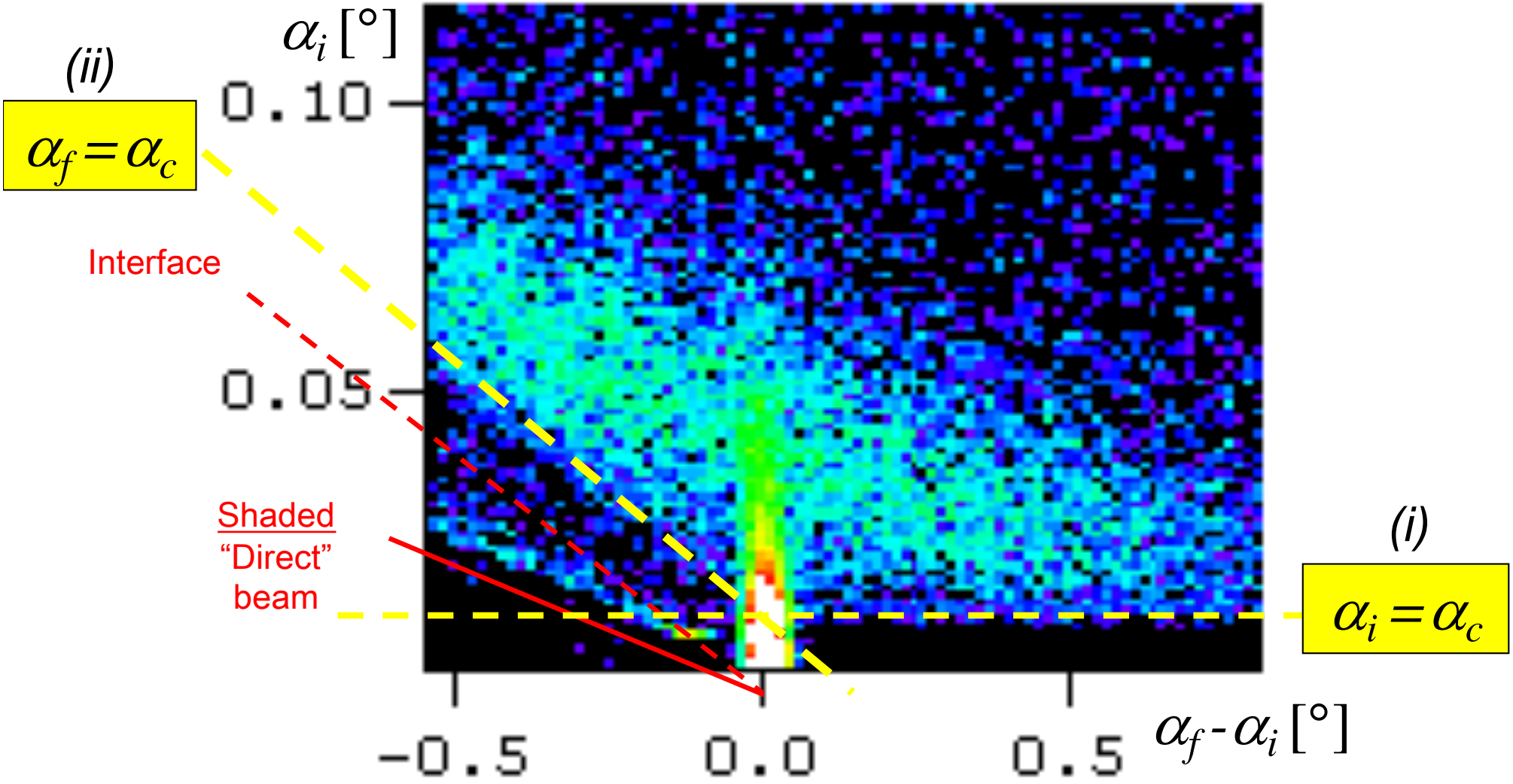
$$Q_x = k\left(\cos\alpha_f \cos\phi - \cos\alpha_i\right)$$

$$\cong -\left(Q_z\left(\sin\alpha_f - \sin\alpha_i\right) + Q_y \sin\phi\right)/2$$

$$\approx -\left(Q_z\left(Q_z - Q_R\right) + Q_y^2\right)/2k = \left(Q_z^2 - Q_z Q_R + Q_y^2\right)/2k$$

NB: typically $Q_x << \begin{cases} Q_y \\ Q_z \\ Q_R \end{cases}$

Generic features: scattering horizons

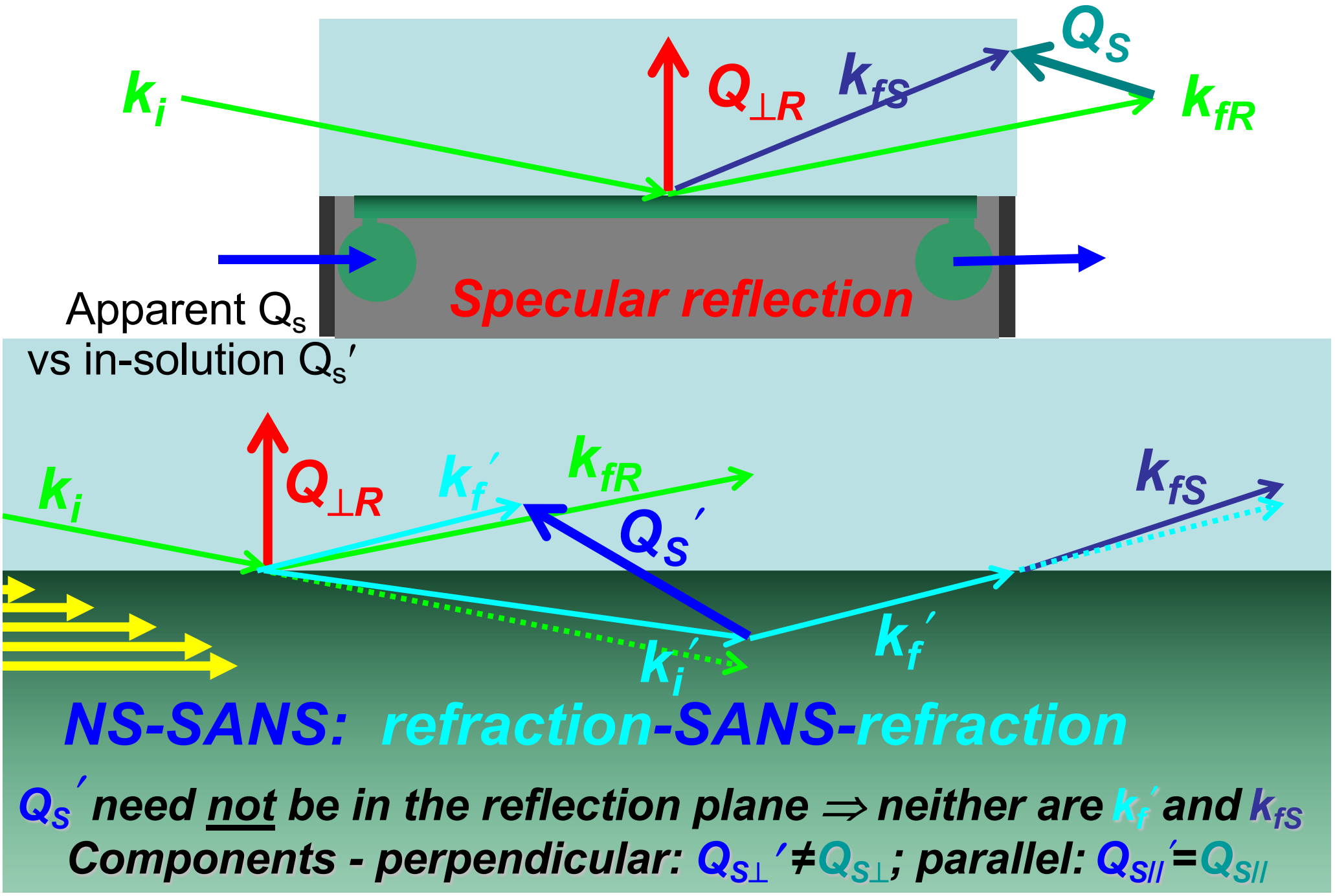


(i) "No" scattering for incident angles below critical (no transmitted beam)

