Membrane phase miscibility gaps and surface constraints

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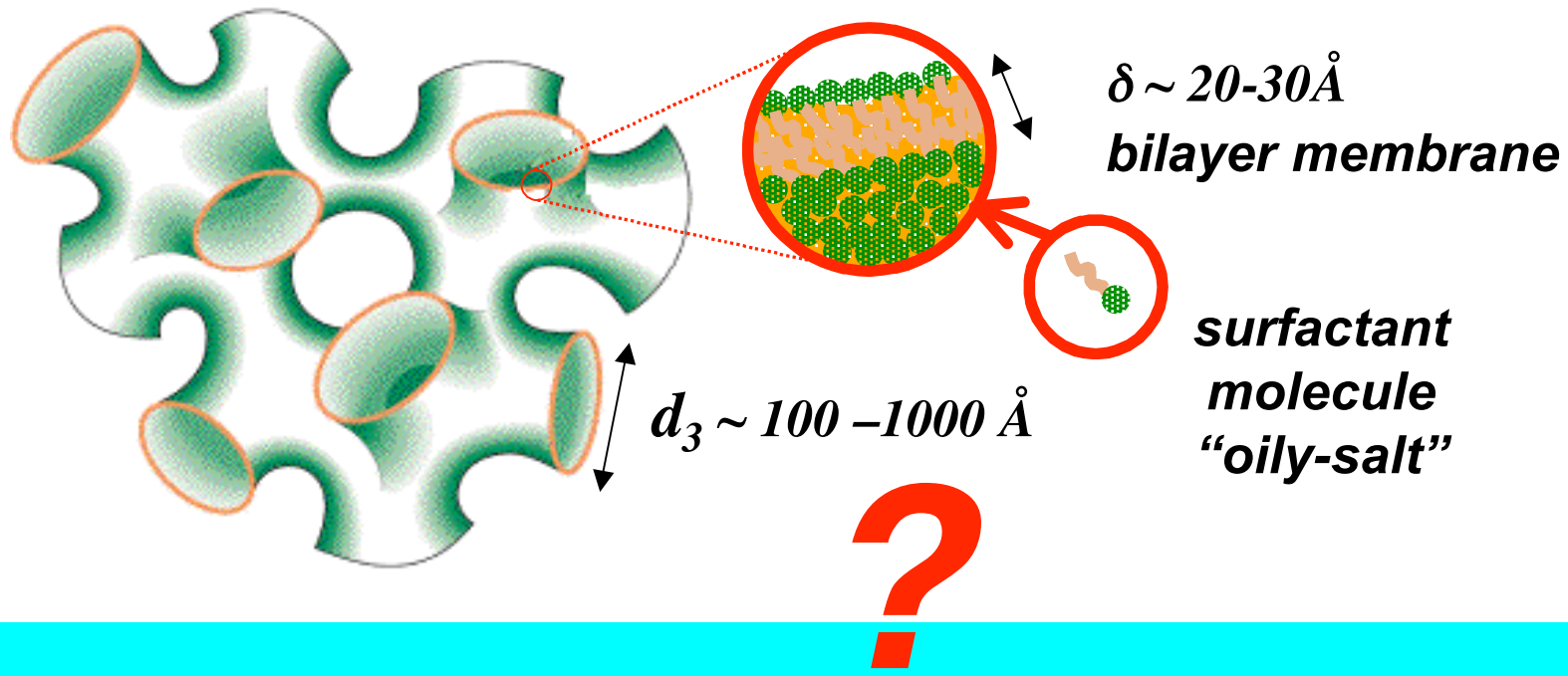
Self-assembled surfactant membrane phase: L_3 "sponge" phase



Quartz surface

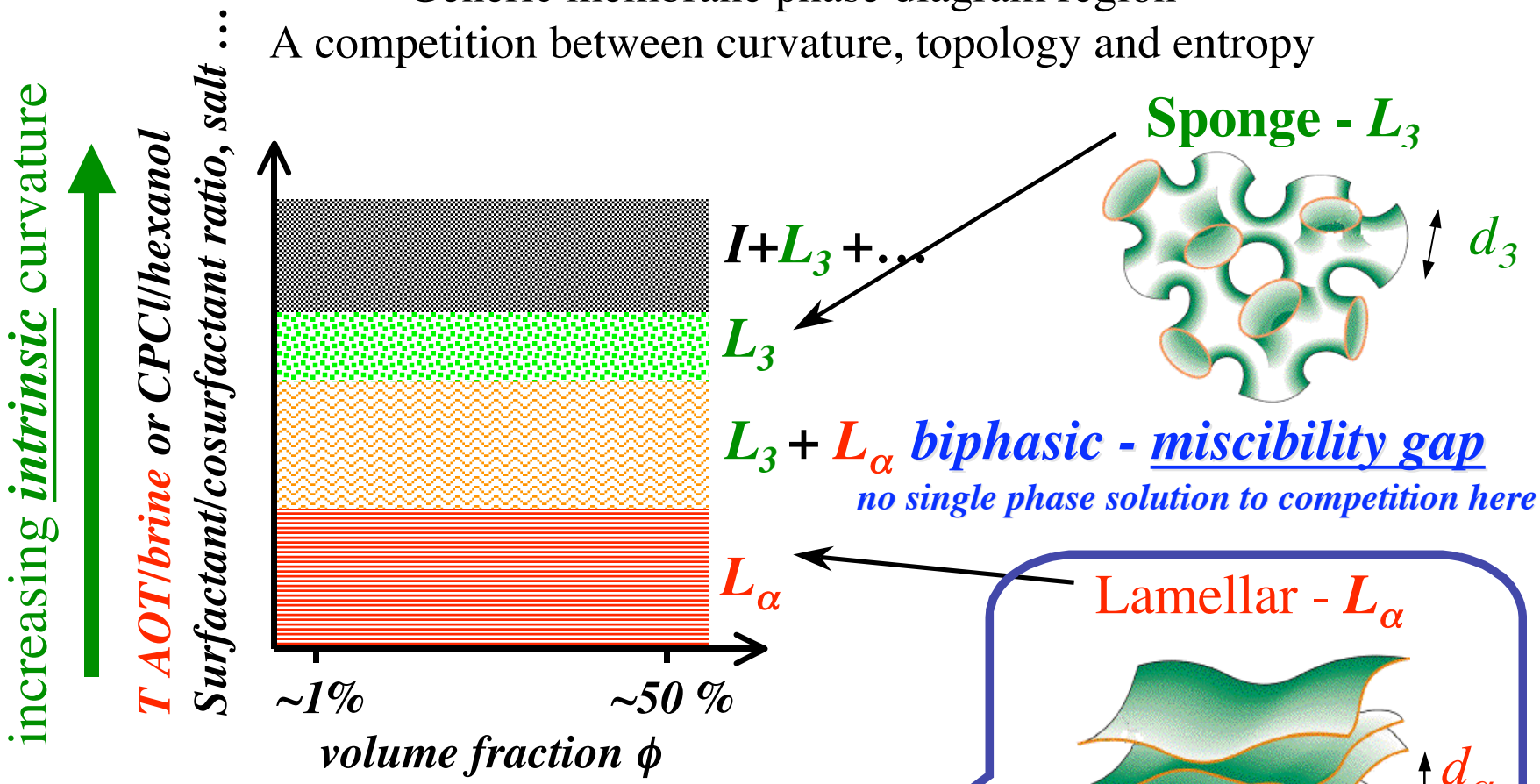
Our simply constraining proximate surface ...

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

A nearby answer in the phase diagram …

Generic membrane phase diagram region

A competition between curvature, topology and entropy



Stacked lamellar phase would fit nicely against a constraining surface ...

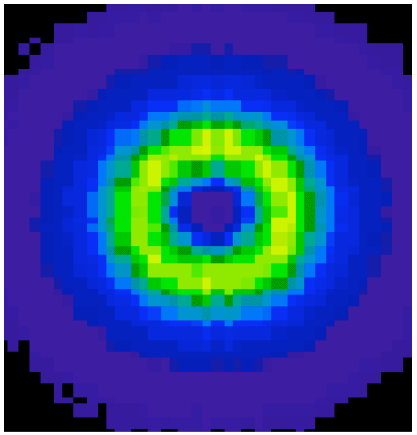
Near surface constraint contributes to F

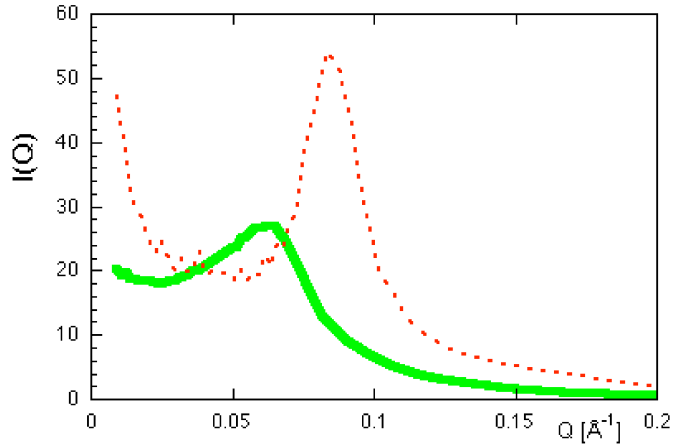
Expect local effect on phase transition and miscibility gap (L_α+L_3 coexistence)

