Reflection Geometry
“Near-Surface” Small Angle Neutron Scattering (NS-SANS)
(but GISANS if you must)
and
Specular Neutron Reflectometry

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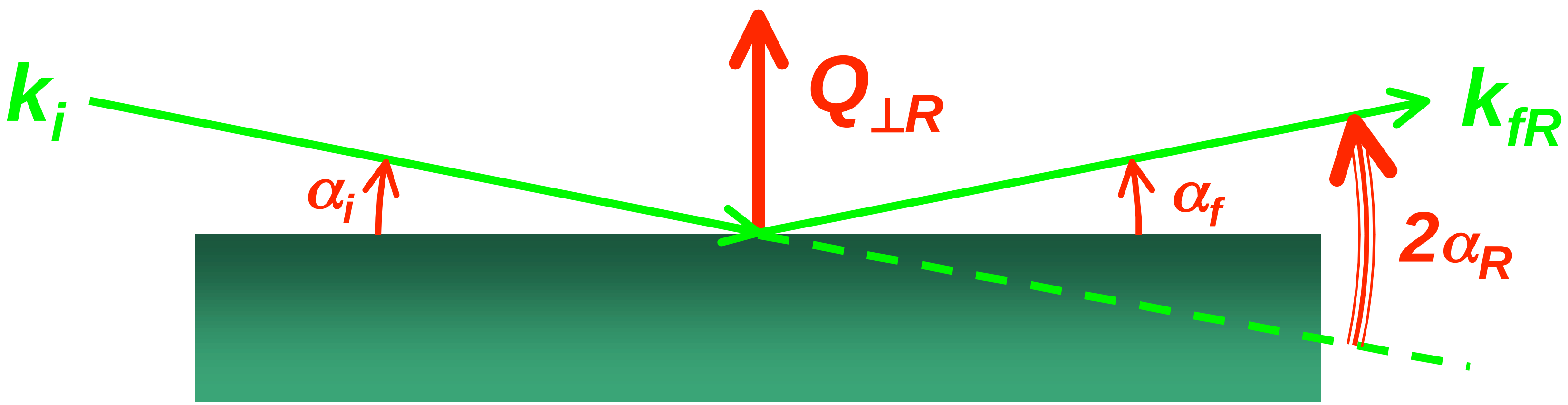
SNS/HFIR User Meeting 11-13 October 2005

Specular Neutron Reflectometry and what it tells us

Neutron reflection at small angles probes larger scale ***depth*** *structure at an interface on depth scales* **~3Å - 3000Å**

Layered structures or correlations relative to a flat interface:
Polymeric, semiconductor and metallic films and multilayers, adsorbed surface structures and complex fluid correlations at solid or free surfaces



Specular reflection

angle of incidence = angle of reflection: $\alpha_f = \alpha_i = \alpha_R$

Reflection scattering vector: $k_{fR} = k_i + Q_{\perp R}$
Perpendicular to surface

Specular Neutron Reflection

Specular Reflection Scattering vector $Q_{\perp R} = 4\pi \sin\alpha_R / \lambda$

Measure: Reflection Coefficient
= Specularly reflected intensity / Incident intensity

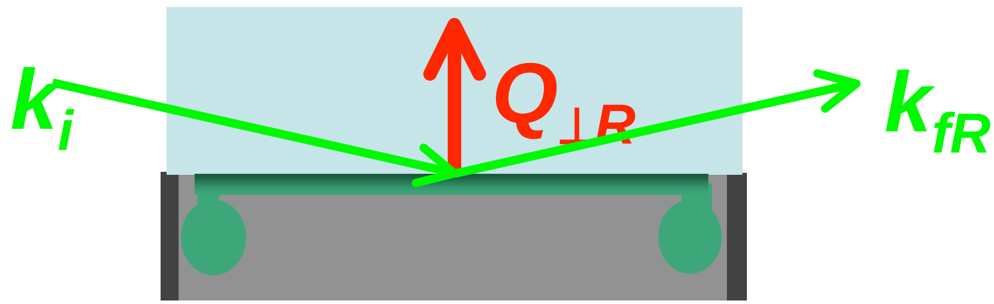
$$R[Q_{\perp R}] \approx \frac{(4\pi)^2}{Q_{\perp R}^4} \left| \int_z \frac{d\Delta\beta[z]}{dz} \exp[iQ_{\perp R} z] dz \right|^2$$

|1-D FT of depth derivative of scattering contrast| $^2 / Q_{\perp R}^4$

Approximation valid at large $Q_{\perp R}$
of an Optical transform - refraction happens
At lower $Q_{\perp R}$ *reaches its maximum R=1 i.e. total reflection*

but mainly $R \sim 1/ Q_{\perp R}^4$ ***so mostly*** $R \ll 1$

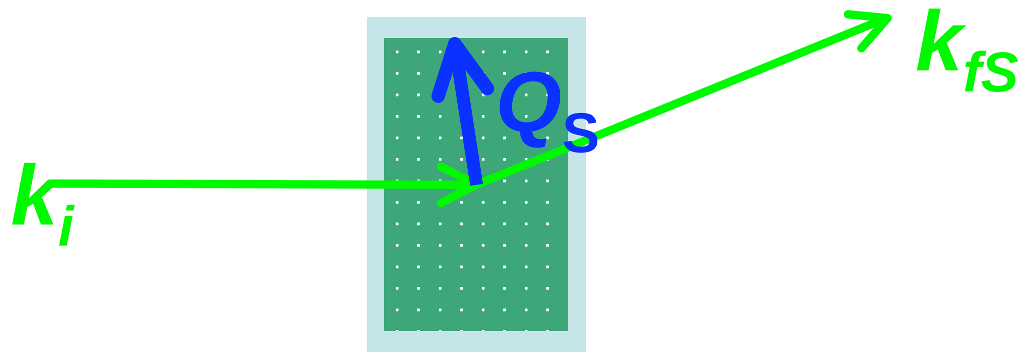
"Near-Surface" (Reflection Geometry) SANS



Neutron Reflectometry (NR)

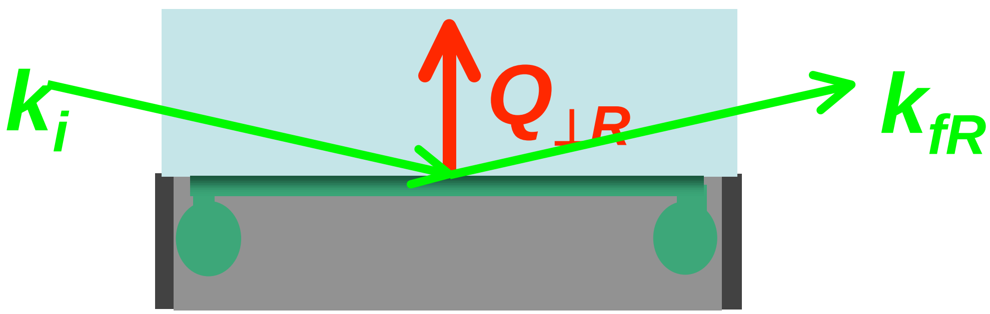
1 mm deep solution trough beneath polished Quartz slab

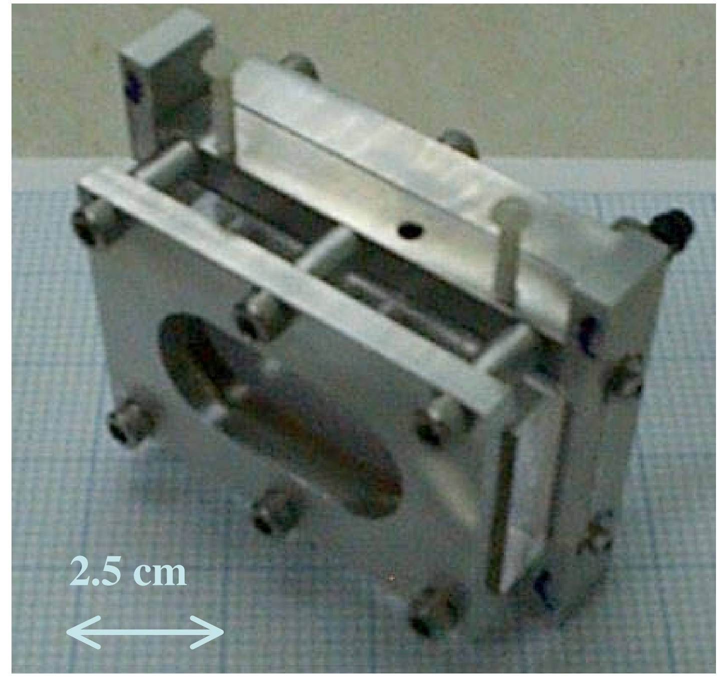
In an NR measurement mostly R<<1, so ...
what happens to the beam transmitted into a sample ?



mostly Small Angle Neutron Scattering (SANS) happens

Reflection geometry Quartz-Solution cell



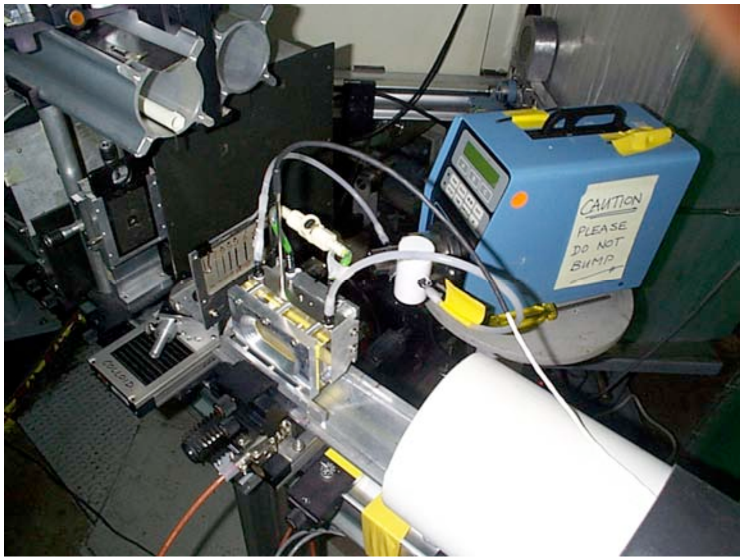


1 mm deep solution trough beneath polished Quartz slab

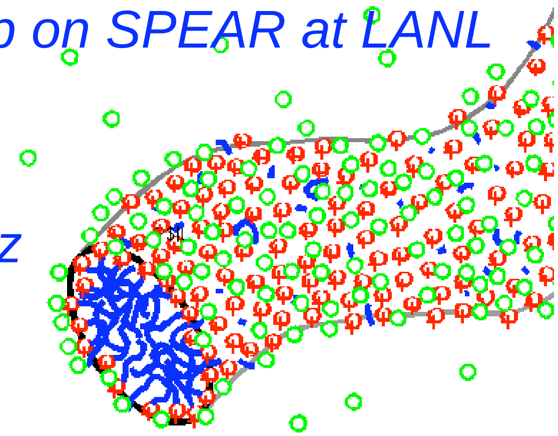
Original idea to simply (and only) use Specular NR to study surface adsorption and constraint effects on complex fluids, in particular under Poiseuille shear so sample flows past quartz surface