(ii) NS-SANS exit angle > critical angle - scattering horizon $\alpha_f = \alpha_c$

(iii) Will manifest differently but predictably for TOF instruments

"Near surface" reflection geometry SANS



Extracting NS-SANS Cross-Sections

$$\frac{d\Sigma_s}{d\Omega'}[Q'] \approx \frac{\frac{d\sigma}{d\Omega}[Q]}{Ad'_{eff}} \frac{\sin\alpha_f}{\sin\alpha'_f} T[\alpha_i]T[\alpha_f]$$

$\frac{d\sigma}{d\Omega}[Q]$ **Cross-section as measured ~normal SANS**

$\frac{\Delta\Omega}{\Delta\Omega'} = \frac{\sin\alpha_f}{\sin\alpha'_f}$ **Refraction correction of solid angle**

$V' = Ad'_{eff}$ **Effective scattering volume in-solution**

$$V' = Ad'_{eff} \rightarrow A/\mu\left[\cot\alpha'_i + \cot\alpha'_f\right]$$

$T[\alpha_i]T[\alpha_f]$

$= (1 - R[\alpha_i])(1 - R[\alpha_f])$ **Interfacial transmission corrections (entry and exit - thank you Stokes)**

All of which we can measure or determine

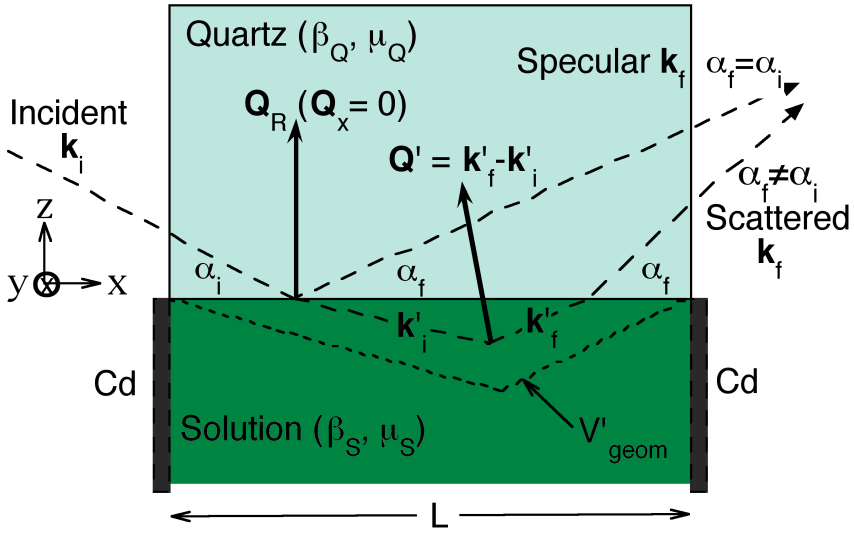
Machinery of "NS-SANS" corrections (1)

Refraction

Correct interface normal component of wavevector in-solution Q_z' from Q_z
Simple Fresnel

$$\alpha_i' \cong \sqrt{\alpha_i^{\,2} - \alpha_c^{\,2}} \qquad \alpha_f' \cong \sqrt{\alpha_f^{\,2} - \alpha_c^{\,2}} \qquad where\ \ \alpha_c \cong \lambda^2 (\beta_s - \beta_Q)/\pi$$

β_S, β_Q: bulk scattering length densities



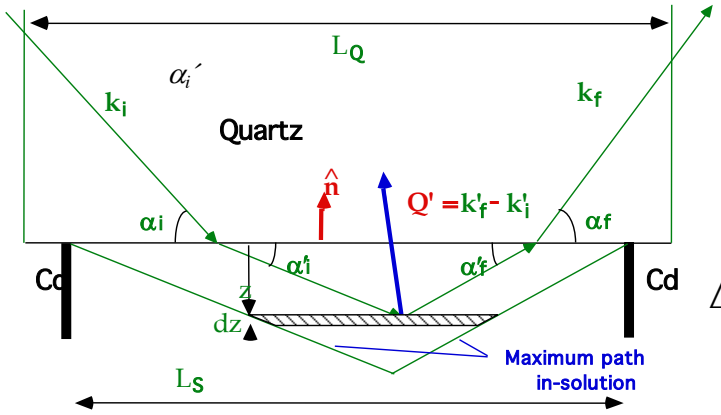
$$Q_z' = k(\sin\alpha_f' + \sin\alpha_i')$$
$$= k(\sqrt{\sin^2\alpha_f - \sin^2\alpha_c} + \sqrt{\sin^2\alpha_i - \sin^2\alpha_c})$$

Do <u>not</u> need to correct in-plane
Wave function continuity condition
$\Rightarrow$ Q_x'=Qx and Qy'=Qy

(there is a – usually - small Qy out of specular plane absorption correction)

Machinery of "NS-SANS" corrections (2)

Cross-sections: NR⇔NS-SANS



Total Specular cross-section:

$$\sigma_R(\lambda,\theta_i) \cong R\left[Q_R = (4\pi/\lambda)\sin\alpha_i\right] \quad \textbf{(specular reflection coefficient)}$$
$$\times\, WL_S \sin\alpha_i \quad (\textit{cell beam acceptance})$$
$$\times\, e^{-\mu_Q L_Q} \quad (\textit{quartz slab absorption})$$
$$\times\, f \quad (\textit{detector beam fraction}\ \ 0.71\pm0.04)$$

NS-SANS macroscopic cross-section per pixel:

$$\Delta\sigma_s(\lambda,\theta_i,\theta_f) \cong \frac{d\Sigma_s}{d\Omega'}\left[Q'_S = (2\pi/\lambda)\left(Sin\alpha'_i + Sin\alpha'_f\right)\right] \quad \textbf{(differential cross section)}$$
$$\times\, \Delta\Omega_{pixel}\left(\sin\alpha_f/\sin\alpha'_f\right) \quad (\textit{refraction corrected pixel solid angle})$$
$$\times\, \tfrac{1}{2}W\, L_S^2 \Big/ \left[\cot\alpha'_i + \cot\alpha'_f\right] \quad (\textit{geometrical sample volume – wedge})$$
$$\times\, e^{-\mu_Q L_Q} \times 2\left[\frac{e^{-(\mu_S-\mu_Q)L_S} + \left([\mu_S-\mu_Q]L_S - 1\right)}{\left([\mu_S-\mu_Q]L_S\right)^2}\right] \quad (\textit{absorption})$$
$$\times\, \left[(1-R(\alpha_i))(1-R(\alpha_f))\right] \quad (\textit{transmission})$$

Full reduction needs measurements of superstrate and sample absorption

NS-SANS needs reflectivity (transmission) corrections
⇔ accurate reflectivity needs NS-SANS background determination