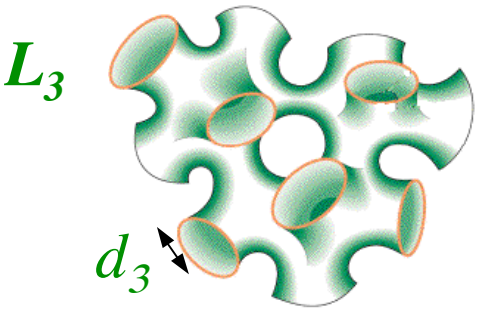
Typical L_3 and L_α SANS at highish volume fraction

e.g. 35% volume fraction CPCl/hexanol sponge in heavy brine
"12m" SANS instrument - ORNL High Flux Isotope Reactor

isotropic

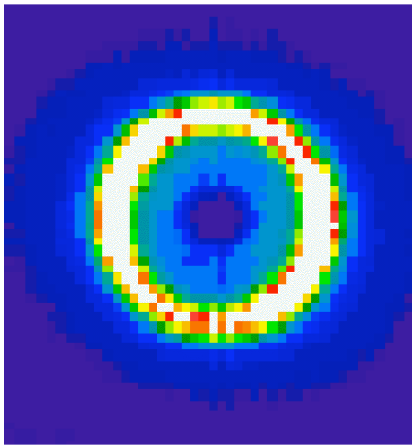


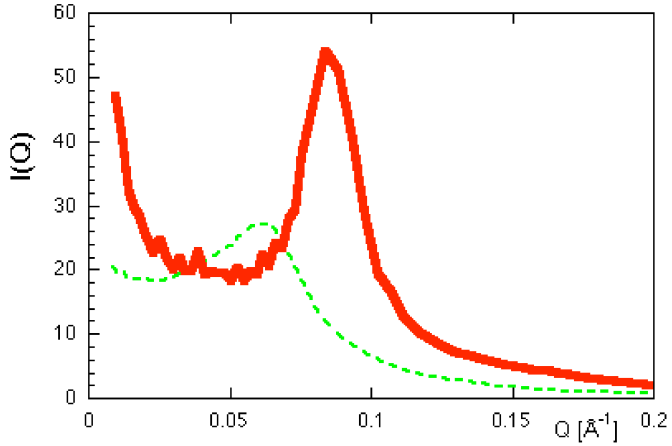


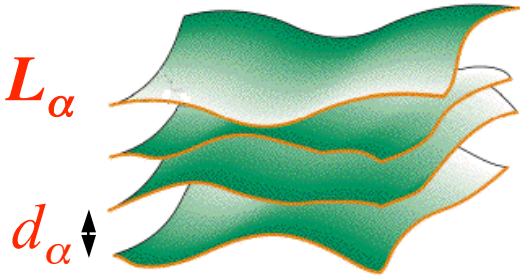


$d_3 \sim 1.25\ d_\alpha$

almost isotropic but …







In chosen Q range Structure factor correlation peaks dominate scattering

- ❑ at lower Q: in-out order parameter and domain scattering (L_α)
- ❑ at higherQ: membrane form factor - first minimum $Q \sim 2\pi/\delta$

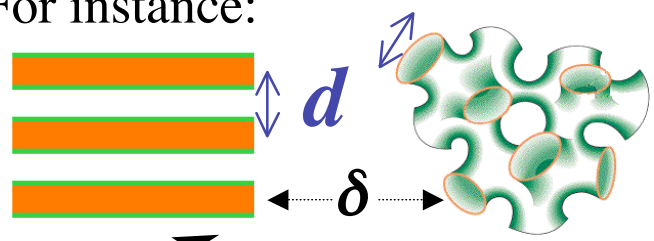
ϕ Scaling: the sheet equation

Correlation length $\boldsymbol{d}$ for structure of sheets of thickness $\boldsymbol{\delta}$ with membrane volume fraction $\boldsymbol{\phi}$

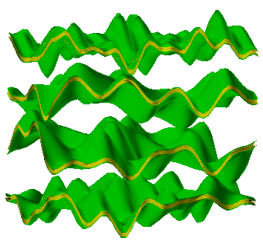
$$\phi = C\ \delta / d$$

G. Porte *et al.*, *J. Phys. (France)* **49**, 511 (1988) and **50**, 1335 (1989)

For instance:



$$d\ \phi = 2\pi\phi / Q_{\text{peak}} = C\ \delta = \textbf{const}$$

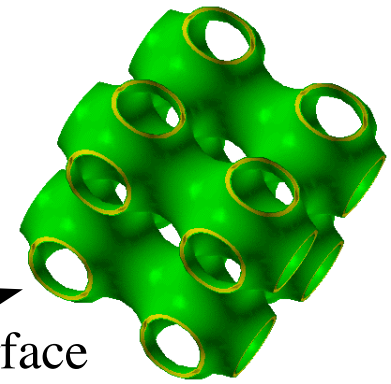


stiff flat L_α lamellae $C_\alpha = 1$

rippled lamellae $C_\alpha > 1$

stiff L_3 sponge $C_3 \geq 1.5$

assuming sponge somewhat disordered cubic minimal surface



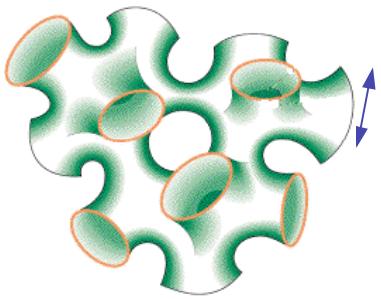
"Schoen P"

L_3 and L_α distorted and fluctuate (excess area) so "typically":

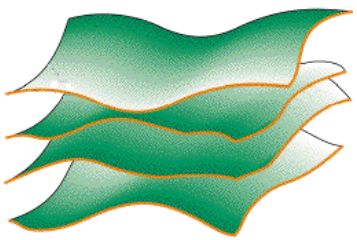
$$C_3 / C_\alpha = d_3[\phi] / d_\alpha[\phi] \sim 1.25 < 1.5$$

OK: so the stacked lamellar structure is a little more distorted wrt its "ground state" ...

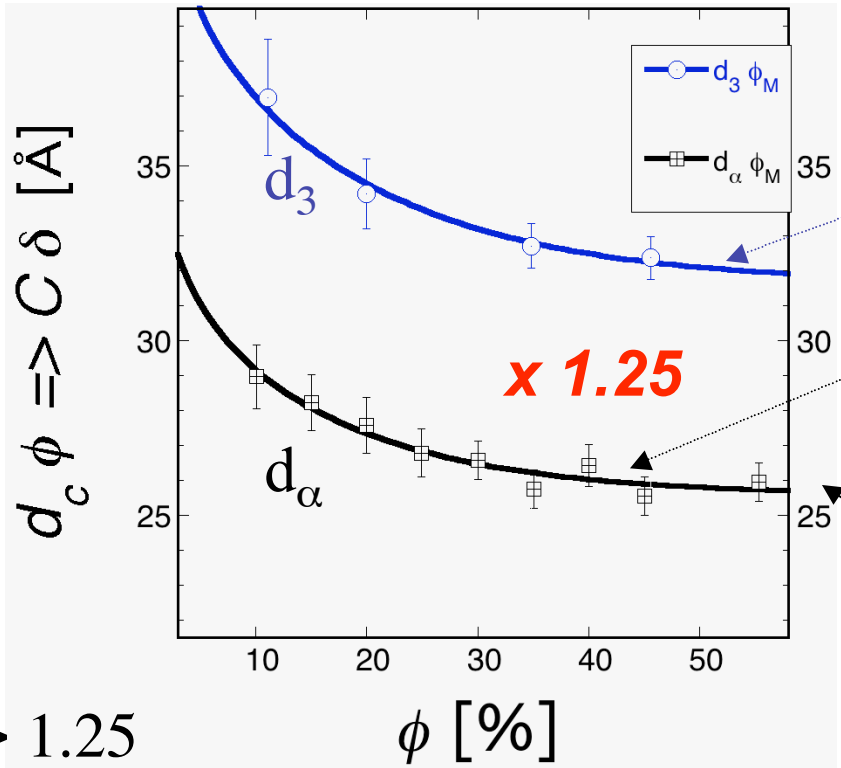
Dilution ("laws") behavior of length scales
CPCl/Hexanol in brine