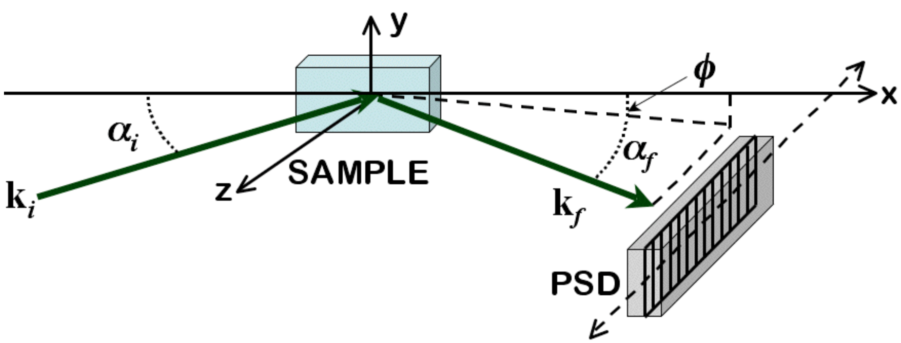
MIRROR Reflecometer HFIR c.1994

Trying to measure Poiseuille Shear effects on a threadlike micellar system with Neutron Reflectometry - we had seen a small bump on SPEAR at LANL



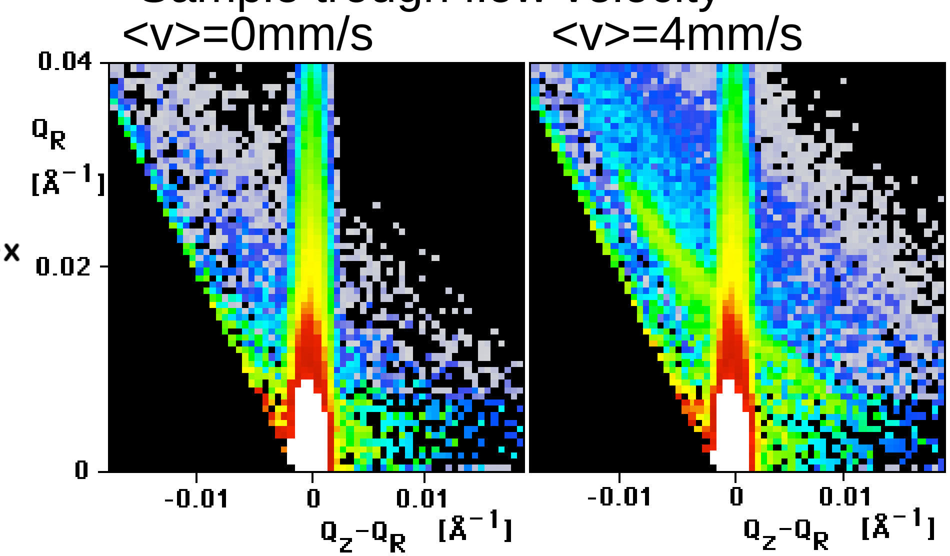
20mM
70% CTA35ClBz
&
30% CTABr



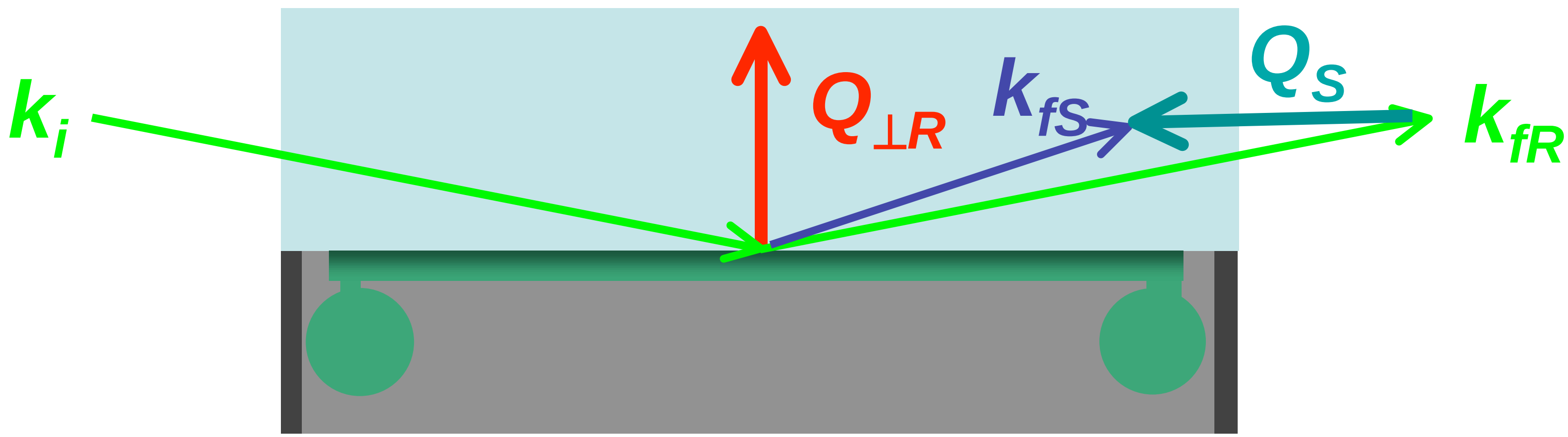


MIRROR Scattering geometry

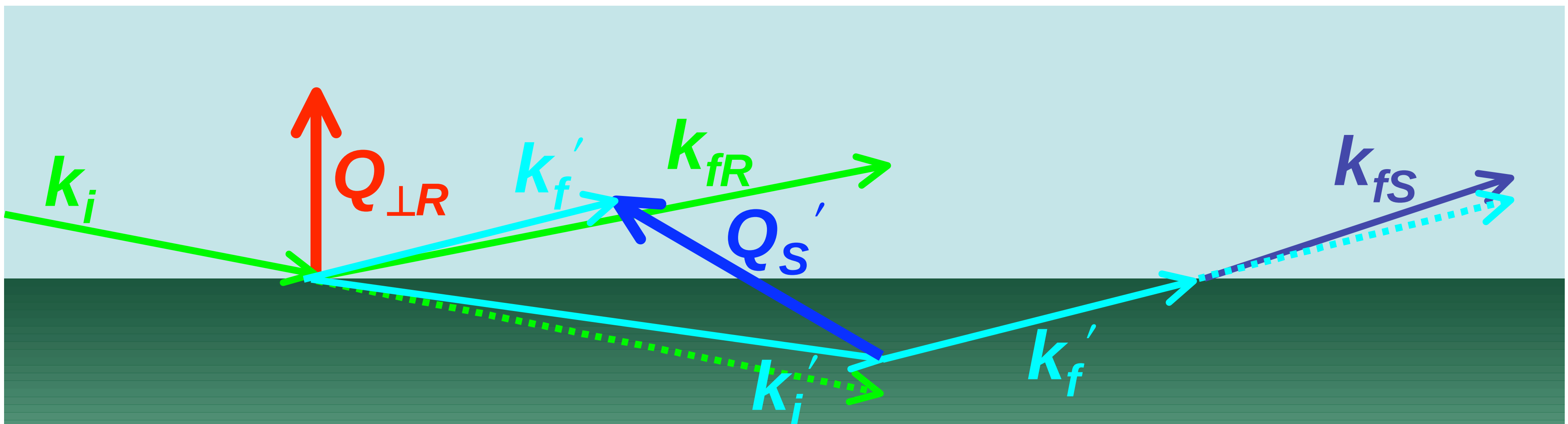
Sample trough flow velocity



bump at Q=0.016Å^{-1} is NOT specular



“NS-SANS” is SANS in reflection geometry



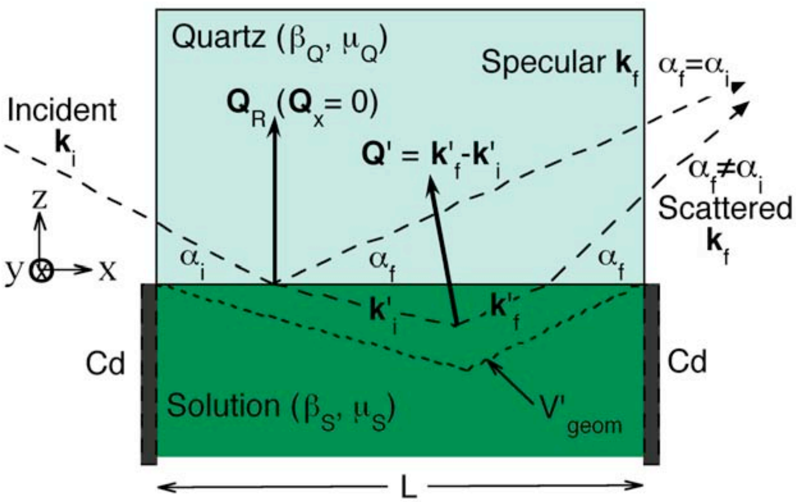
NS-SANS: refraction-SANS-refraction

Q_S' need not be in the reflection plane ⇒ neither are k_f' and k_{fS}

Components - perpendicular: $Q_{S\perp}' \neq Q_{S\perp}$; parallel: $Q_{S//}' = Q_{S//}$