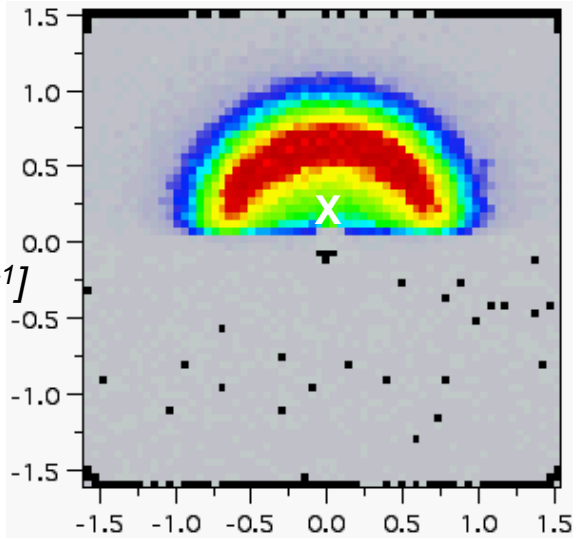
*So **ITERATIVE** correction*

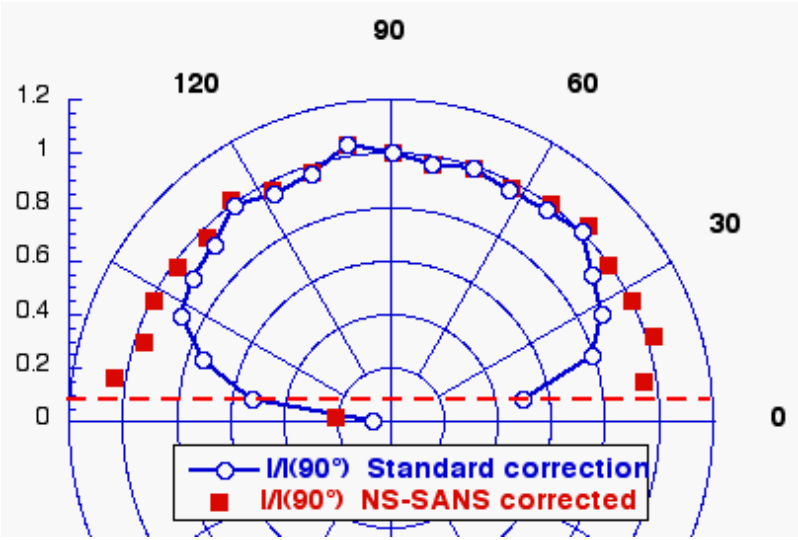
2D Reduction Correction test 2D SANS (out of plane $\phi > 0$)

Spherical micelle interaction peak: NS-SANS

Simply corrected data
background subtraction
volume const
and convert to Q

NR signal subtracted from the NS-SANS and kept out of the way (index matched for this test)





NS-SANS corrected data
background subtraction

volume depends on Q_z,

interfacial transmissions (i.e. reflectivities),

convert to Q correcting for refraction

recover interaction peak ring to scattering horizon

NS-SANS correction converts arc to half of interaction ring above cell "horizon"

ring radius Q_{peak} ~ 0.62nm^{-1}

$\Rightarrow$Micelle separation = $2\pi/0.62$nm^{-1} = 10 nm

cf. W.A. Hamilton, P. Butler, J.B. Hayter. L.J. Magid and P.J. Kreke, *Physica B* **221**, 309 (1996) – SXNS4 (mostly correct)

NS-SANS / GISANS … 2D Hexagonal Lattice Crystallography

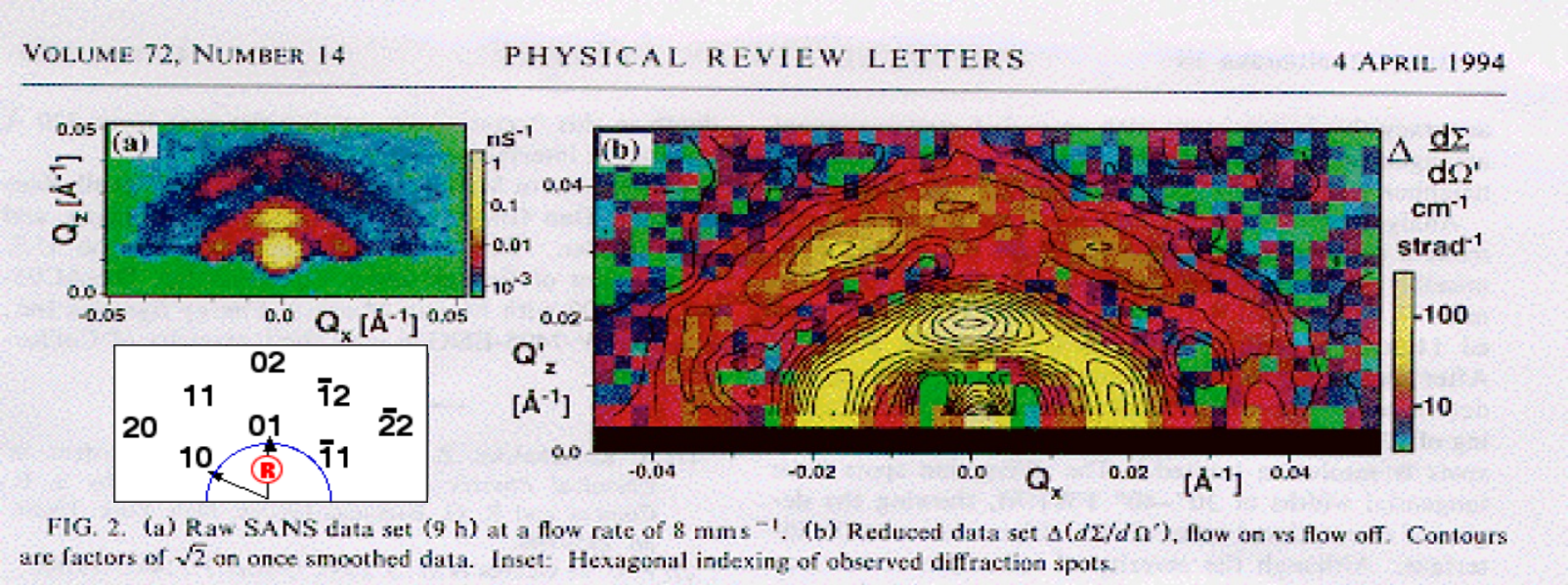
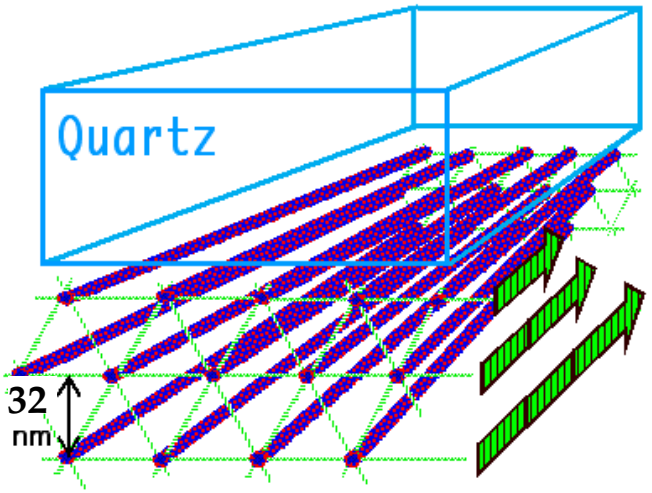
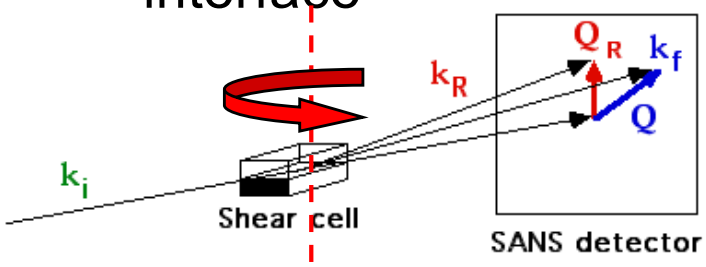
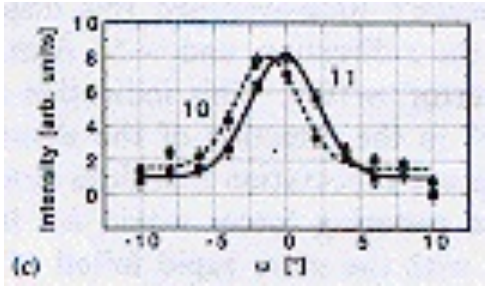


FIG. 2. (a) Raw SANS data set (9 h) at a flow rate of 8 mms^{-1}. (b) Reduced data set $\Delta(d\Sigma/d\Omega')$, flow on vs flow off. Contours are factors of $\sqrt{2}$ on once smoothed data. Inset: Hexagonal indexing of observed diffraction spots.