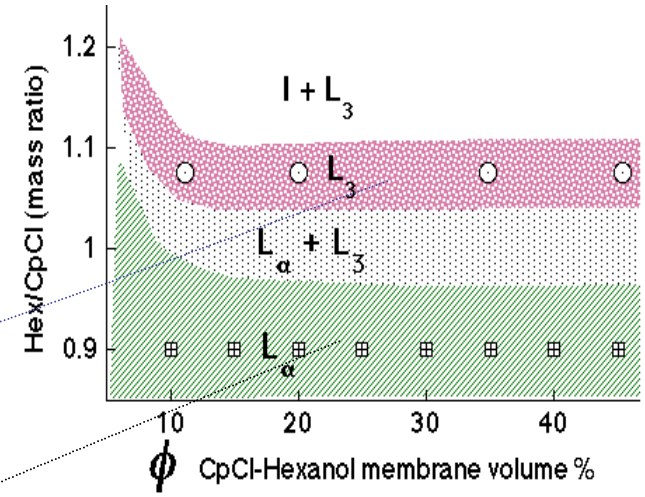


SANS



SANS





Consistent fit params

$\kappa_o/k_BT = 0.8\pm0.2$

$\delta = 25.6 \pm0.5$ Å

$\Lambda_{min}/x \sim 50$Å $\sim 2\delta$

$d_3/d_\alpha \rightarrow 1.25$

as "$\phi_M \rightarrow 1$"

Fluctuations damped $\Rightarrow$ ~ideal dilution $\phi > 25\%$

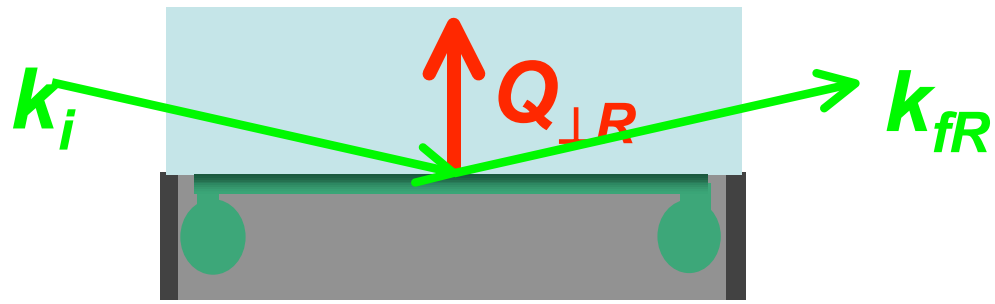
$C'_\alpha = 1 \Rightarrow C'_3 = 1.25 \pm 0.04$

W. Helfrich, *Z. Natuforsch* **33a**, 305 (1978)

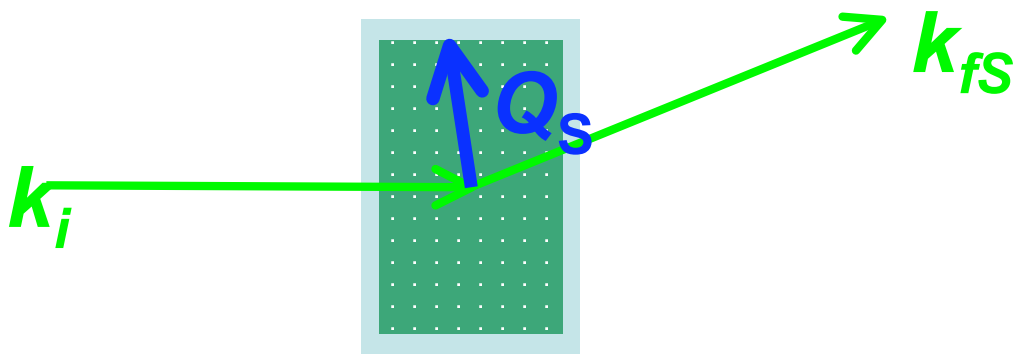
D. Roux *et al.*, *Europhys. Lett.* **17**, 575 (1992)

W.A. Hamilton *et al.*, *J. Chem. Phys.* ***116,*** 8533 (2002)

"Near-Surface" (Reflection Geometry) SANS

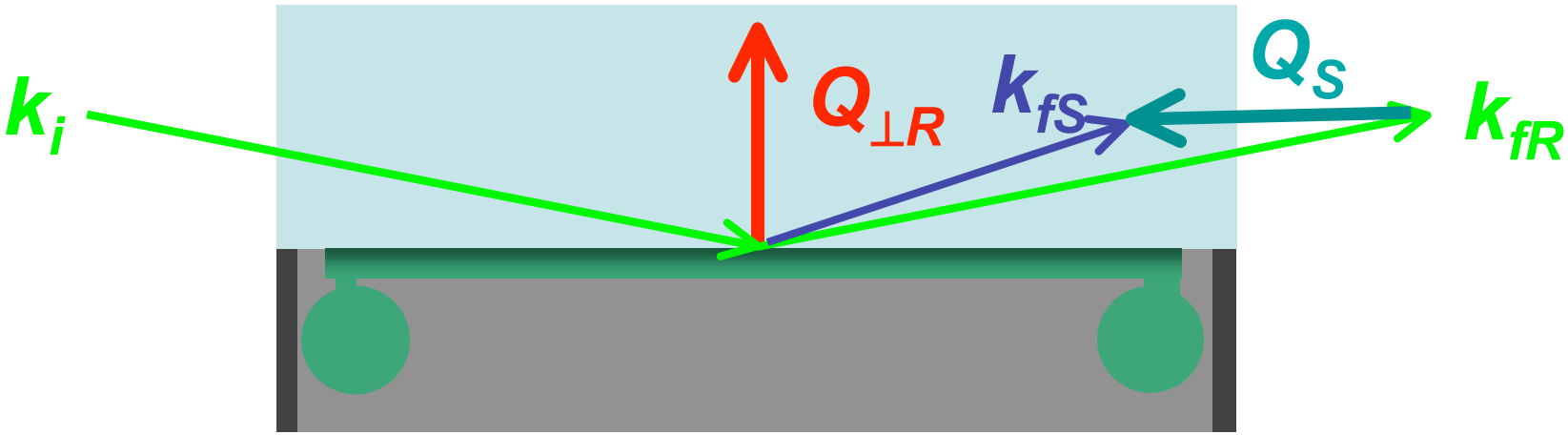


Neutron Reflectometry (NR)

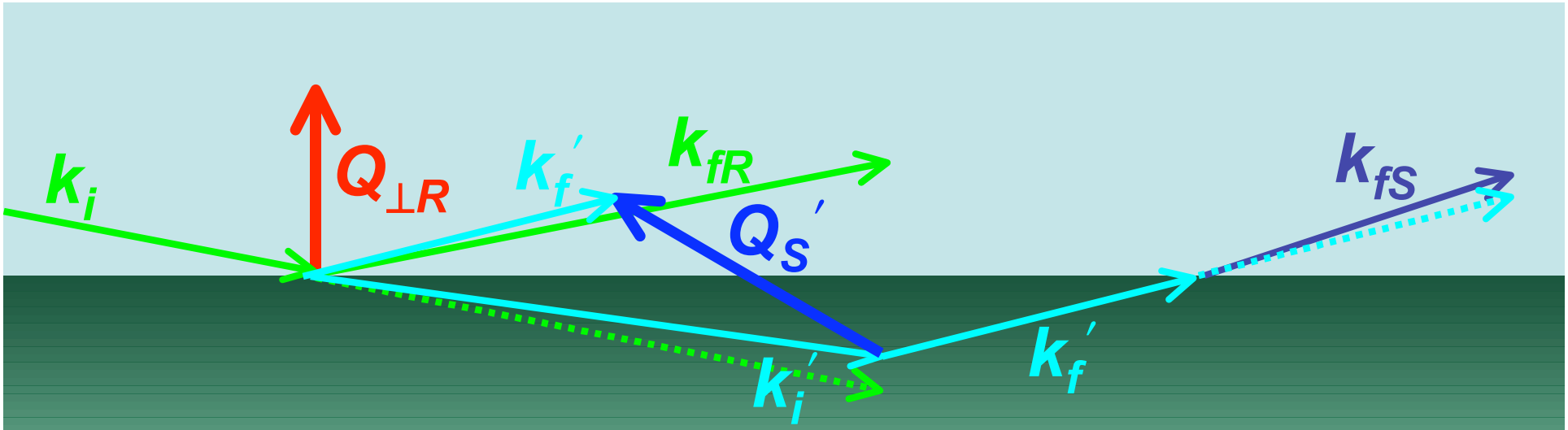


Small Angle Neutron Scattering (SANS)

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



"NS-SANS" is SANS in reflection geometry



NS-SANS: refraction-SANS-refraction

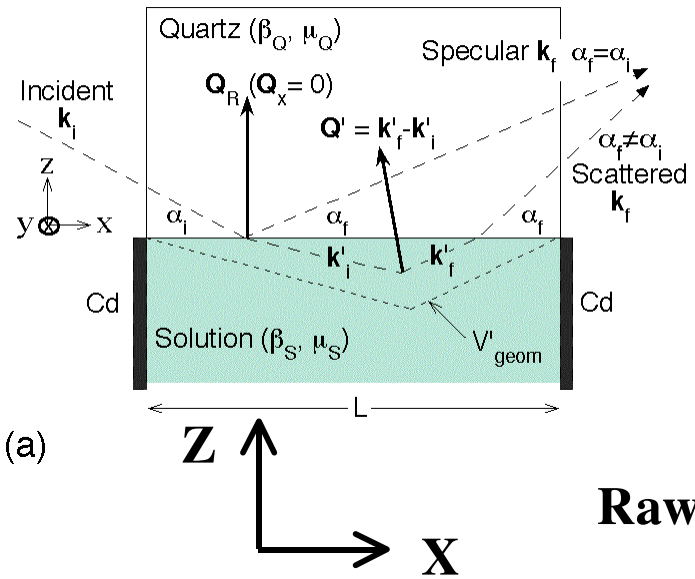
Q_S' need <u>not</u> be in the reflection plane ⇒ neither are k_f' and k_{fS}