Machinery of "NS-SANS" corrections (1)

Refraction



Need to correct interface normal component of wavevector in-solution Q_z' from Q_z

$$\theta'_i \cong \sqrt{\alpha_i^{\,2} - \alpha_c^{\,2}} \qquad \theta'_f \cong \sqrt{\alpha_f^{\,2} - \alpha_c^{\,2}} \qquad where \;\; \alpha_c \cong \lambda^2\left(\beta_s - \beta_Q\right)/\pi$$

β_S, β_Q: bulk scattering length densities

Simple Fresnel

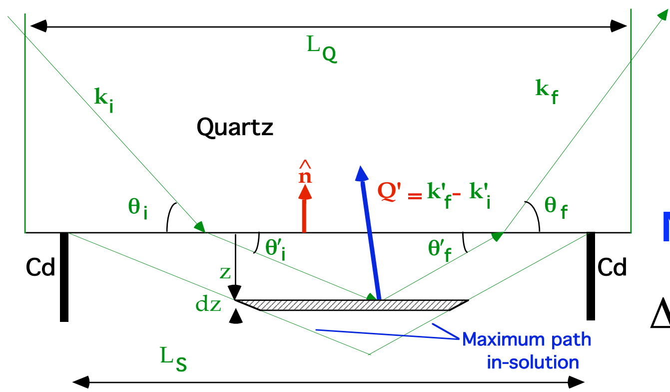
$$Q'_z = k(\sin\alpha'_f + \sin\alpha'_i)$$

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

Do not need to correct in-plane
Wave function continuity condition
=> Q_x'=Qx and Qy'=Qy

Machinery of "NS-SANS" corrections (2)

Cross-sections: NR⇔NS-SANS



Total Specular cross-section:

$$\sigma_R(\lambda,\theta_i) \cong R\left[Q_R = (4\pi/\lambda)Sin\theta_i\right] \qquad (\textbf{specular reflection coefficient})$$
$$\times\, WL_S \sin\theta_i \qquad (\textit{cell beam acceptance})$$
$$\times\, e^{-\mu_Q L_Q} \qquad (\textit{quartz slab absorption})$$
$$\times\, f \qquad (\textit{detector beam fraction}\ \ 0.71 \pm 0.04)$$

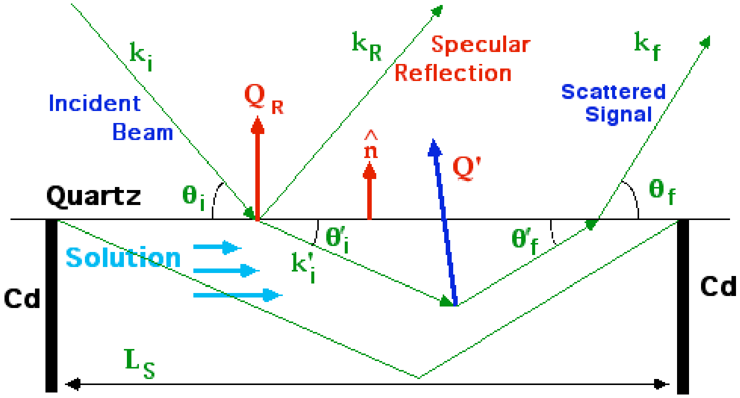
NS-SANS macroscopic cross-section per pixel:

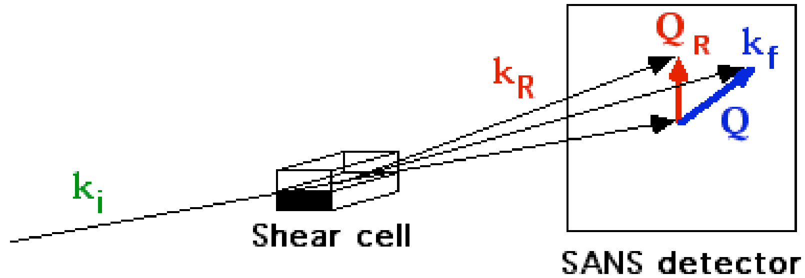
$$\Delta\sigma_s(\lambda,\theta_i,\theta_f) \cong \frac{d\Sigma_s}{d\Omega'}\left[Q'_S = (2\pi/\lambda)(Sin\theta'_i + Sin\theta'_f)\right] \qquad (\textbf{differential cross section})$$
$$\times\, \Delta\Omega_{pixel}\,(\theta_f/\theta'_f) \qquad (\textit{refraction corrected pixel solid angle})$$
$$\times\,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

Need measurements of superstrate and sample absorption also
ITERATIVE

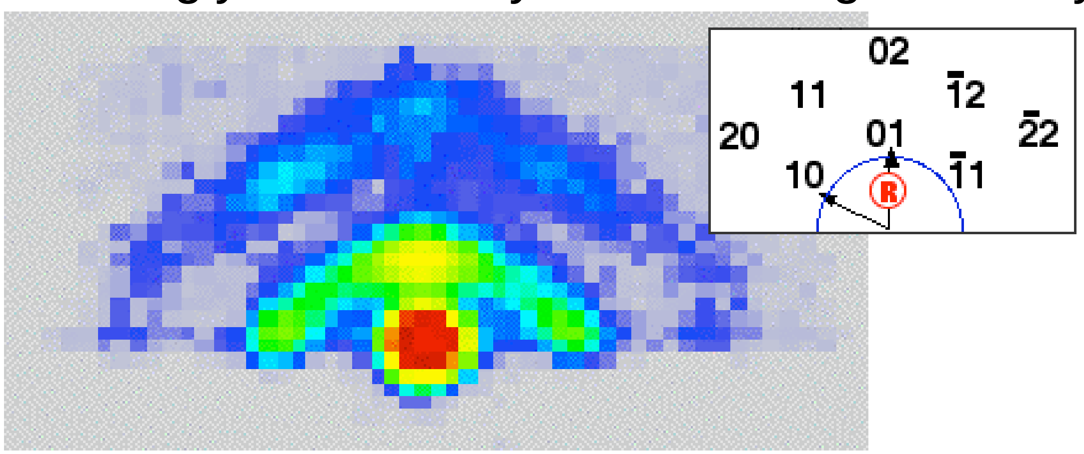
"Local membrane ordering of sponge phases at a solid-solution interface", W.A. Hamilton, L. Porcar, P.D. Butler and G.G. Warr, *Journal of Chemical Physics* **116**, 8533 (2002)* [and *Virtual Journal of Biological Physics Research* **3** (2002) [http://www.vjbio.org].

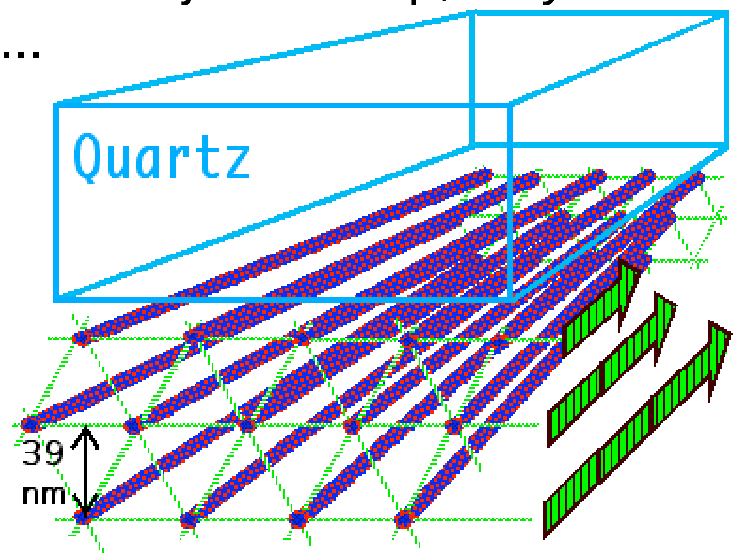
Poiseuille shear response of mixed counterion 20mM 70% CTA35ClBz & 30% CTABr threadlike micelles





In Poiseuille shear past a surface the micelles don't just line up, they form a strongly oriented crystalline hexagonal array...



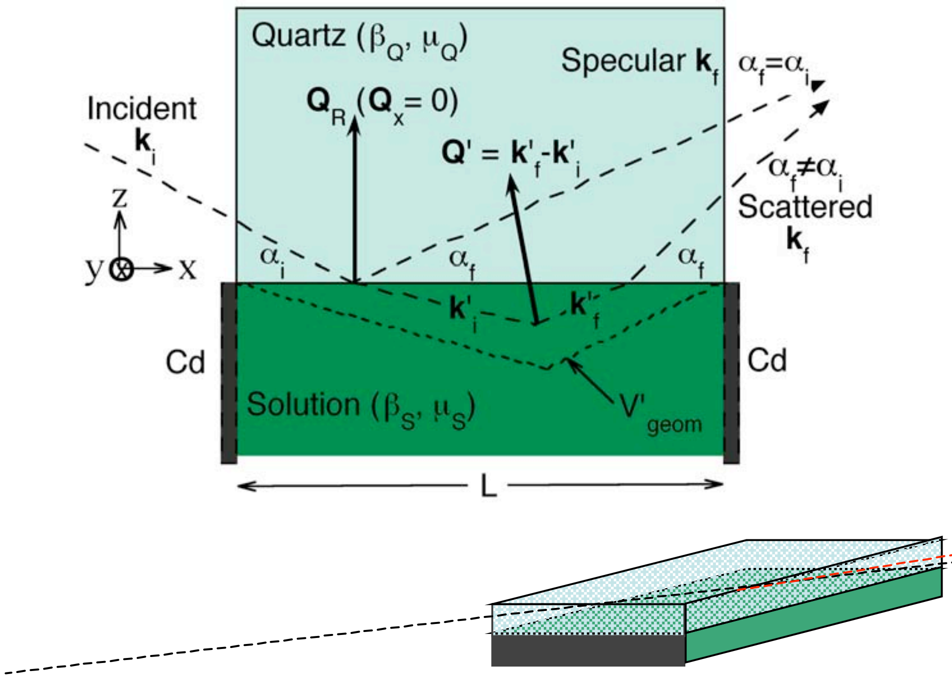


Our 0.016Å^{-1} bump was the 01 hexagonal peak above seen from Grazing incidence "Near Surface" SANS data (<~100micron) from surface