Our strongest 0.023Å^{-1} bump was the 01 hexagonal peak Q_{corr}=0.0195Å^{-1} above seen from scattering of transmitted neutron beam within <~100μm of interface







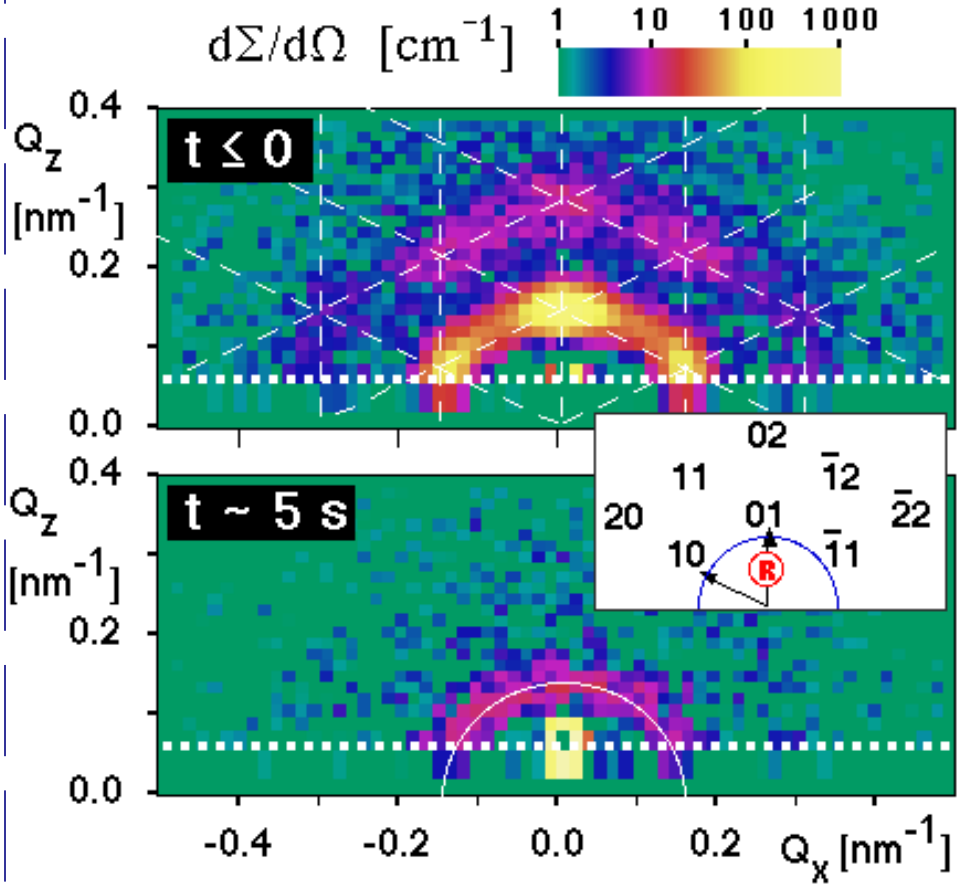
Rocking curve on **10** and 11 indexed peaks indicates that Xtal "mosaic" and/or threadlike micelle length is >300nm (~10 layer separations)

W.A. Hamilton, P.D. Butler, S.M. Baker, G.S. Smith, J.B. Hayter, L.J. Magid and R. Pynn, *Physical Review Letters* **72**, 2219 (1994)
W.A. Hamilton, P. D. Butler, John B. Hayter, L. J. Magid and P. J. Kreke, *Physica B* **221, 309 (1996)**

And finally some kinetics : 2D melting

Shear-induced threadlike micelle lattice relaxation

Time sliced NS-SANS analysis (NIST 30m SANS)



Shear moves adjacent layers past each other at 1000's Å/s

Hexagonal pattern rapidly gives way to an even liquid ordering ring of scattering reaching to the horizon
⇒ 2D melting
(consistent peak shift)

Liquid ring persists for many minutes as the micelles must re-entangle

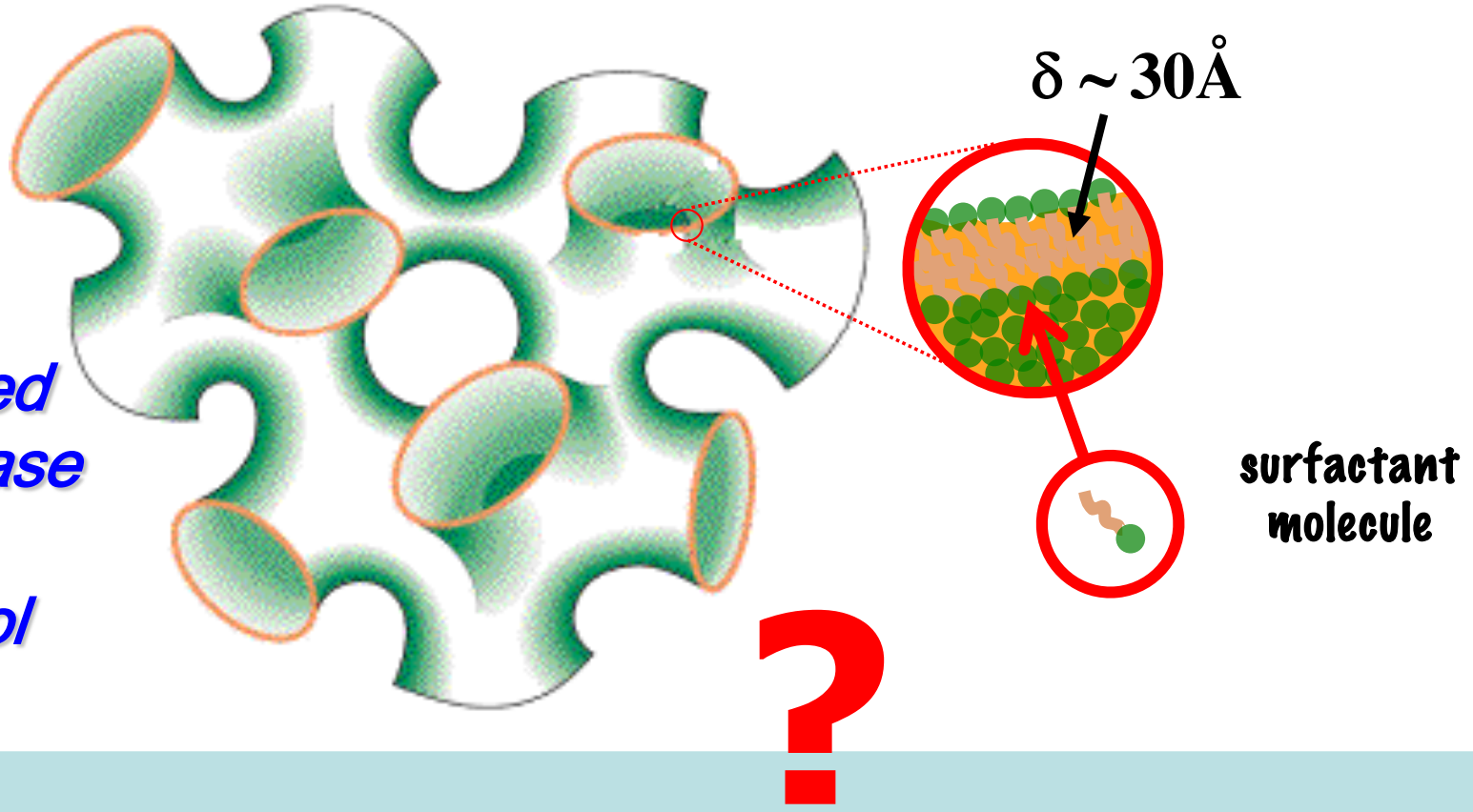
Xtal phase 01 peak fast decay time 0.7±0.2s