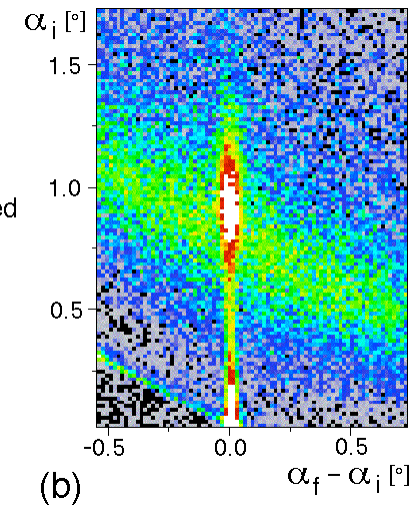
Components - perpendicular: $Q_{S\perp}' \neq Q_{S\perp}$; parallel: $Q_{S//}' = Q_{S//}$

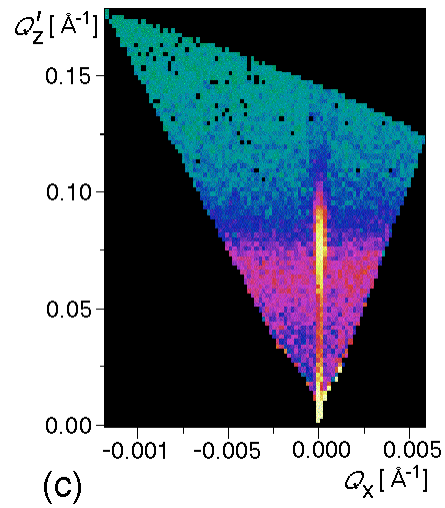
NS-SANS data reduction at constant wavelength

e.g. 35% volume fraction CPCl/hexanol sponge in heavy brine
on HFIR reflectometer MIRROR at ORNL (1D PSD in reflection plane - as per SPEAR)

Correct raw angle/angle data for incident beam (monitor), refraction, **absorption/volume**, interface transmissions and converting to **(Q_x,Q_z)** coordinates





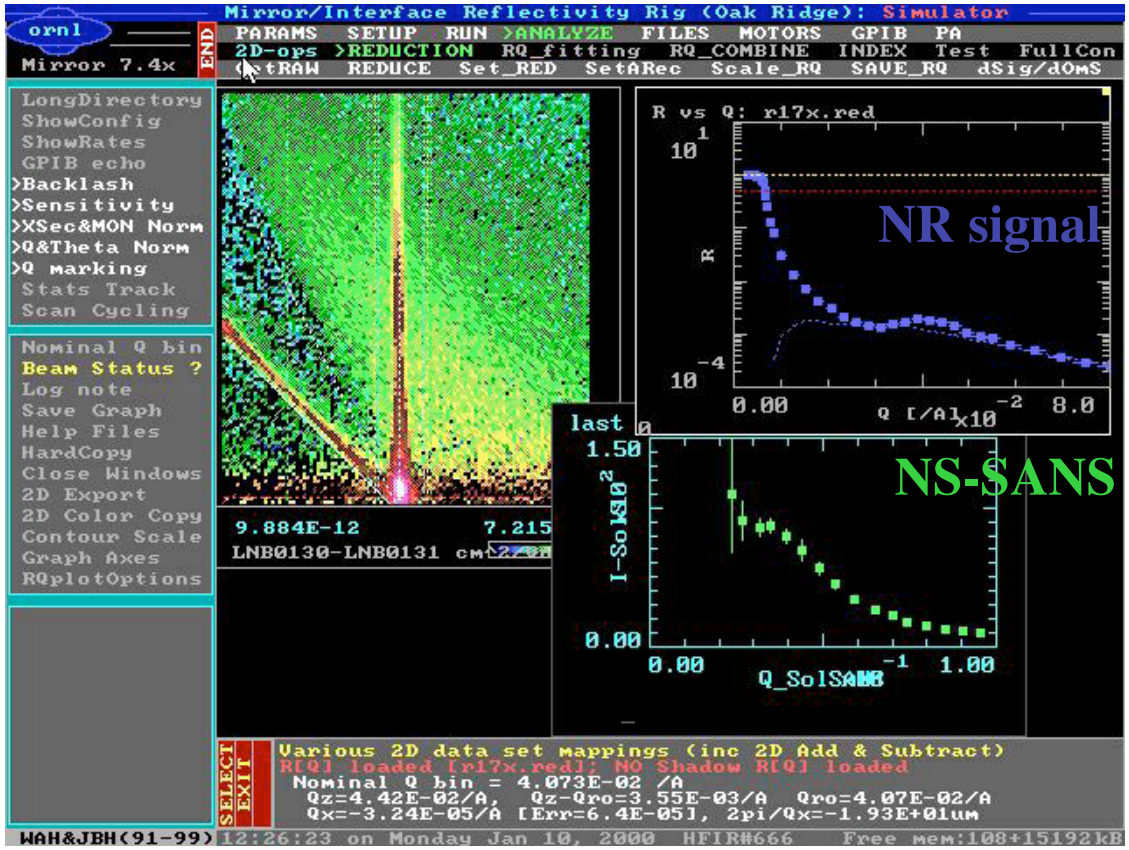


Raw/Mon ($\alpha_f - \alpha_i$, α_i) => (Q_x,Q_z) map

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

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

MIRROR data (collection and) reduction program



NR signal => $R[Q_R]$ vs Q_R

(correctly) subtracts NS-SANS background

NS-SANS => $d\Sigma/d\Omega$ vs Q_S

Refraction, Absorption /sample volume, Interface Transmissions, Detector/instrument resolution …

NR

$$\sigma_R = R[Q_R[\alpha_i]] \times WL \sin\alpha_i \times \exp[-\mu_Q L_Q] \times f, \quad \text{(A1)}$$

NS-SANS

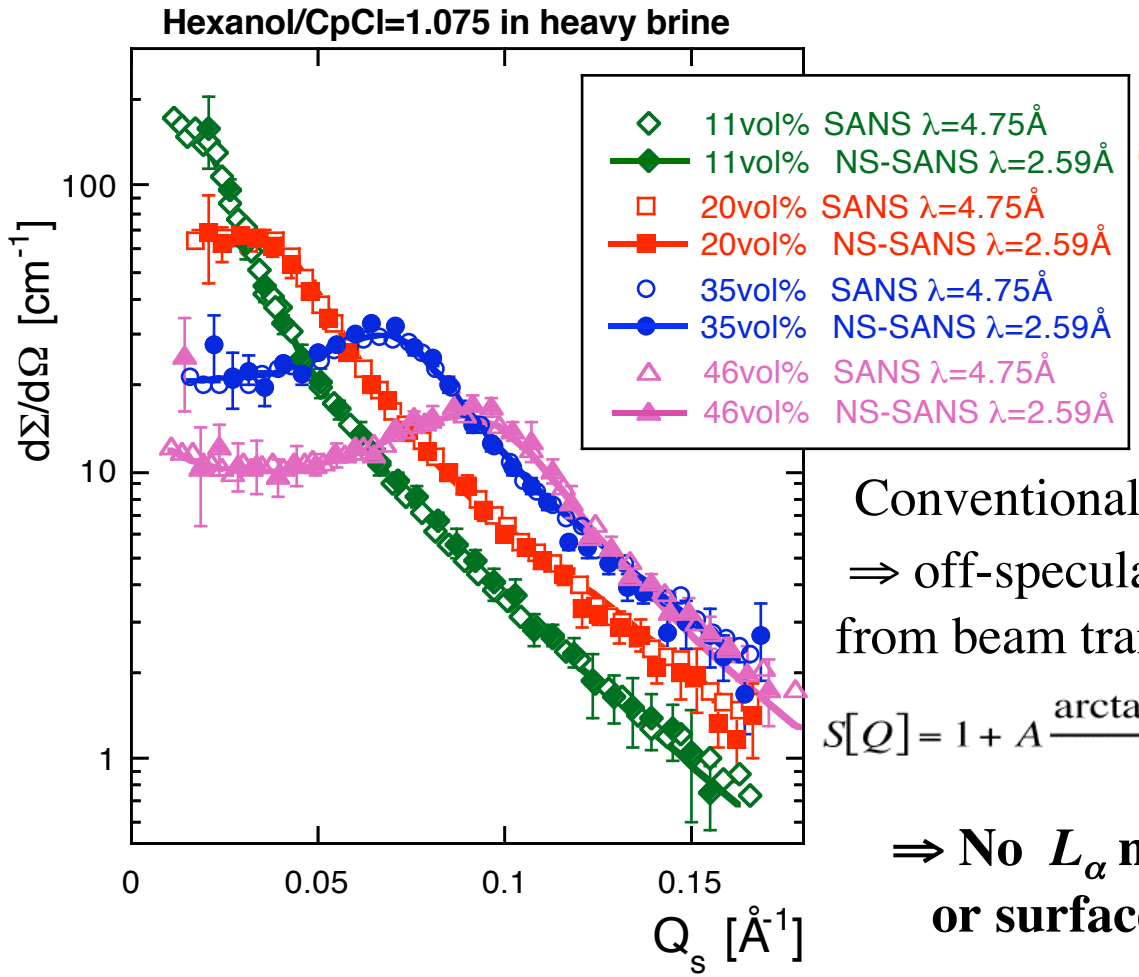
$$\sigma_S \cong d\Sigma_S/d\Omega' \times \Delta\Omega_{\text{pixel}}(\sin\alpha_f/\sin\alpha_f') \times \frac{WL^2}{2(\cot\alpha_i' + \cot\alpha_f')} \times \exp[-\mu_Q L_Q] \times \frac{2((\mu_S-\mu_Q)L - 1 + e^{-(\mu_S-\mu_Q)L})}{(\mu_S-\mu_Q)^2 L^2} \times (1 - R[Q_R[\alpha_i]])(1 - R[Q_R[\alpha_f]]). \quad \text{(A2)}$$