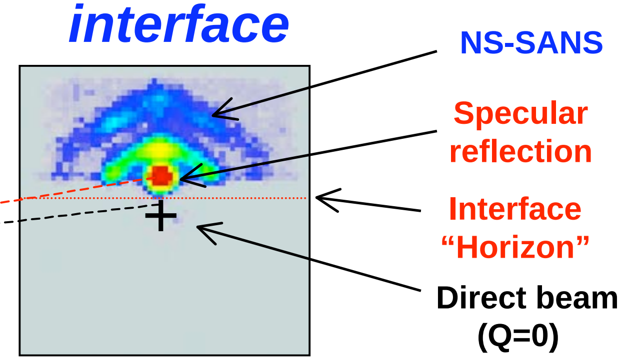
W.A. Hamilton, P.D. Butler, S.M. Baker, G.S. Smith, J.B. Hayter, L.J. Magid and R. Pynn, *Physical Review Letters* **72**, 2219 (1994)

W.A. Hamilton, P. D. Butler, John B. Hayter, L. J. Magid and P. J. Kreke, *Physica B* 221, 309 (1996)

NR/NS-SANS



Simultaneously (unavoidably) measure Near Surface SANS from solution and Specular neutron reflection from quartz-solution interface



SANS 2D Detector

Penetration of beam into solution ~cm, low angles ~degrees

⇒"Near Surface"-SANS probes <~100 μm from interface

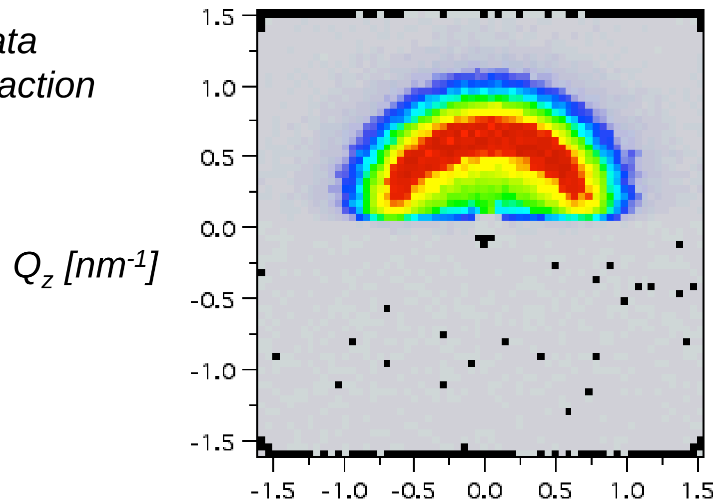
$$d_{eff} \cong \frac{1}{\mu_s\left(\cot\alpha'_i + \cot\alpha'_f\right)}$$

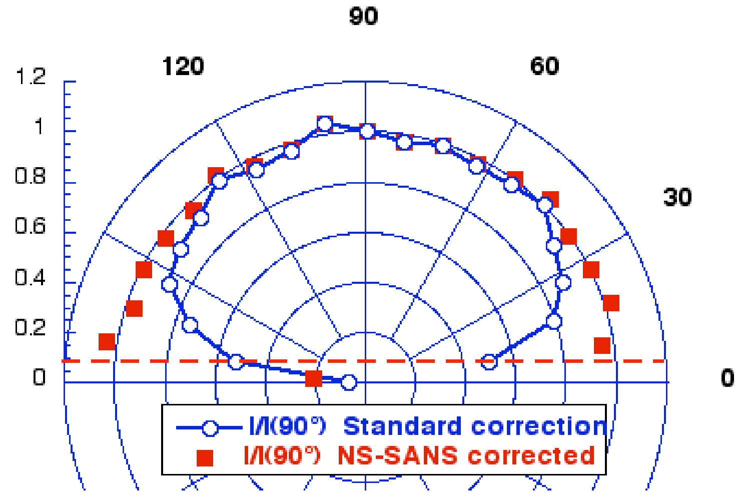
~ Effective penetration depth in terms of sample absorption coefficients

and <u>in-solution</u> grazing angles

Micellar separation (interaction) peak: NS-SANS

Simply corrected data
background subtraction
volume const
and convert to Q





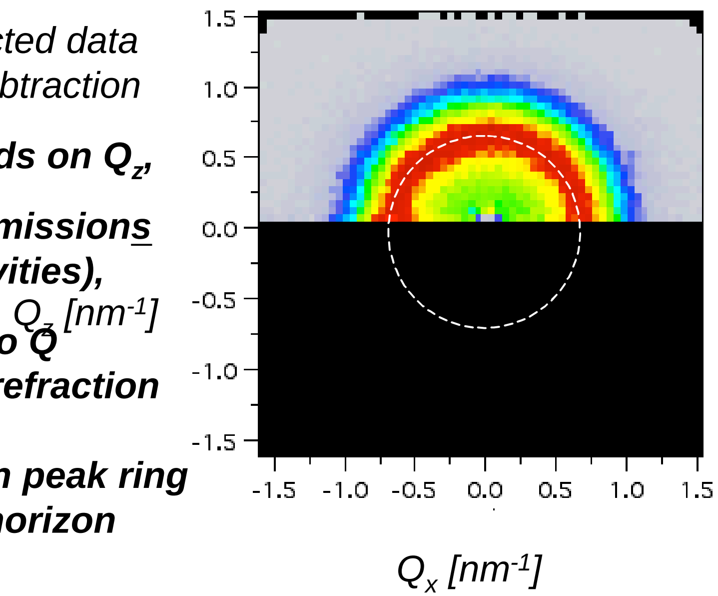
NS-SANS corrected data
background subtraction

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"

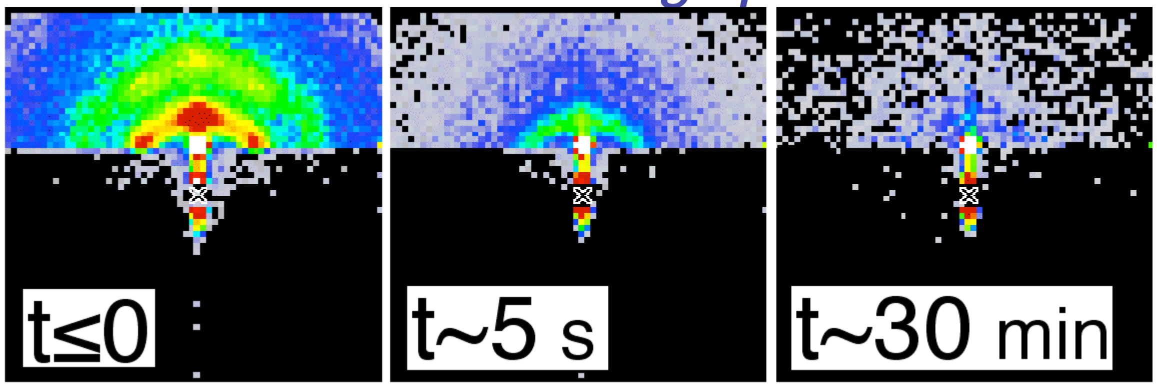
ring radius Q_{peak} ~ 0.62nm^{-1}

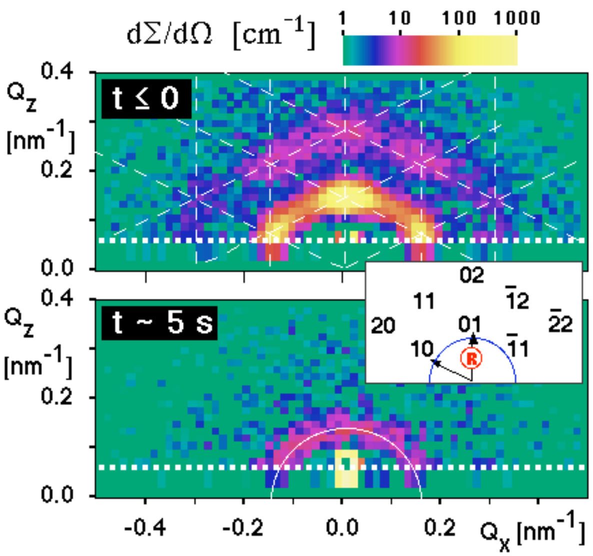
⇒Micelle separation = $2\pi/0.62nm^{-1}$ = 10 nm

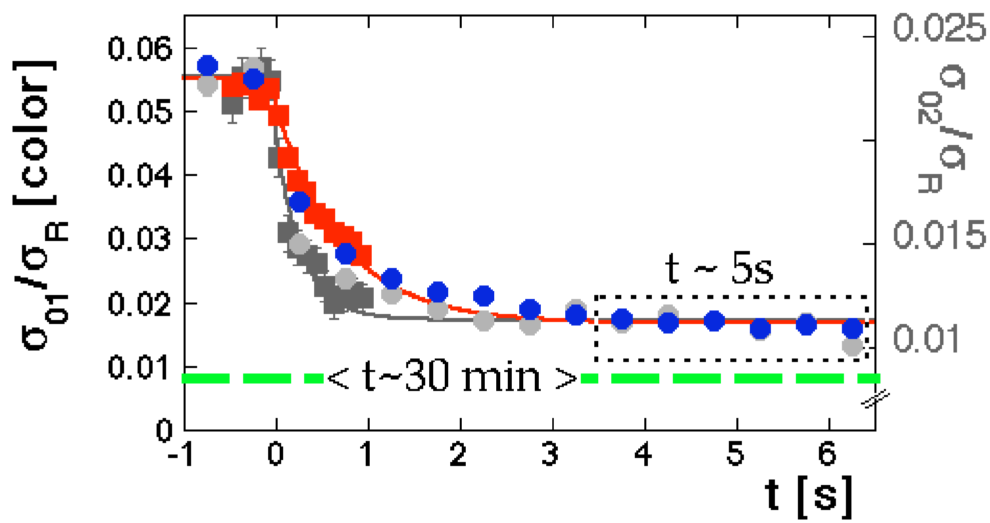
Volume, Refraction, Interface reflectivity corrections => SANS $d\Sigma/d\Omega$