NS-SANS Corrections + analysis ⇒ initial relaxation is 2D melting

"Fast Relaxation of a Hexagonal Poiseuille Shear-induced Near-Surface Phase in a Threadlike Micellar Solution",
W.A. Hamilton, P.D. Butler, L.J. Magid, Z. Han and T.M. Slawecki, *Physical Review E (Rapid Communications)* **60**, 1146 (1999)

Another question we asked:

What does an isotropic phase do in an anisotropic situation?



Self-assembled L_3 "sponge" phase

CpCl-Hexanol in D_2O

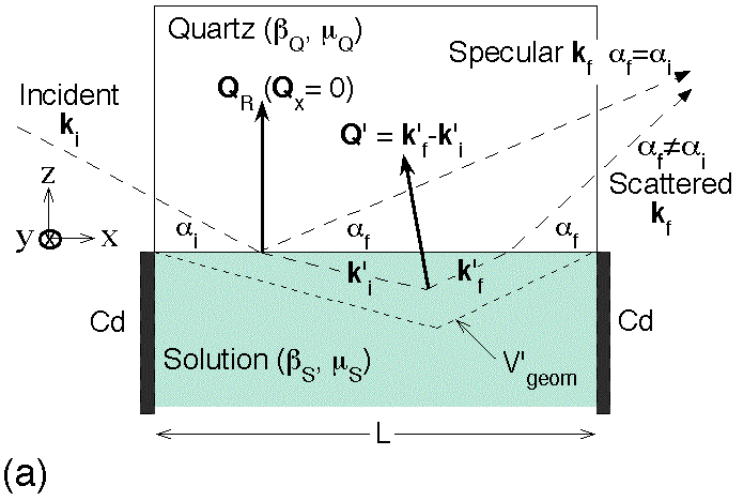
Geometric constraint of a proximate surface (SiO_2)

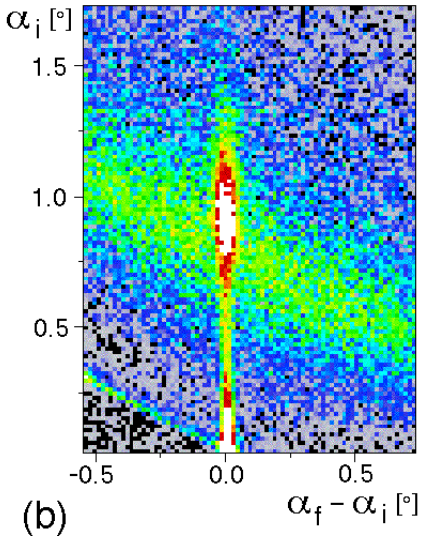
Simultaneous NR and NS-SANS MIRROR 1-D PSD

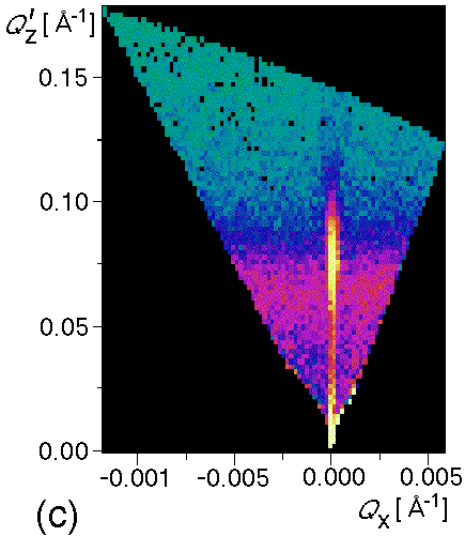
with Lionel Porcar, PaulButler (ORNL) and G.G. Warr (University of Sydney)

Sponge at surface: NR/NS-SANS 1-D PSD data

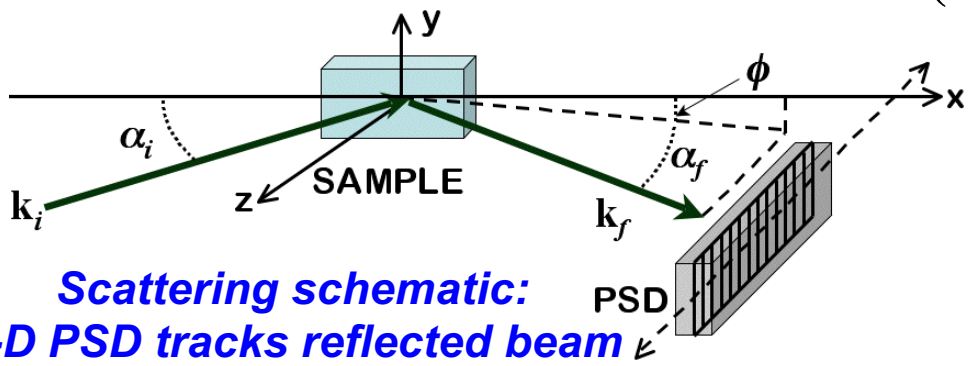
Corrected for refraction, ***absorption/volume****, interface transmissions and converted to in-solution* ***(Q_x,Q_z)*** *coordinates*







Raw ($\alpha_f - \alpha_i$, α_i) => (Q_x,Q_z) map



Scattering schematic:
1-D PSD tracks reflected beam

MIRROR - ORNL / HFIR: λ=2.59Å
SD=3.4m Ordela 1150N PSD
100mm x 1mm (0.3mrad) in reflection
(k_i,k_f) plane

"Slit correction" for transverse (y) resolution:

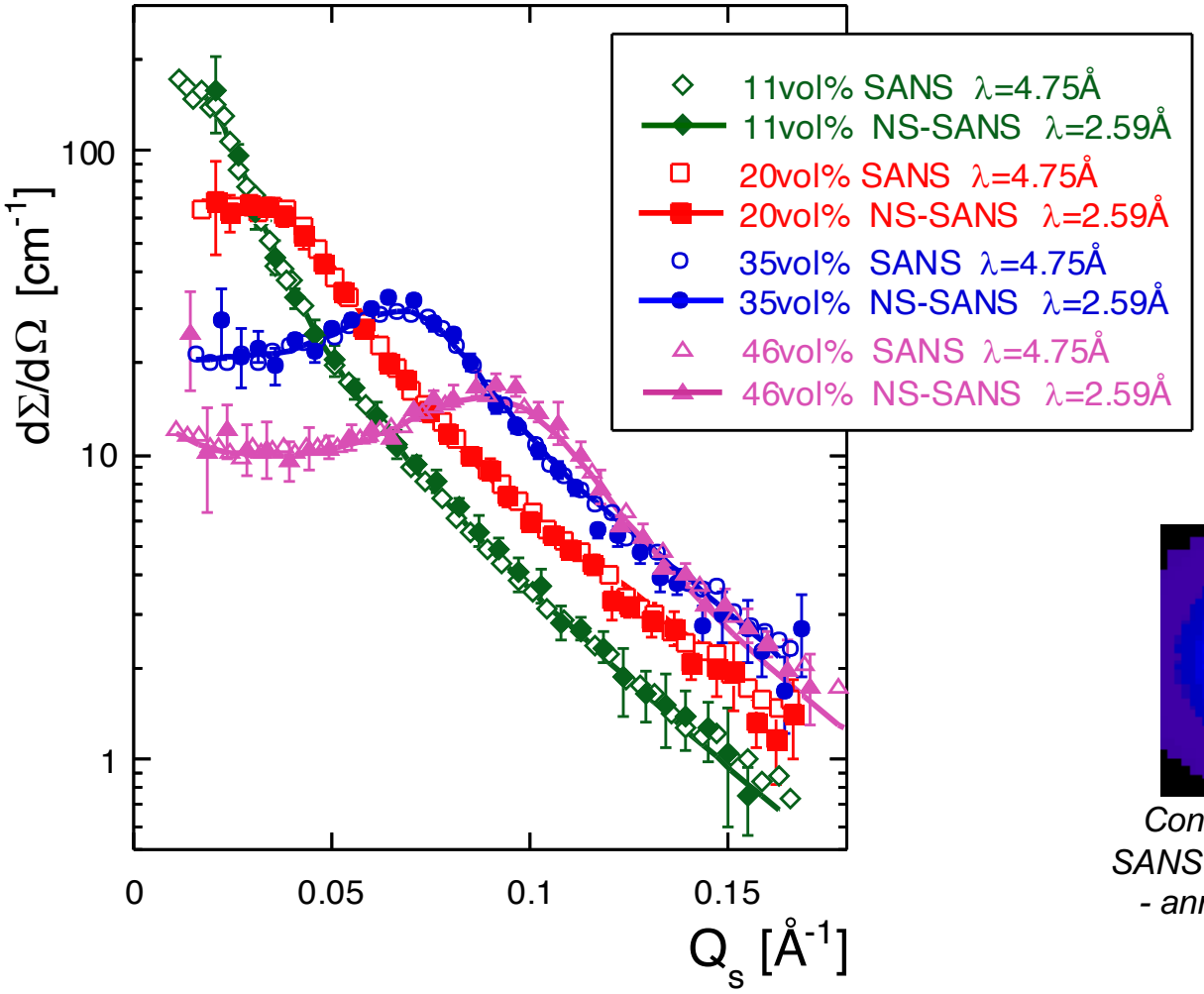
$$Q_S \cong \sqrt{Q_x^2 + (\delta Q_y)^2 + Q_z^2} \quad \cdots$$

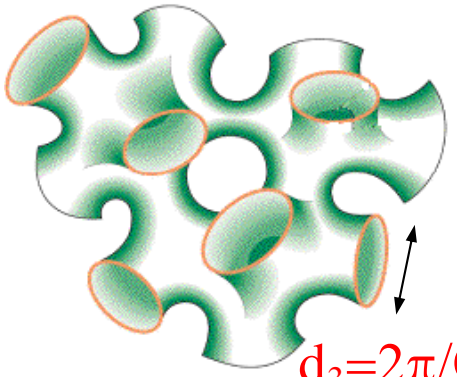
"Local membrane ordering of sponge phases at a solid-solution interface",
W.A. Hamilton, L. Porcar, P.D. Butler and G.G. Warr,
Journal of Chemical Physics **116**, 8533 (2002)* [and *Virtual Journal of Biological Physics Research* **3** (2002) [http://www.vjbio.org].

NS-SANS reduction vs conventional SANS

Conventional bulk SANS "12m" SANS instrument
vs. NS-SANS Reflection Geometry cell MIRROR

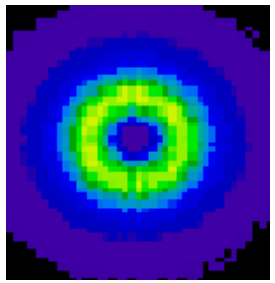
λ=4.75Å (open symbols)
λ=2.59Å (solid symbols)



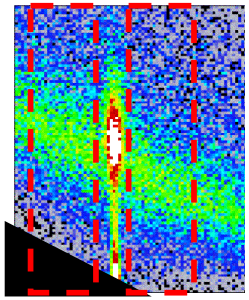


$d_3 = 2\pi/Q_3$

$$S[Q] = 1 + A\frac{\arctan[Q\xi_{io}/2]}{Q} + \frac{B}{1+(Q-Q_3)^2\xi_3^2}$$



Conventional L3 SANS measurement - annular binning



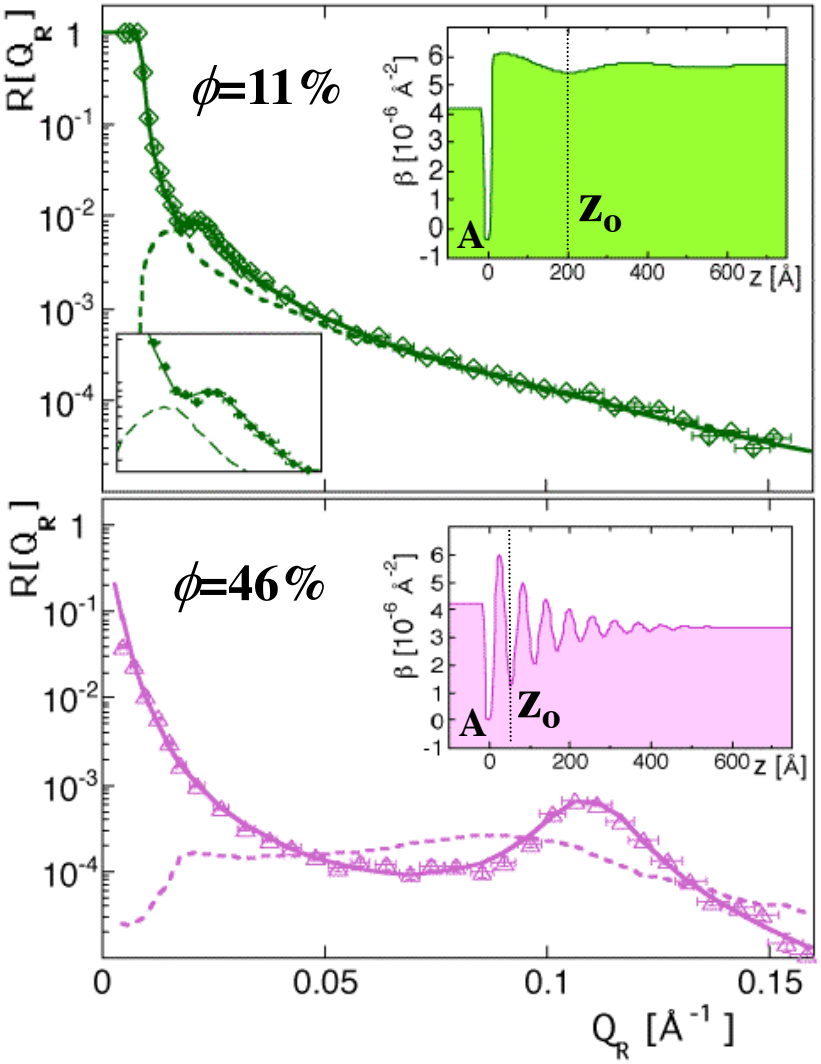
L3 NS-SANS Reduction regions With direct beam masked

Conventional SANS ≅ NS-SANS

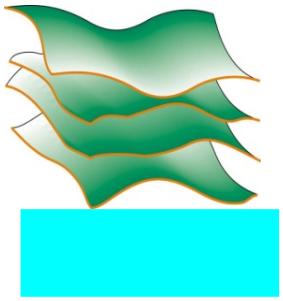
⇒ In this case off-specular is simply L_3 "bulk" SANS from beam transmitted into solution