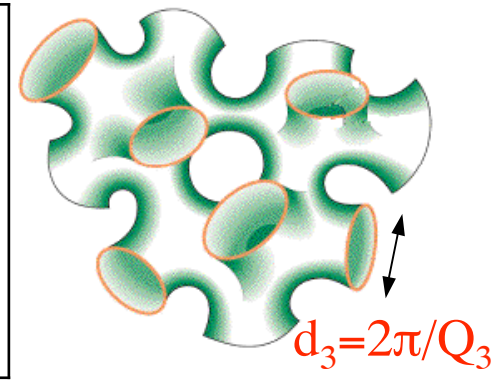
NS-SANS data analysis: *PRL* 72, 2219(1994) , *Physica B*. 221, 309(1996) , *PRE* 60, R1146(1999) …

NR/NS-SANS data analysis: Hamilton *et al.* *J. Chem. Phys.* 116, 8533 (2002)

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

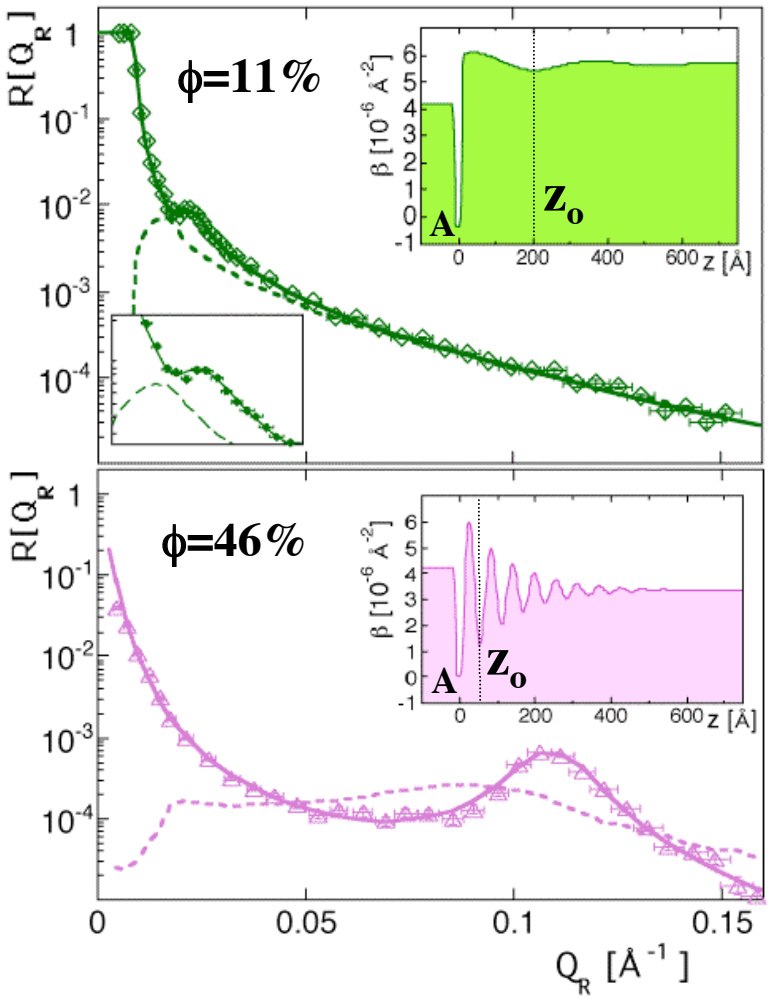
⇒ off-specular is simply L_3 SANS from beam transmitted into solution

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

⇒ 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 picture shows.

Specular Neutron Reflectivity Analysis



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

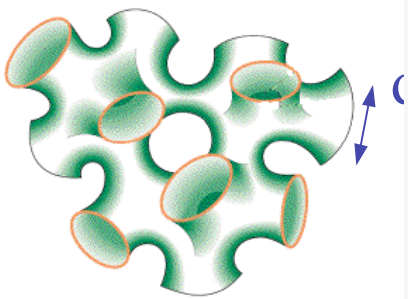
ξ_Z / $\mathbf{d_Z}$

increases with ϕ_M

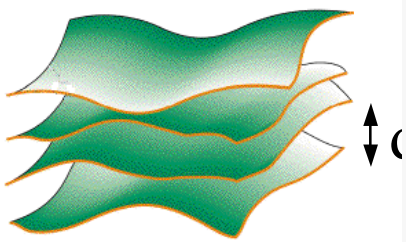
More surface "layering"

Dilution law behavior of bulk and surface L_3 length scales

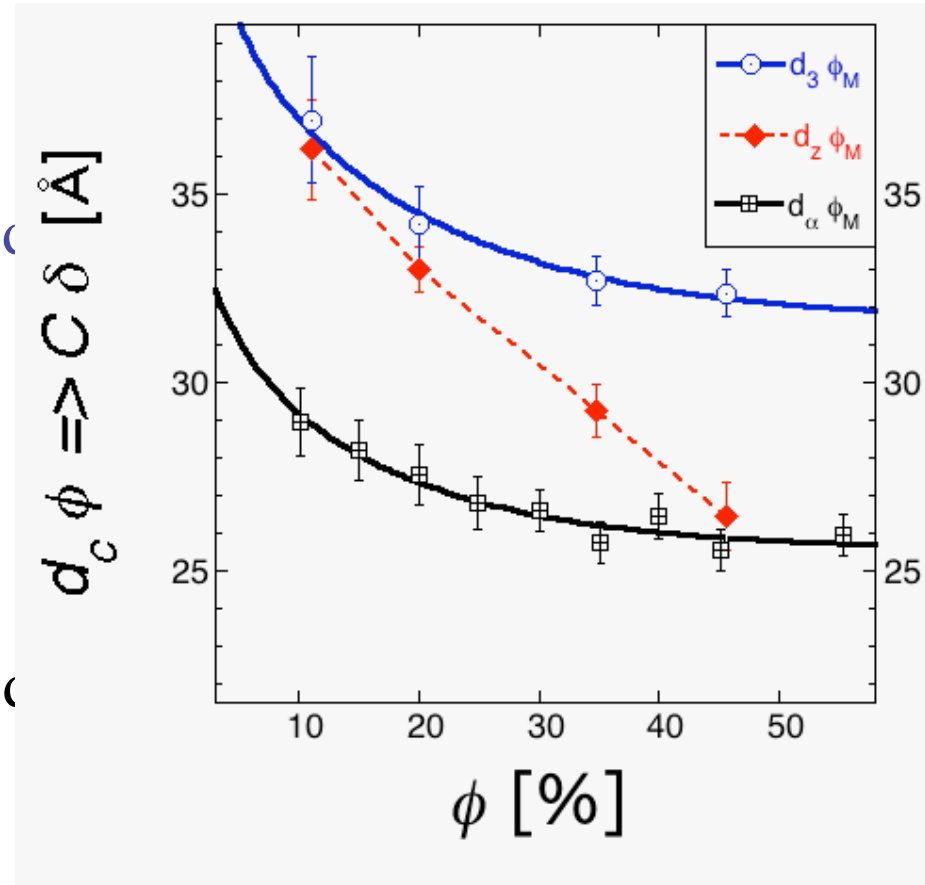
BULK (again)