What we saw in threadlike micelle relaxation

0.1s and 0.5s multiplexed data and NS-SANS analysis reveals a two stage process







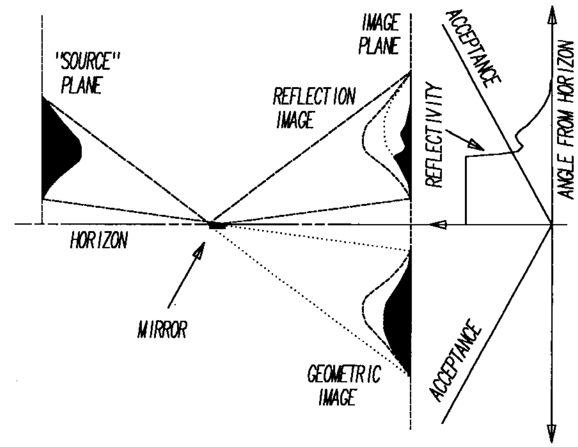
Xtal phase 01 peak fast decay time 0.7±0.2s

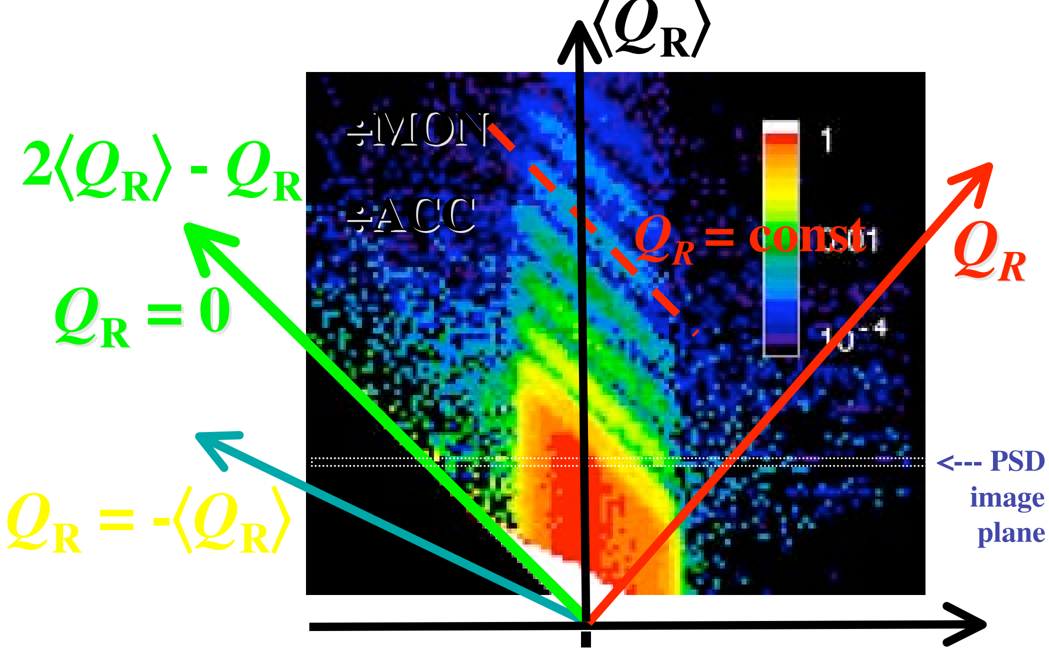
NS-SANS Corrections + analysis ⇒ initial relaxation is 2D melting

“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)

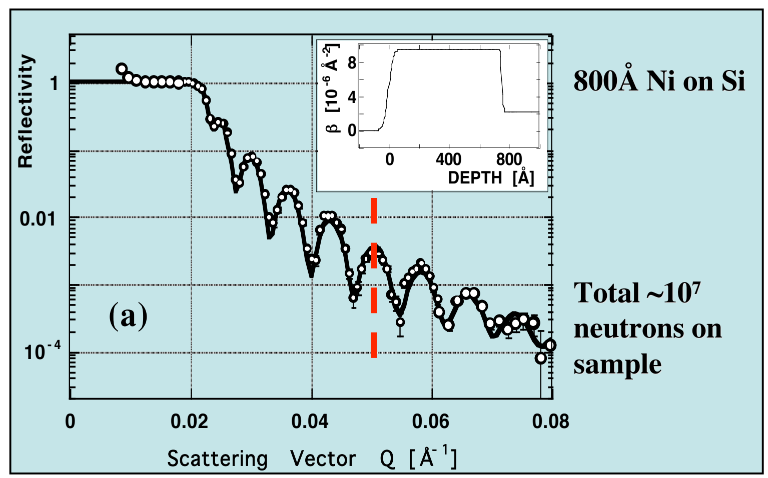
Imaging Analysis of NR data
NB: "Specular" $\alpha_i \equiv \alpha_f$ is a selection rule

- ***Mirror is equipped with a 1-D Position Sensitive Detector in reflection plane. Signal is product of source intensity, sample acceptance and reflectivity.***
- ***High resolution Specular R[Q] can be recovered from data collected across a loosely collimated wide beam. Reduction "automatic" in instrument software.***



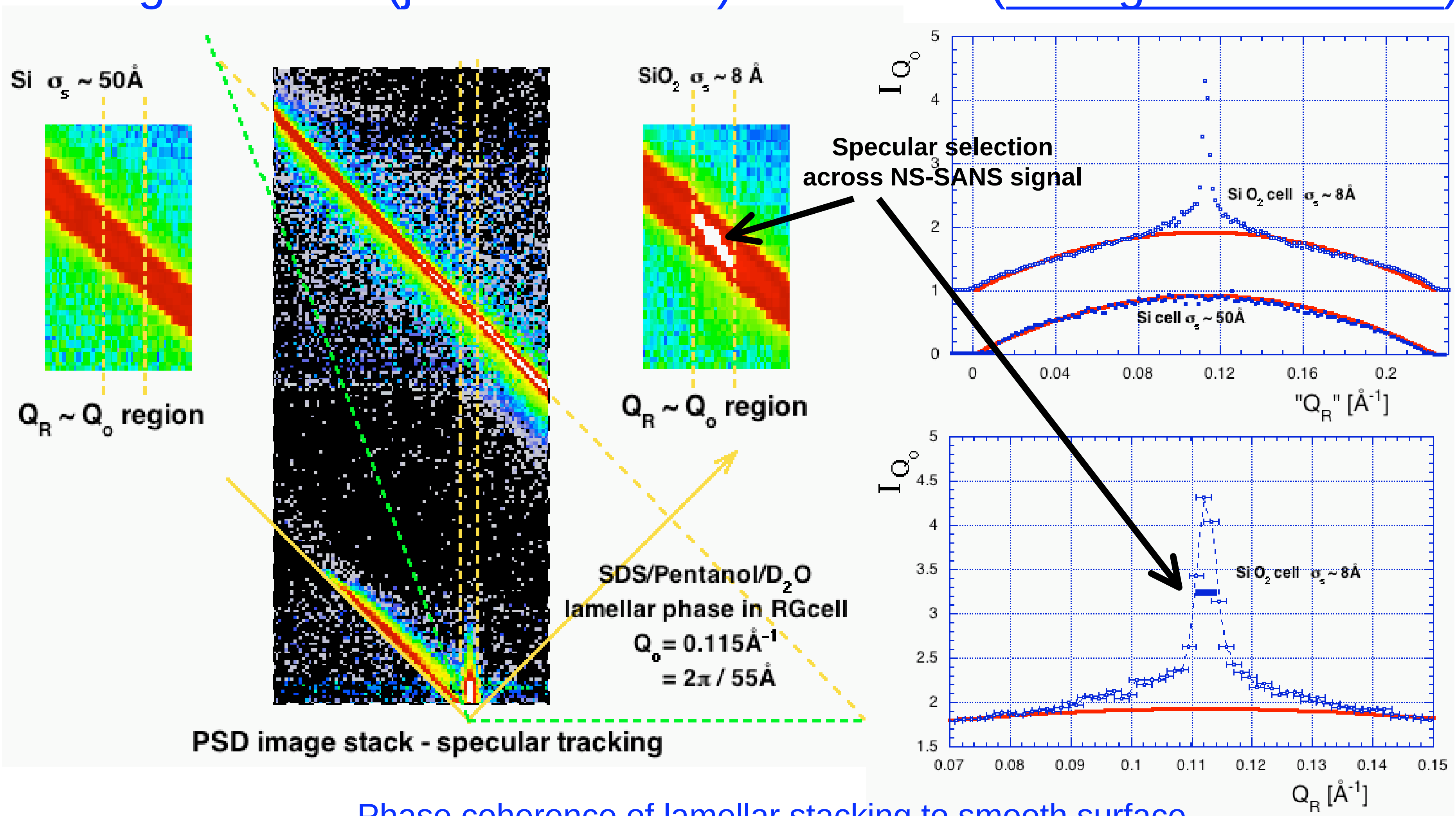


HFIR reflectomer MIRROR: data after normalization for monitor and sample acceptance (30m SANS satellite 4.75Å - 1993)



"Neutron Reflectometry as Optical Imaging", W. A. Hamilton, J. B. Hayter, and G. S. Smith, *Journal of Neutron Research* 2, 1 (1994)

Back to NR - why you might care ...
NR-NSSANS on lamellar phase in reflection geometry cell
Rough surface (just NS-SANS) vs smooth (<u>strong NR selection</u>)



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 **<u>not</u>** coherent)