NS-SANS ≡ conventional SANS (uninteresting "monitor" result, but √ technique)

Specular results for sponges at surface



NR analysis reveals adsorption and lamellar phase like layering of membranes at surface



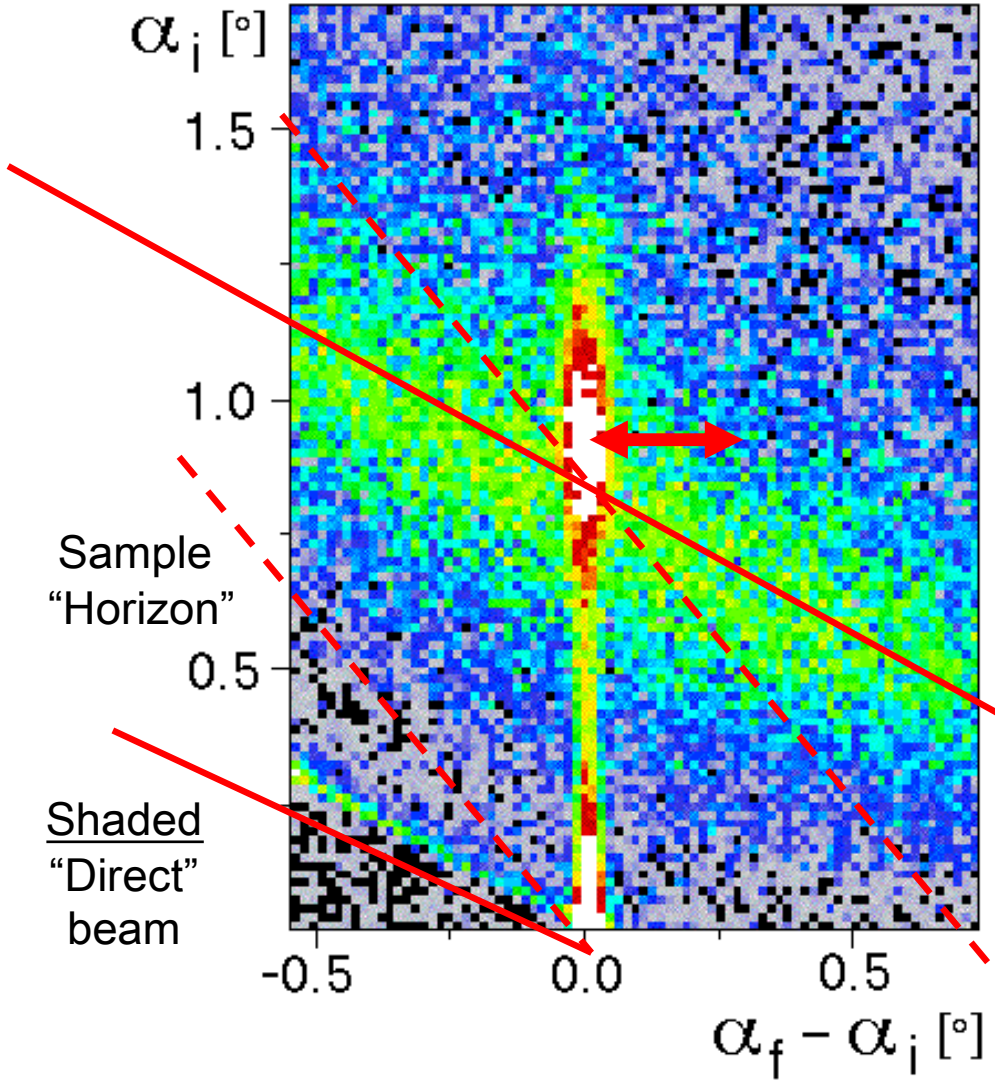
L_α

But this isn't a SNR talk …

For our current purposes:
Compare <u>strong</u> NS-SANS "background" (dashed lines) to specular signal
- to get a NR measurement right you needed to subtract this signal correctly

"Local membrane ordering of sponge phases at a solid-solution interface",
W.A. Hamilton, L. Porcar, P.D. Butler and G.G. Warr,
Journal of Chemical Physics **116**, 8533 (2002)* [and *Virtual Journal of Biological Physics Research* **3** (2002) [http://www.vjbio.org].

Scattering geometries are different … i



Tendency in NR to measure background at offset angle. With off-specular SANS that may not be the appropriate subtraction …

Constant NS-SANS Qs ~parallel to (projection) of Direct (incident) beam

$$Q_z = k\left(\sin\alpha_f + \sin\alpha_i\right)$$

NB: Constant Reflectivity Q_R Parallel to projected horizon

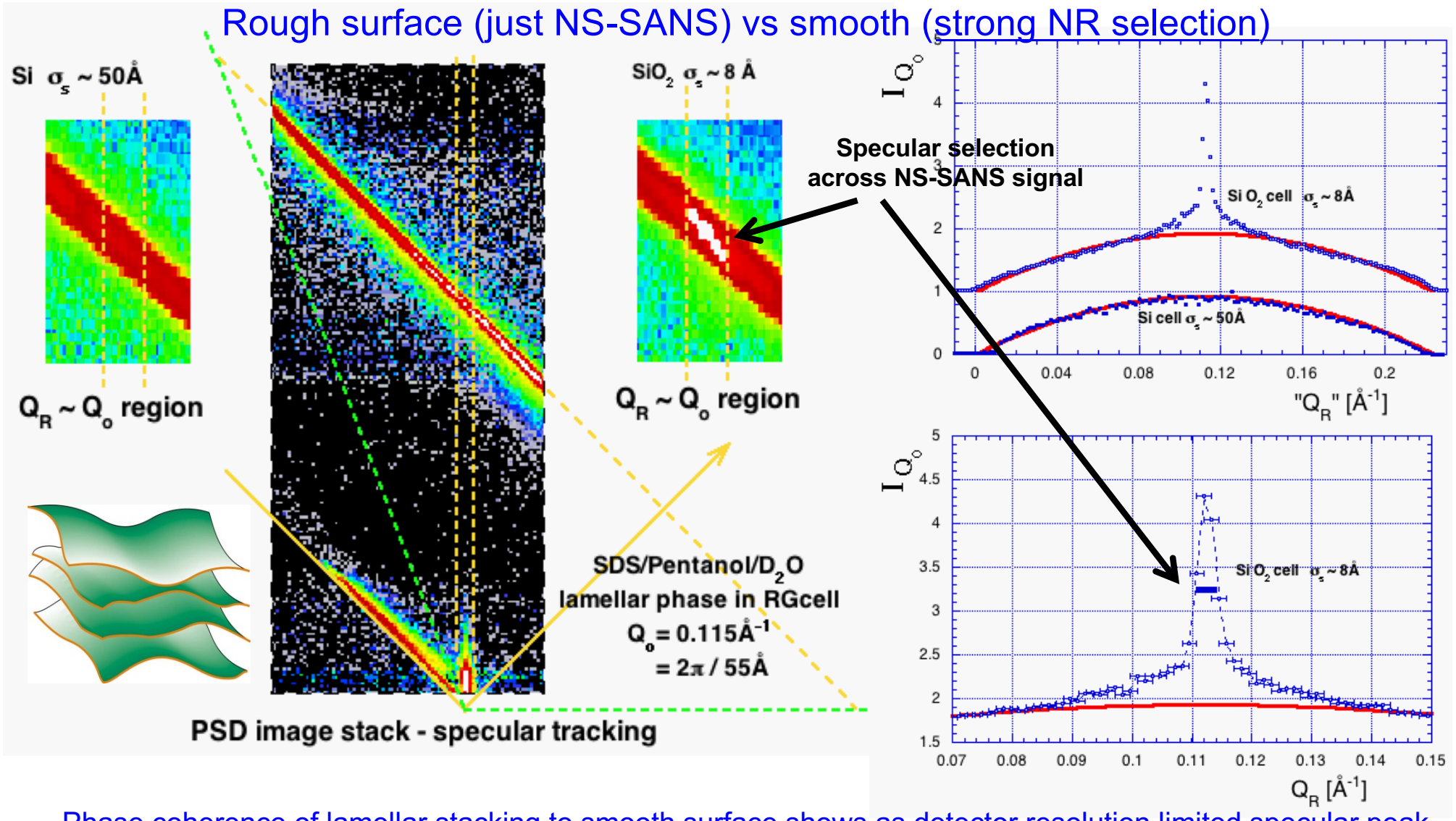
$$Q_R = 2k\sin\alpha_i$$

(ignoring refraction for the moment)