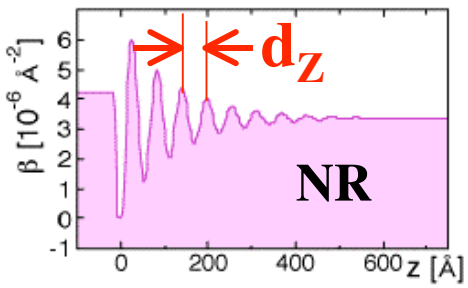


SANS & **NS-SANS**



SANS



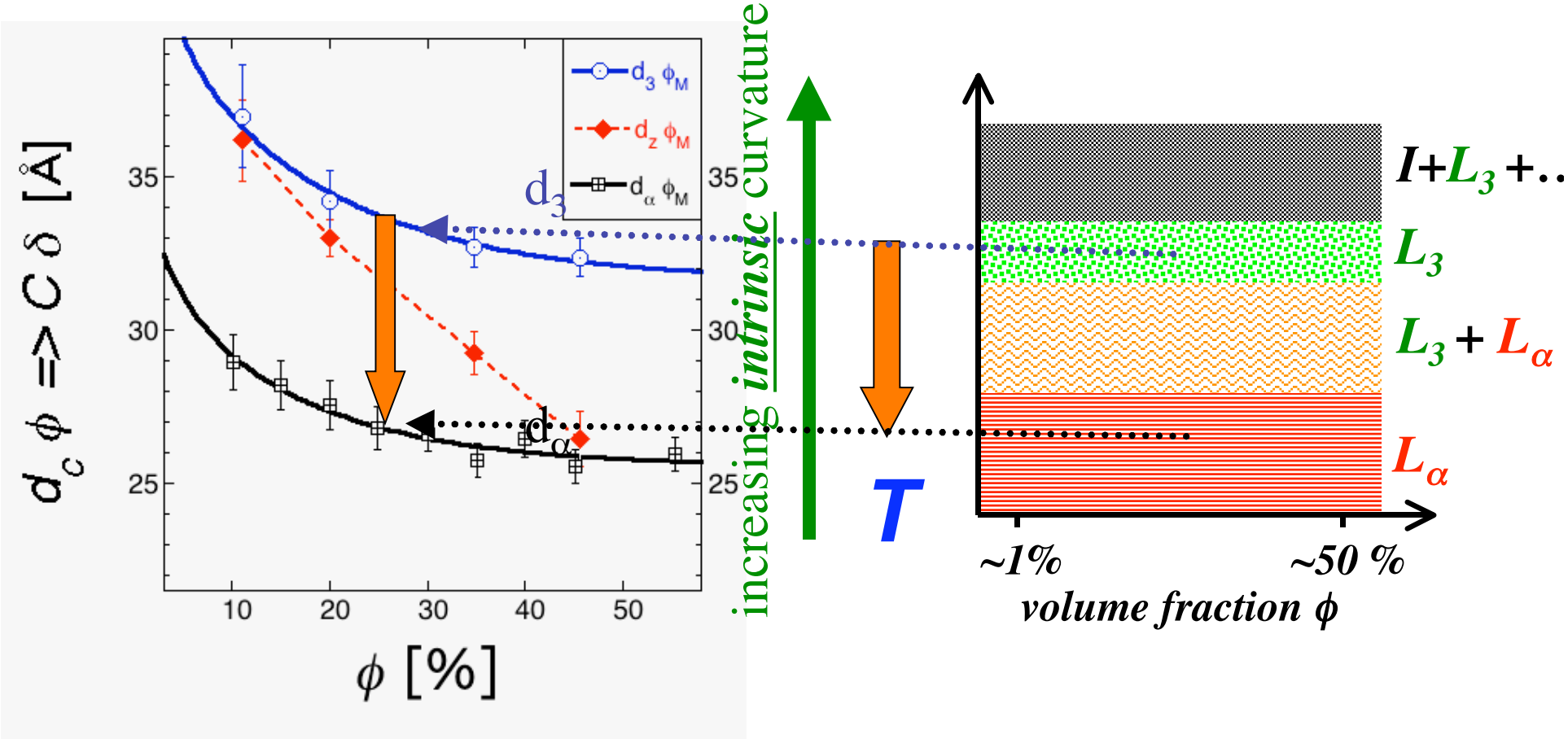


SURFACE L_3 STATE

Surface ordering becomes more like L_α as ϕ increases

So now what ?

NR/NS-SANS scan across the biphasic region
Effect of intrinsic curvature alone on surface state

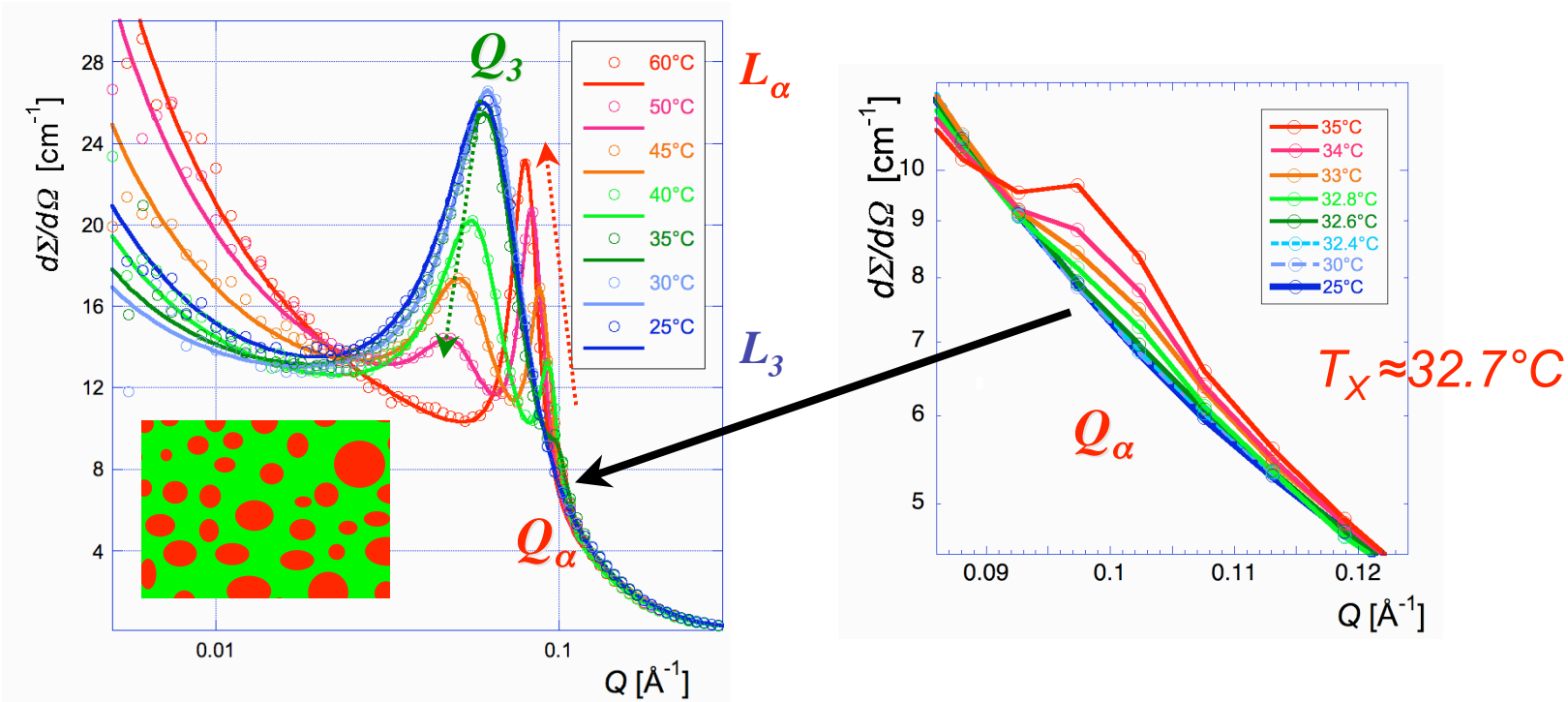


AOT/Brine topological control wrt T (tune with salt)
Stiffer than CpCl/Hexanol (double tail & no cosurfactant)
Expect less distortion of scaling by fluctuations

Transition across a miscibility gap: Conventional Bulk SANS

SANS 25%Aerosol-OT in 1.5vol% heavy brine vs T (25-60°C)

SAND instrument at IPNS



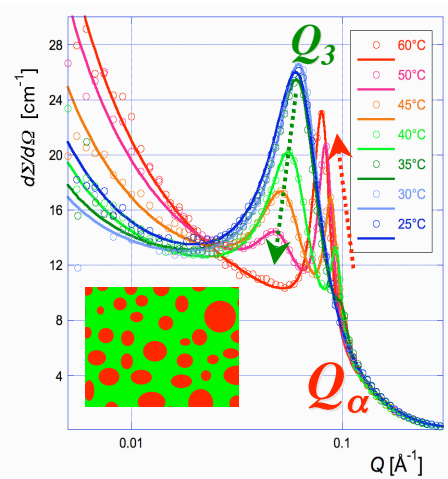
As temperature of initial L_3 phase is increased an L_α quasi-Bragg peak emerges from L_3 scattering at high Q, and strengthens as the L_3 correlation peak weakens, both peaks move to lower Q as T crosses biphasic region