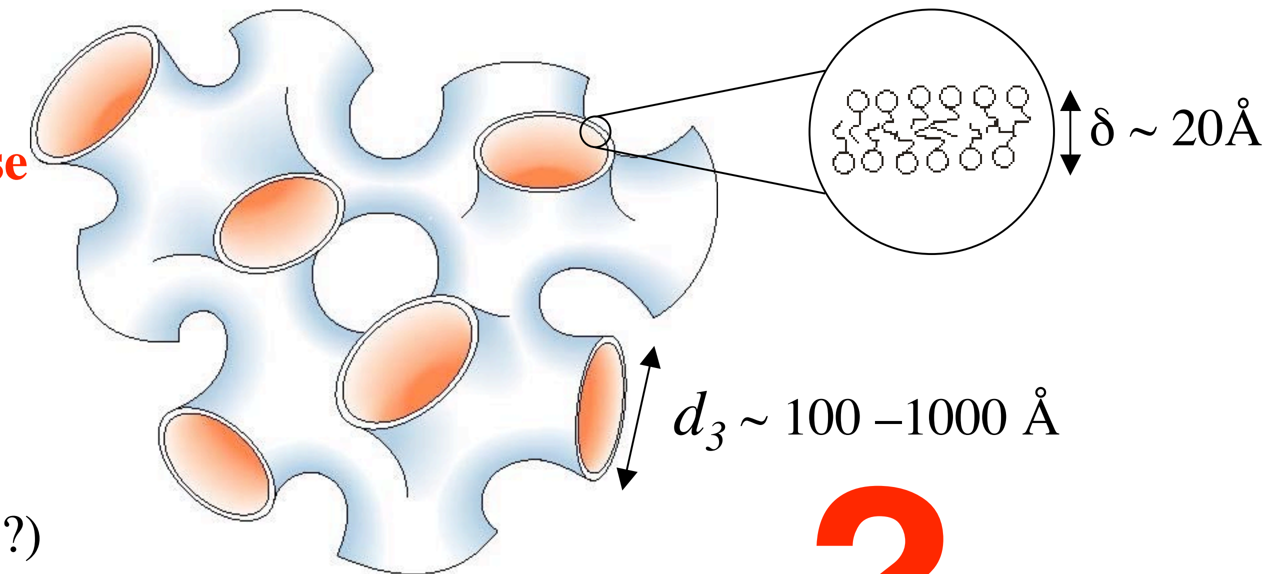
NS-SANS as NR background and monitor: Sponges at a surface ...

Surfactant "sponge" phase - L_3

Isotropic membrane phase

Low viscosity

Transient birefringence under flow ($L_3 \rightarrow L_\alpha$, lamellar ?)



?

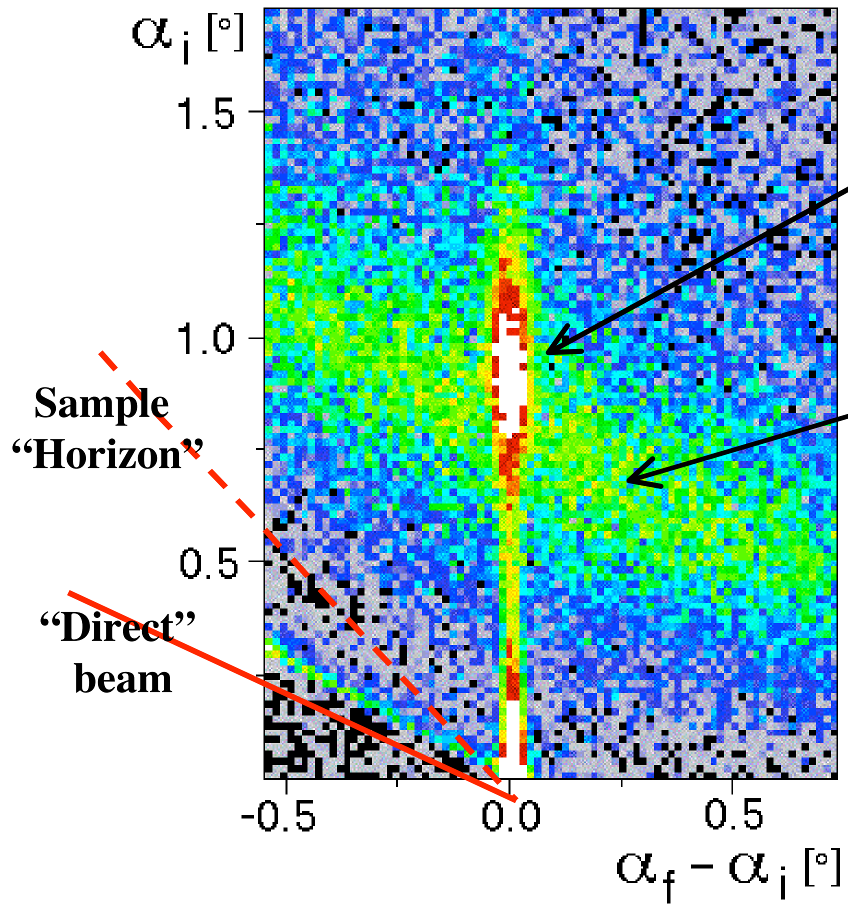
Quartz surface

What does an isotropic bulk phase do in an anisotropic situation?

Neutron Reflectometry (NR) and "Near Surface" SANS (NS-SANS) - MIRROR Reflectometer
Conventional bulk SANS - "12m" SANS instrument
ORNL High Flux Isotope Reactor

NR and Off-Specular NS-SANS (in plane) analysis implemented on MIRROR reflectometer

35vol% CetylpyridiniumCl/Hexanol sponge in static Quartz-Solution cell "raw" data



Specular NR signal ($\alpha_i = \alpha_f$) peak at higher Q than and at noticeable offset to …

Off specular NS-SANS signal (~ parallel to "direct" beam) Sharper than one might have expected for sponge scattering background?

NS-SANS: "L_α" near surface?

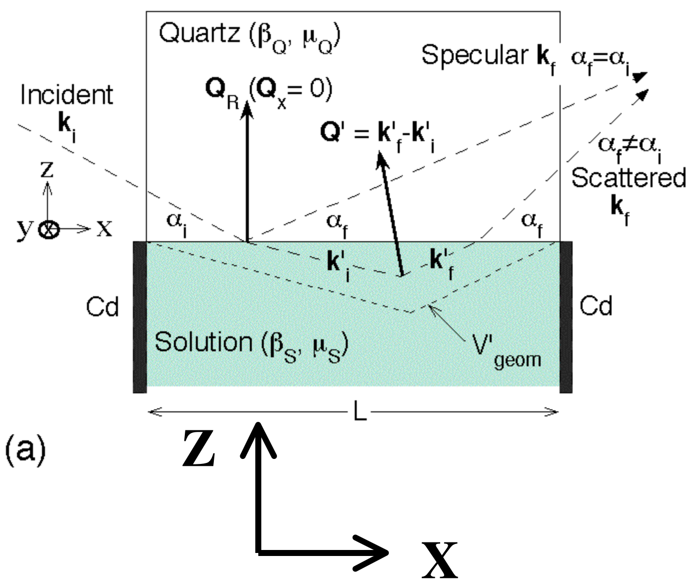
NR: Suppression of membrane fluctuations near interface?

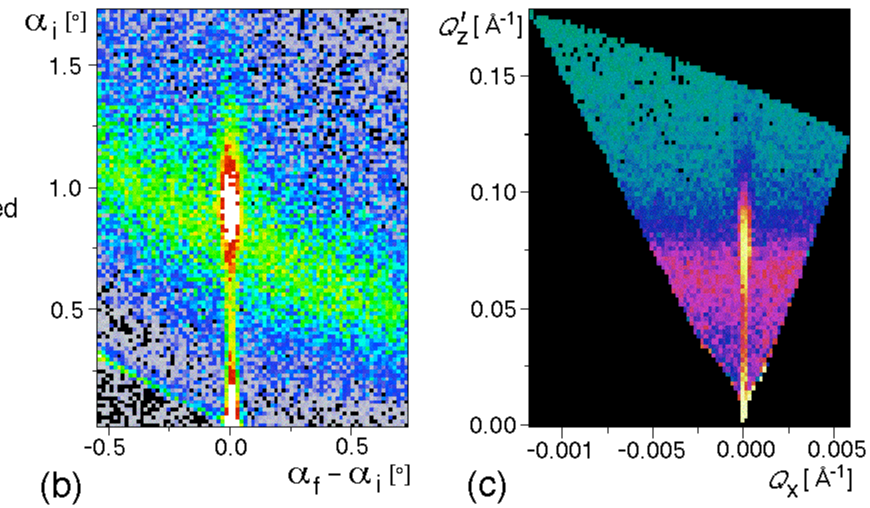
MIRROR Reflectometer - ORNL High Flux Isotope Reactor

J. Neutron Research **2, 1 (1994) and** http://neutrons.ornl.gov

After partial NS-SANS reduction:

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





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

> NS-SANS a lot less sharply peaked – now obviously similar to sponge bulk SANS signal, but still offset from NR peak.