So an extreme, but not unlikely, case

NR-NSSANS on lamellar phase in reflection geometry cell

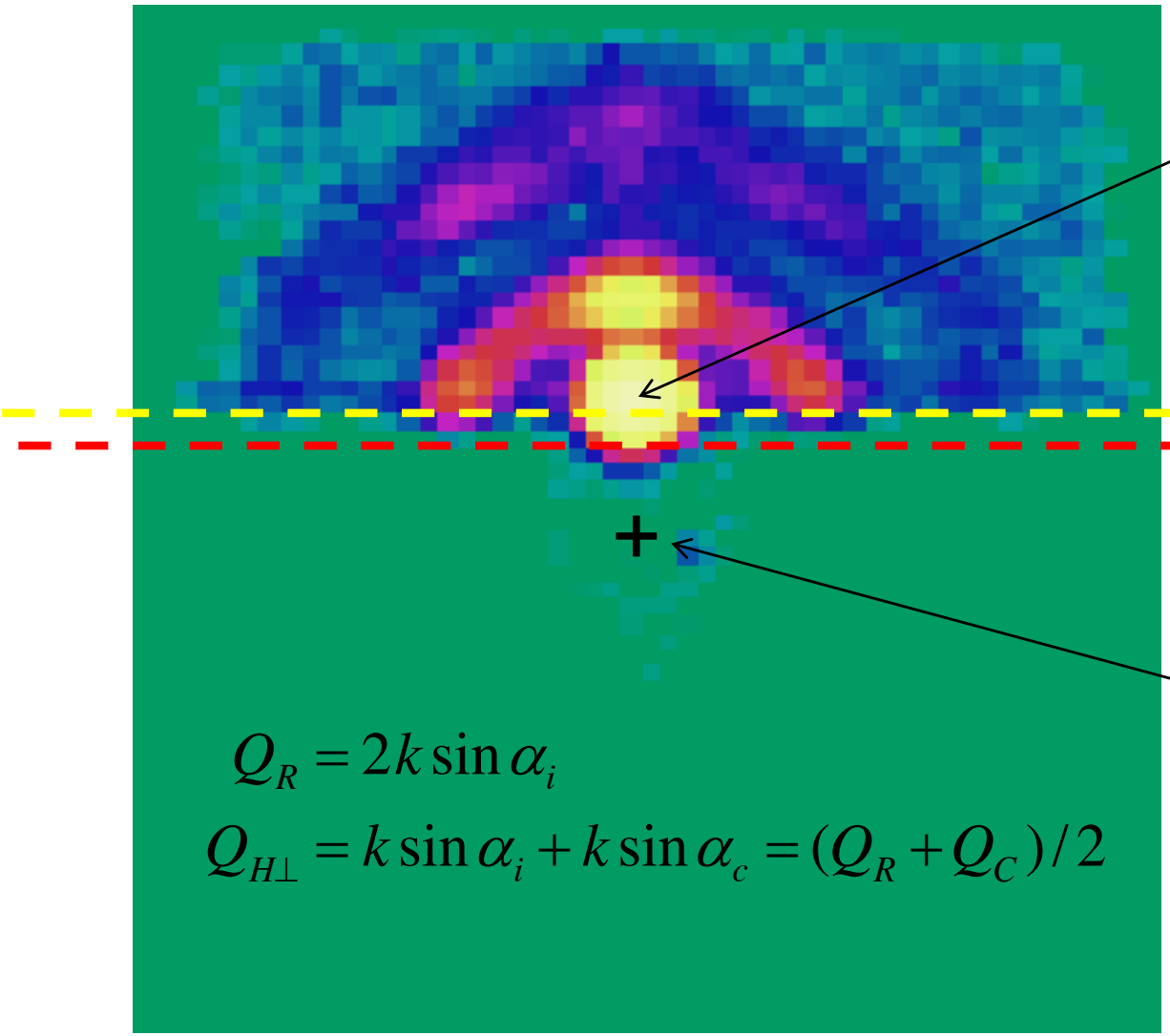
Rough surface (just NS-SANS) vs smooth (strong NR selection)



Phase coherence of lamellar stacking to smooth surface shows as detector resolution limited specular peak within incident collimation limited NS-SANS width (surface aligned, but **not** coherent)

NR & NS-SANS are indistinguishable until instrument collimation (at least) matches its angular resolution limit

A note about the scattering horizon ↔ Software



Specular Reflection (Q=Q_R) $\alpha_f = \alpha_i$

Scattering Horizon (H) $\alpha_f = \alpha_c$

Sample Interface (projected) $\alpha_f = 0$

Direct beam (Q=0) $\alpha_f = -\alpha_i$

$$Q_R = 2k \sin \alpha_i$$

$$Q_{H\perp} = k \sin \alpha_i + k \sin \alpha_c = (Q_R + Q_C)/2$$

$$Q_C = 2Q_{H\perp} - Q_R$$

Trivial, but useful for on the fly SANS corrections before the reflectivity is done

Manifests differently but predictably for TOF

NS-SANS GISANS limit conclusions

Surface states can be quite different to bulk states (under flow or not)
at ranges beyond you might expect from various ordering potentials

NS-SANS is often unavoidable in NR measurements (and visa versa)
Can be significant even in thin liquid films ~20-50micron)
You might as well understand it to account for it properly
even if only for background subtraction
(exercise for the reader - search for reflectivity measurements
in which this has not be done correctly - what are the symptoms?)

Also note that NS-SANS can also be
a rather useful "bulk" sample state monitor
So you can be sure of your bulk state in an NR measurement,
since scattering can probe where a sensor might not fit
Cautionary tale (a "Poiseuille shear effect" that wasn't):

"Using Neutron Reflectometry and reflection geometry "Near-Surface" SANS to investigate surfactant micelle organization at a solid-solution interface",
W. A. Hamilton, L. Porcar and L.J. Magid, Physica B 357, 88-93 (2005)

Instrumentality and what I didn't cover

The "Near-Surface" or Reflection Geometry SANS (whatever …)
treatment is simple transport process. The processes (refraction, transmisssion/absorption, scattering, transmission/absorption, refraction)
are sequential and separably measurable.

For surface coherent rather than correlated structures we have to calculate the scattering of a wave function source that can vary dramatically within the structure.
Local interaction between reflectivity and scattering is important.
So: DWBA &c later in this workshop

Either way
A dedicated GISANS instrument needs:
To be both a good (polarizable?) Reflectometer and a goodish SANS
Resolution and absolute normalization are important,
but sample geometries and environments are not always convenient
So you will want pretty capable sample handling and flexible instrument software …
Also allowing
Some degree of on-the-fly data reduction and analysis (Neutrons=$)
And a reasonable "standard" data reduction/analysis package
But also export of semi-raw data …
… other people's students have more time and different challenges to yours

Speaking of challenges:
Inelastic GISANS? (the surface wave stuff back in the day was a bit of a cheat)
Exponential wave/beam penetration as a Laplace Transform term of a sample's depth profile?

& Thankyou for your attention