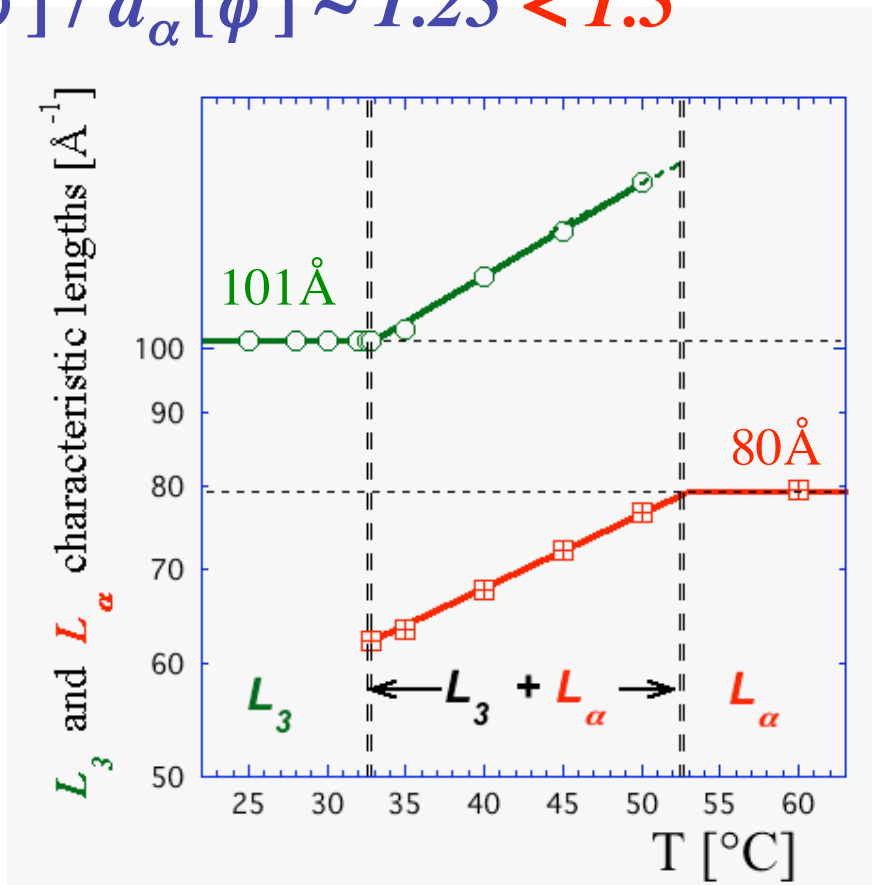
$$I[Q] = N\,P[Q]\,S[Q] + I_{bg} \cong \left(\frac{\pi\phi\sigma^2(\Delta\rho)^2}{(t_o+t_h)}\right)\left(\frac{4\left(1-\cos[Qt_o]\exp\left[-Q^2\delta_o^2/2\right]\right)}{Q^2\left(Q^2\sigma^2+2\exp\left(-Q^2\sigma^2/6\right)\right)}\right)\left(1+\frac{A_3}{Q}+\frac{B_3}{1+(Q-Q_3)^2\xi_3^2}+\frac{\left(A_\alpha/\xi_{OZ}^2\right)}{Q^2}+\frac{B_\alpha}{1+(Q-Q_\alpha)^2\xi_\alpha^2}\right)+I_{bg}$$

All you need to remember about this fit: Sponge correlation peak at Q_3 is described by a Lorenztian peak of amplitude ***"B_3"*** in the structure factor term ….

? Peak positions versus T across miscibility gap ?

$$\text{“ } C_3 / C_\alpha = d_3[\phi] / d_\alpha[\phi] \sim 1.25 < 1.5 \text{ ”}$$





L_3 and L_α peaks move more or less in unison across miscibility gap

<u>But</u> Ratio Q_α / Q_3 for coexistence varies from about **1.6** to **1.7** across the gap ($>1.5 \Rightarrow \phi_\alpha > \phi_3$)

Ratio Q_α / Q_3 between monophasic regions is (0.079±0.001)/(0.062±0.001) = 1.27±0.04

(for CPCl/Hexanol in Brine sponges we found 1.25 ±0.04 [Hamilton *et al.* *J. Chem. Phys.* **116**, 8533 (2002])

L_3 phase volume f_3 and volume/mass fraction X_3 in biphasic region

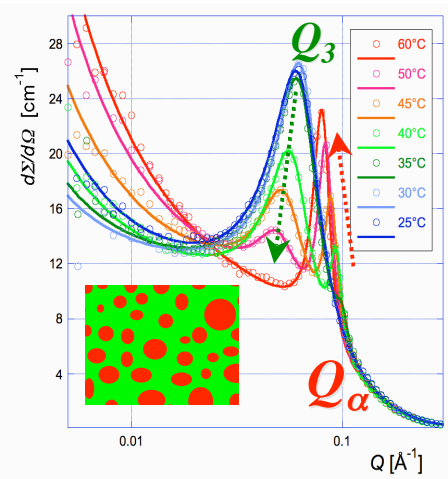
Isotropic sheet scattering scales as: $S(Q)\,\phi$ vs. Q/ϕ

G. Porte *et al.*, *J. Phys. (France)* **49**, 511 (1988) and **50**, 1335 (1989)

Assuming scaling holds for sponge over biphasic region can show:

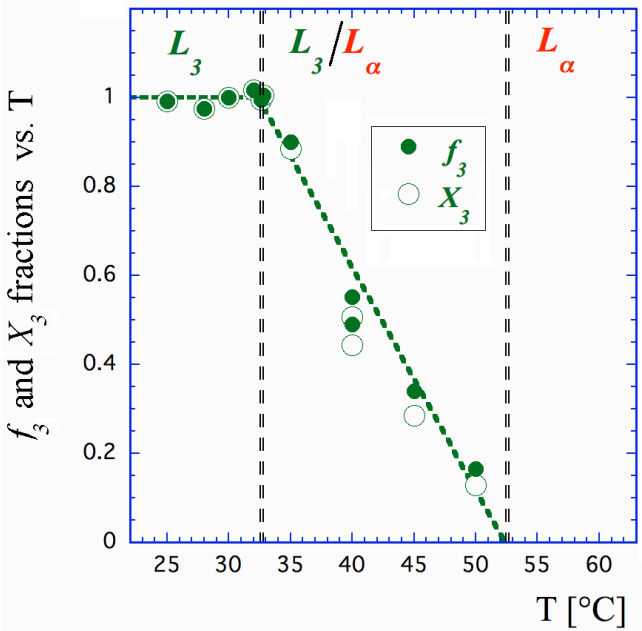
Phase occupancy fraction: $f_3[T] = (I_{33}[T]/I_{33}[T_3])(Q_3[T]/Q_3[T_3])$

Membrane volume/mass phase fraction: $X_3[T] = (I_{33}[T]/I_{33}[T_3])\,(Q_3[T]/Q_3[T_3])^2$



$I_{33}[T]=V_3\,S_3[Q_3\,[T]]$

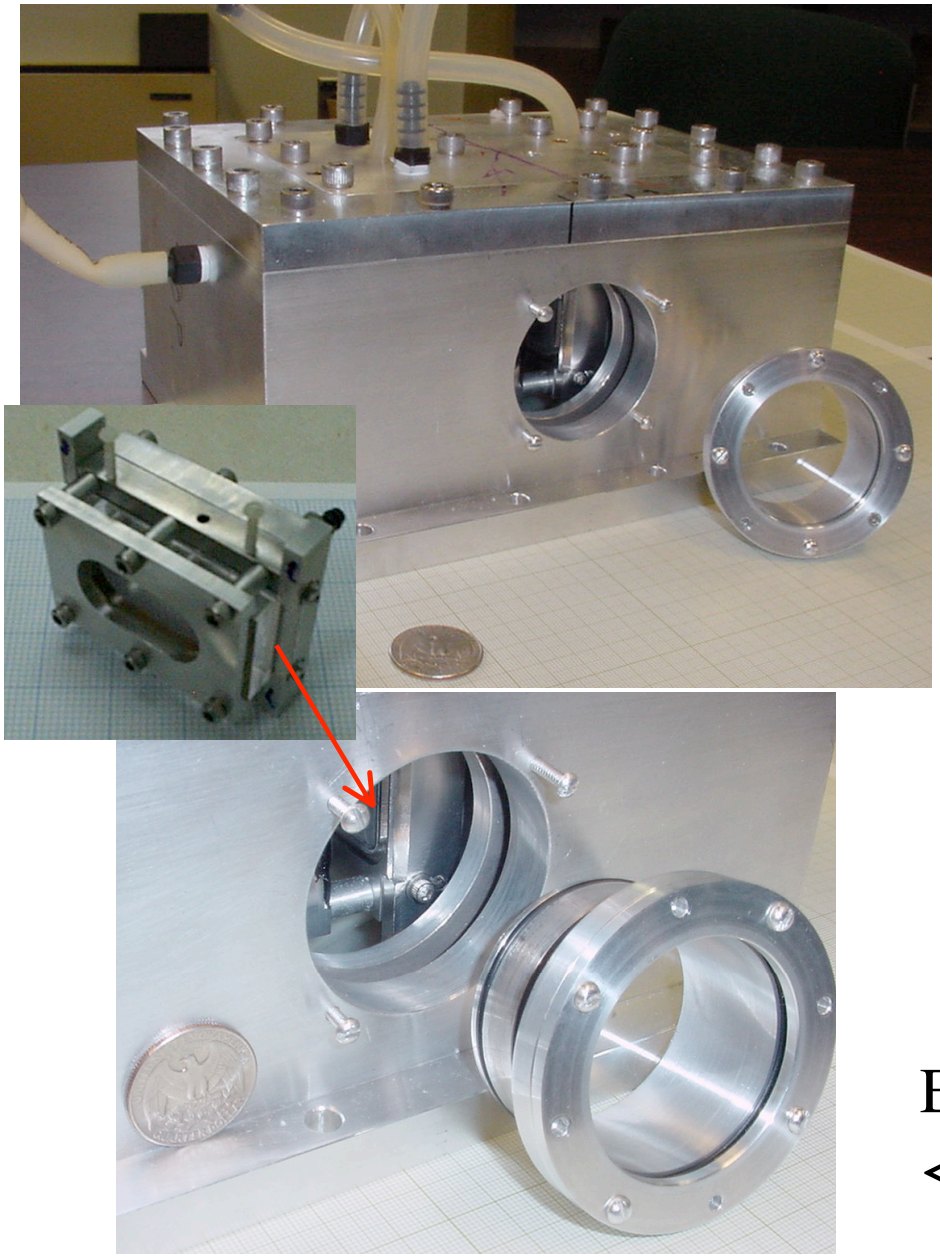
height of sponge structure factor peak in fits