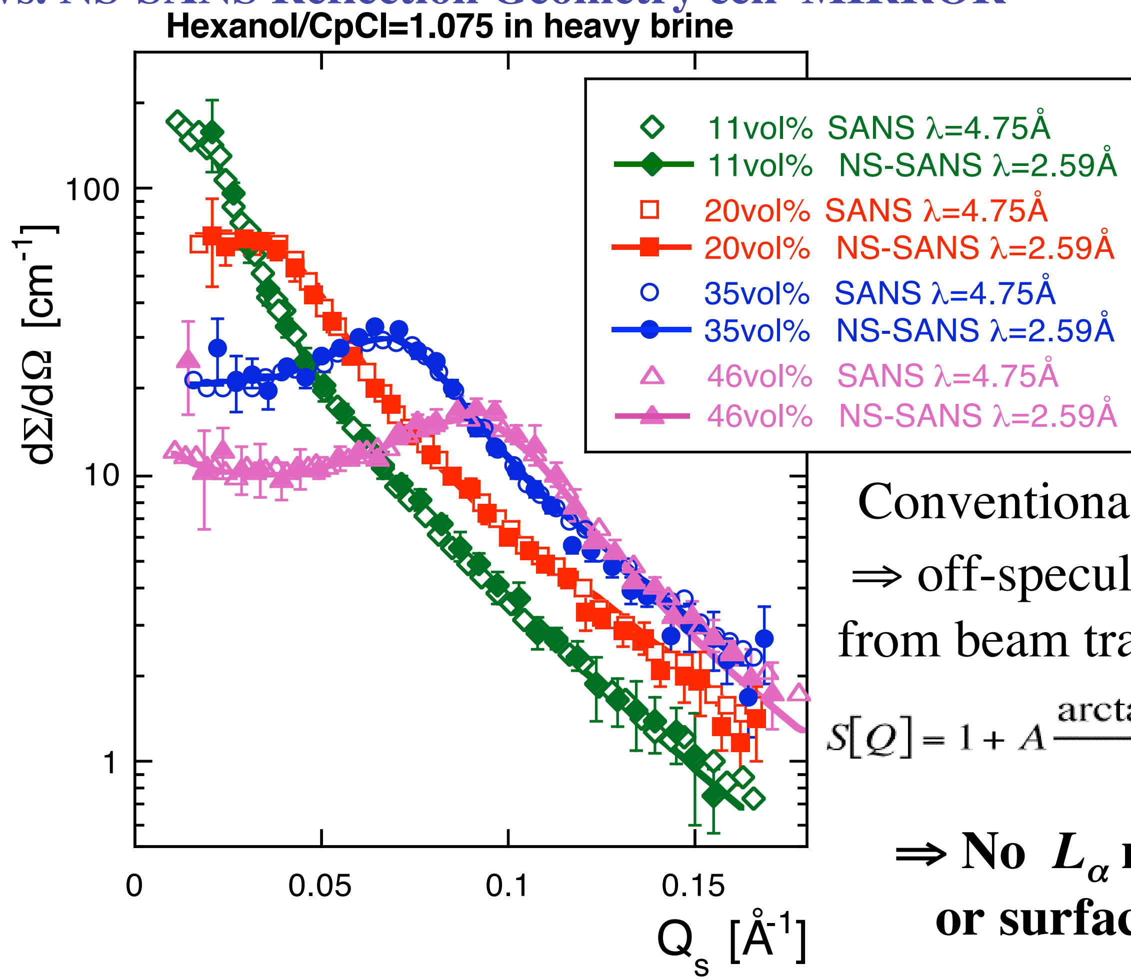
1-D PSD Correct for transverse (y) resolution: $Q_S \cong \sqrt{Q_x^2 + (\delta Q_y)^2 + Q_z^2}$ …

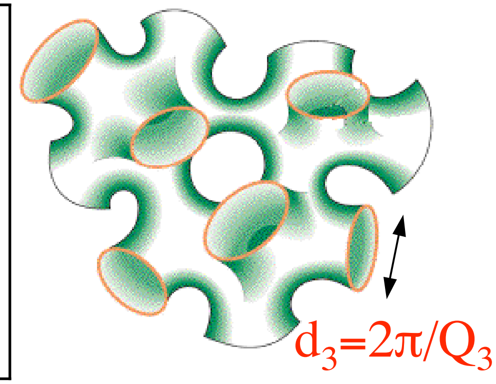
"Local membrane ordering of sponge phases at a solid-solution interface",
W.A. Hamilton, L. Porcar, P.D. Butler and G.G. Warr,
Journal of Chemical Physics **116**, 8533 (2002)* [and *Virtual Journal of Biological Physics Research* **3** (2002) [http://www.vjbio.org].

“A comparison shows MIRROR NS-SANS reduction works (can be trusted√)...”

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

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





Conventional SANS ≅ NS-SANS

⇒ off-specular is simply L_3 SANS from beam transmitted into solution

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

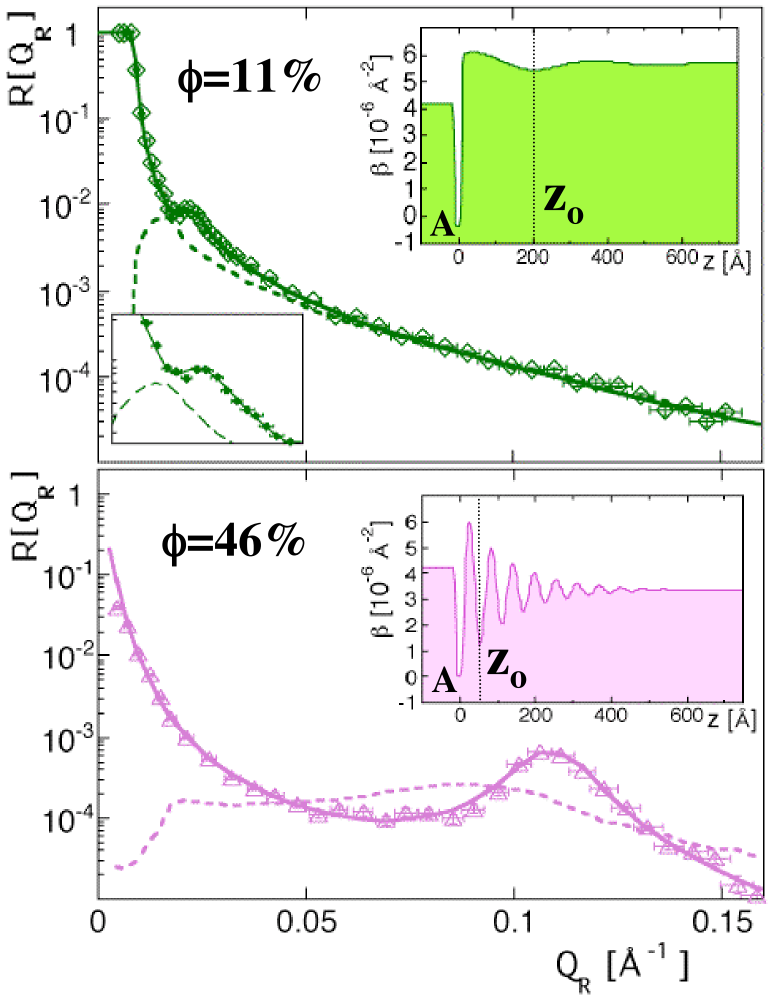
⇒ No L_α nucleation (<0.1μm) or surface-induced phase shift

Quick take home corollary:

Interesting *looking* off-specular scattering isn’t necessarily.
Analyze your data & Beware of “interpretative” picture shows.

“ ... results are less different than they at first appeared”

Specular Neutron Reflectivity Analysis for sponges at surface



Scattering length density ($\beta[z]$) profile normal to interface:

Quartz (β_Q)

Adsorbed bilayer

(expected: since CpCl is a cationic surfactant and quartz a negatively charged surface)

Symmetric decaying oscillation to bulk solution membrane concentration (β_s)

Periodicity $\mathbf{d_Z}$

Exponential decay ξ_Z

$\mathbf{z_o}$ offset ⇔ "1st" in-solution membrane

ξ_Z / $\mathbf{d_Z}$

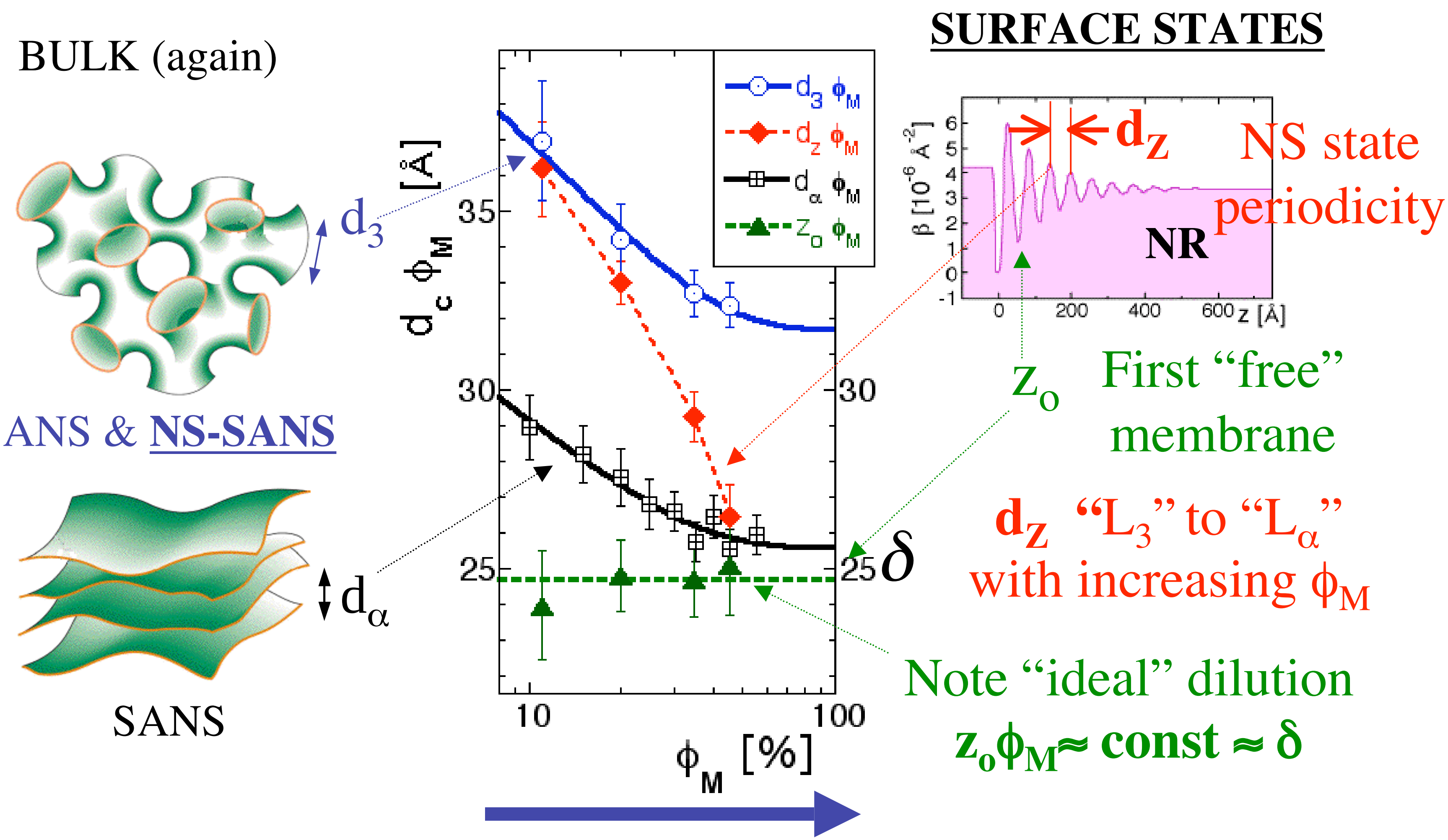
increases with ϕ_M

More surface "layering"

"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].

Simultaneous NR/NS-SANS analysis => layering only at surface and we can be confident about our NR results

Dilution law behavior of length scales



decreasing fluctuations (ϕ_X ~ 30%)

A possible Poiseuille surface shear effect that probably isn't:
NS-SANS as a monitor

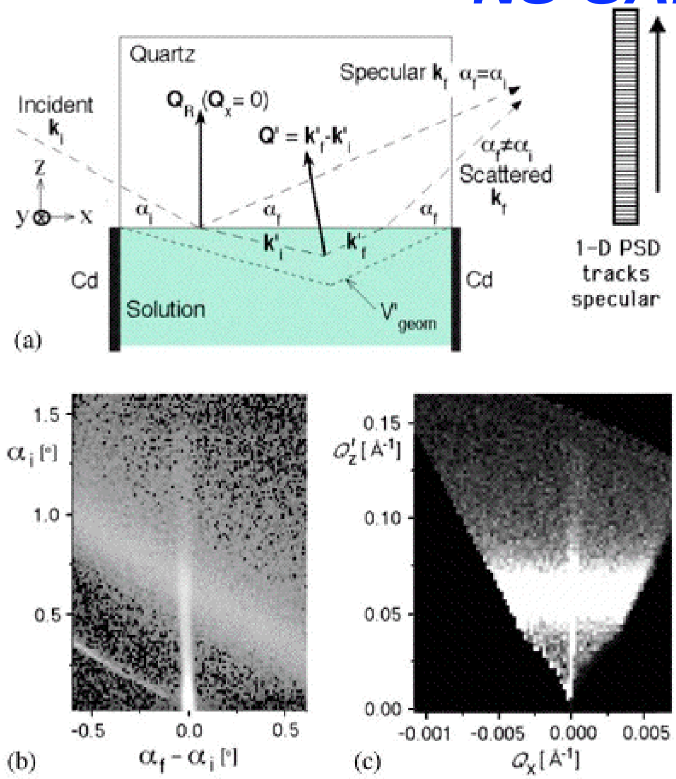


Fig. 1. (a) Schematic of NR/NS-SANS solution cell and measurement geometry. (b) Raw NR/NS-SANS data set 400 mM CTAB in D_2O at 30 °C. (c) Corrected NS-SANS.

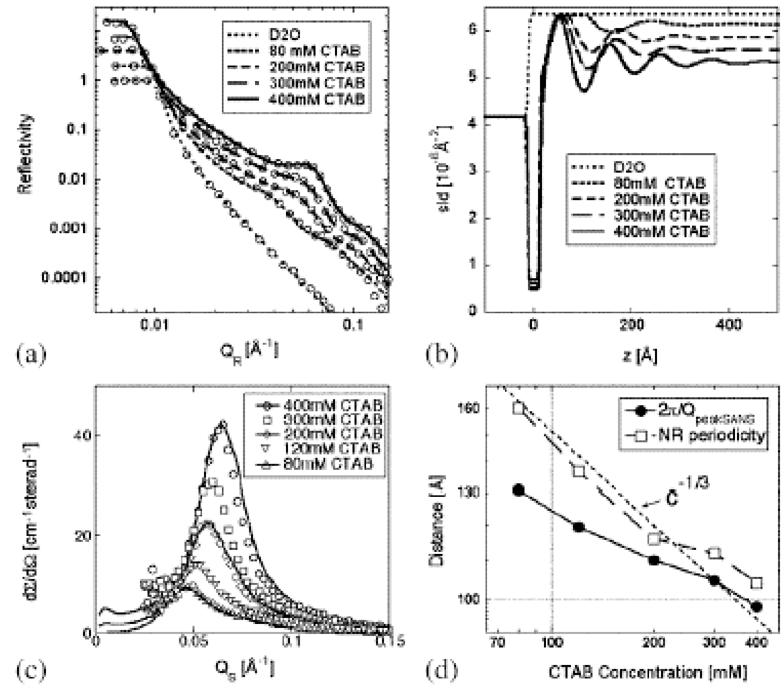
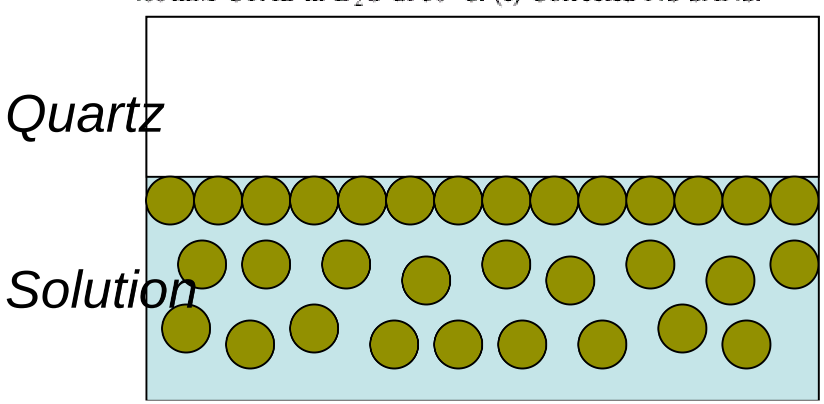


Fig. 2. Concentration series: (a) NR scans—rms resolution approximately indicated by data point width; (b) quartz-solution sld profiles; (c) reduced NS-SANS and bulk SANS data; and (d) characteristic lengths vs. concentration.



2(a)&(b) NR: CTAB micelle absorption and some surface ordering

2(c) NS-SANS: (data points) simply agrees with bulk SANS (solid lines)

A possible Poiseuille surface shear effect that probably isn't:
NS-SANS as a monitor

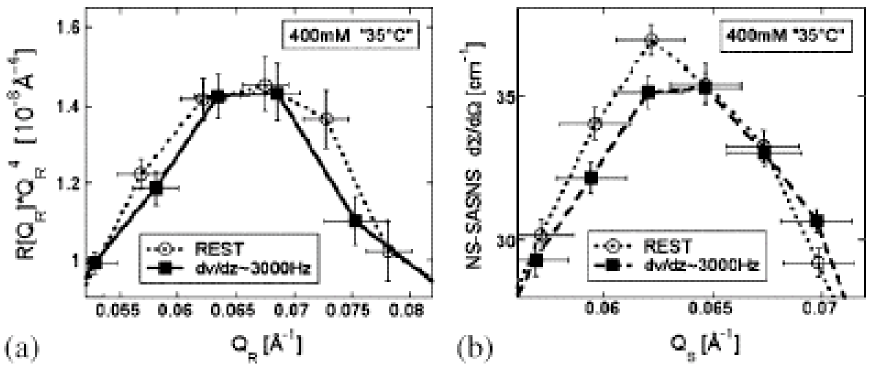


Fig. 4. Temperature/"shear" effects on 400 mM CTAB in D2O at a nominal temperature of 35 °C at rest and at an applied Poiseuille surface shear ~3000 Hz: (a) NR measurement in surface layering peak region scaled as RQ_R^4, and (b) NS-SANS cross-section over the micelle interaction peak region.

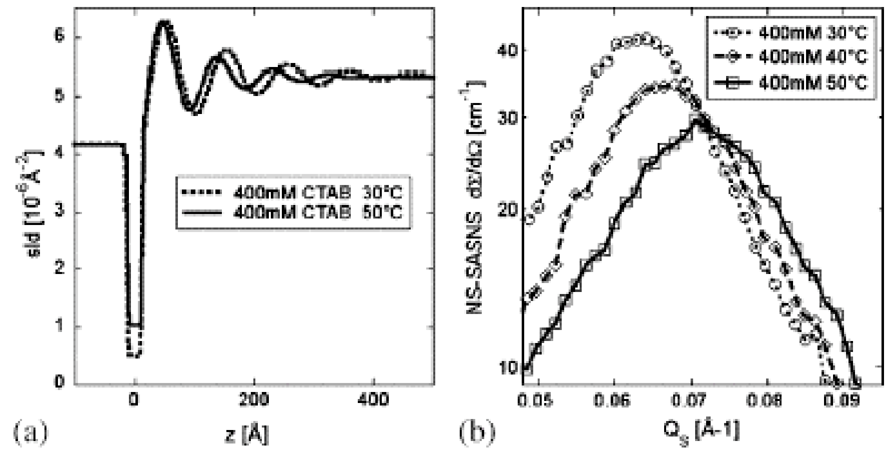


Fig. 3. 400 mM CTAB in D_2O temperature series: (a) sld profiles at 30 and 50 °C, and (b) reduced NS-SANS cross-section at 30, 40, and 50 °C over interaction peak region.

4(a) For concentrated 400mM solutions 3000Hz shear apparently sharpens the NR layering peak (consistent with expectations)

but

4(b) corresponding NS-SANS peak shift 0.001Å^{-1} and -1.5cm^{-1}

&

3(b) previous temperature series show that this could simply correspond to a 2°C temperature rise ... 0.0005Å^{-1}/°C and -0.7cm^{-1}/°C

so

no premature (or false?) report of a shear-induced effect

"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)

Things to think about

NS-SANS is quite often unavoidable in NR measurements
(can be true even in thin liquid films ~20-50micron)
You might as well understand it to account for it properly
even if only for background subtraction

A rather useful "bulk" sample state monitor
So you can be sure of your bulk state
and scattering can probe where a sensor might not fit

NR/NS-SANS Analysis:
Easy for constant wavelength reactor reflectometers
e.g. MIRROR at HFIR-CNS
and
Can be done with SNS Liquids reflectometer (with a few more corrections)
NB: and in TOF case fully simultaneous NR and NS-SANS

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