Very near expected tie line => Scaling still works (similarity), but 1.6-1.7 ... ?

Also phase separation is slow (expected $\rho_{AOT} > \cong \rho_{D_2O}$)

AOT: Temperature gradients are a problem, so …



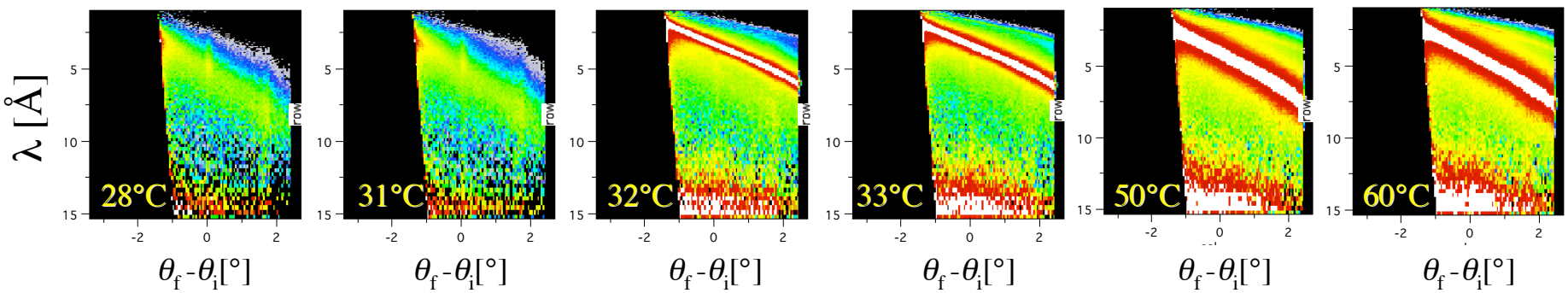
External temperature control box
<0.1°C over dimensions of Rcell

NR/NS-SANS for transition across miscibility gap

SANS 25%Aerosol-OT in 1.5vol% heavy brine vs T (28°C-60°C)

1st TOF attempt: **POSY-II/IPNS** (Raw/Spectrum/Vsol θ_R=1.5°)

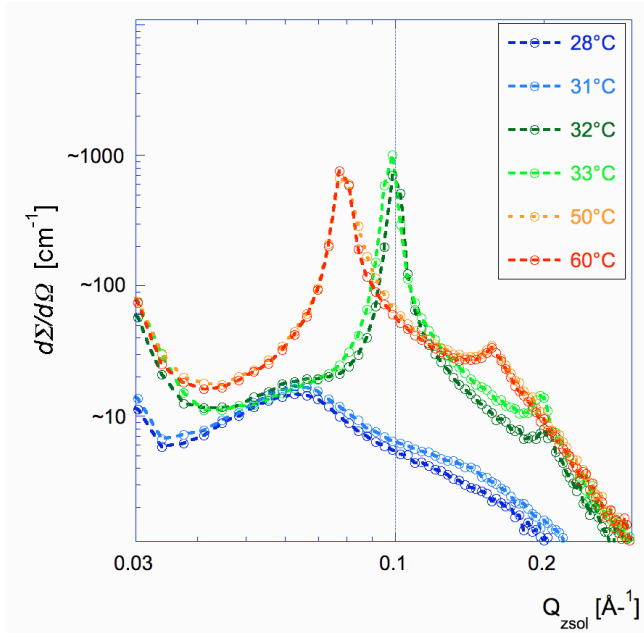
λ [Å] vs. θ_f-θ_i[°]: so specular is vertical at 0°



====== L_3 ===== || = $L_3(?)/L_\alpha$ ========== >>>>

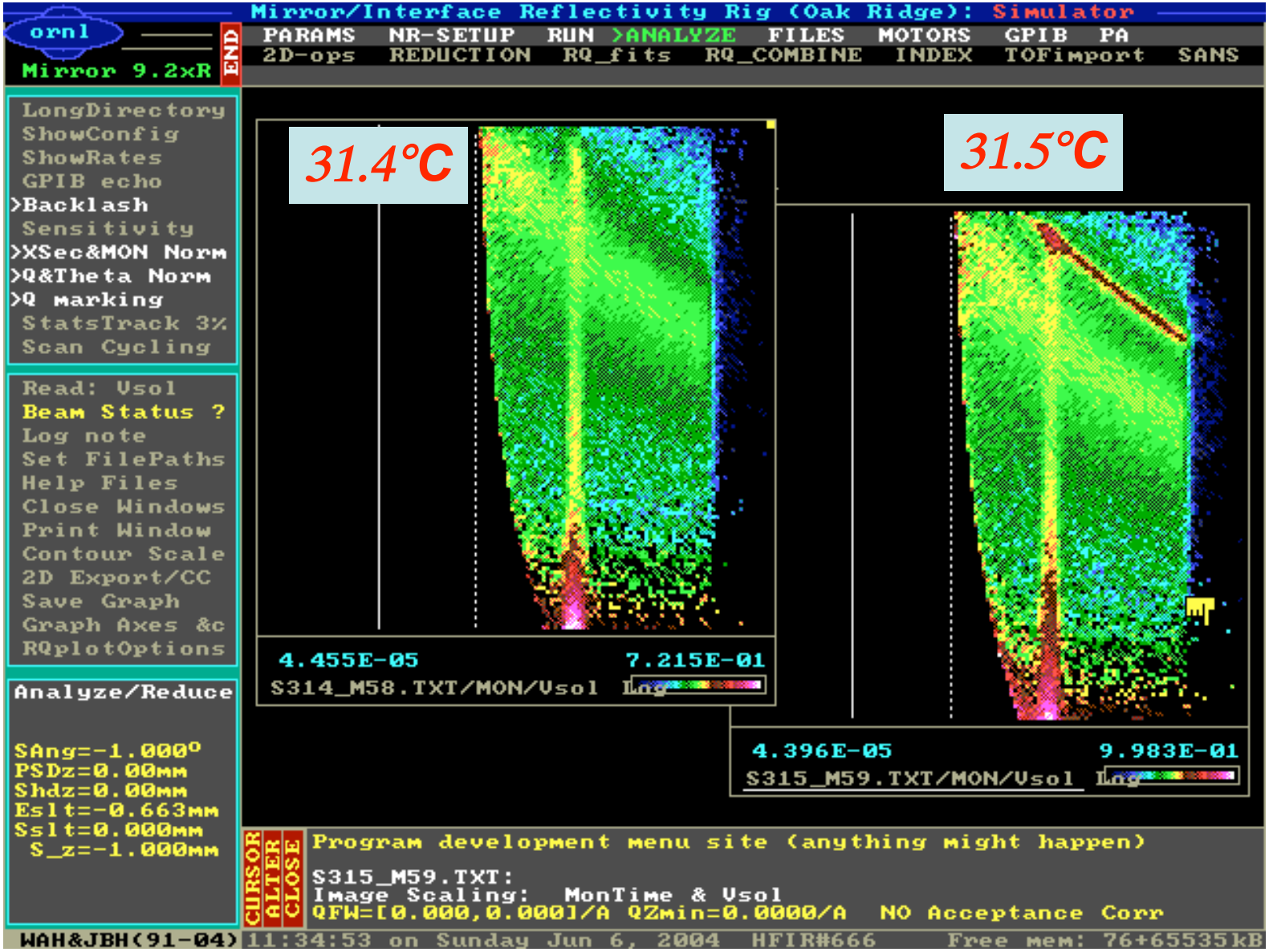
Some collimation/normalization problems (ours)
and a "hot spot" on the detector's RHS
and some pincushion distortion at the edges
but avoiding these:

- General progression with T as per bulk
- 1° L_α peak (0.1Å^{-1}->0.08Å^{-1}), get 2°
- Strong surface alignment
- L_α scattering overwhelming (MS√)



40°C
MIA …

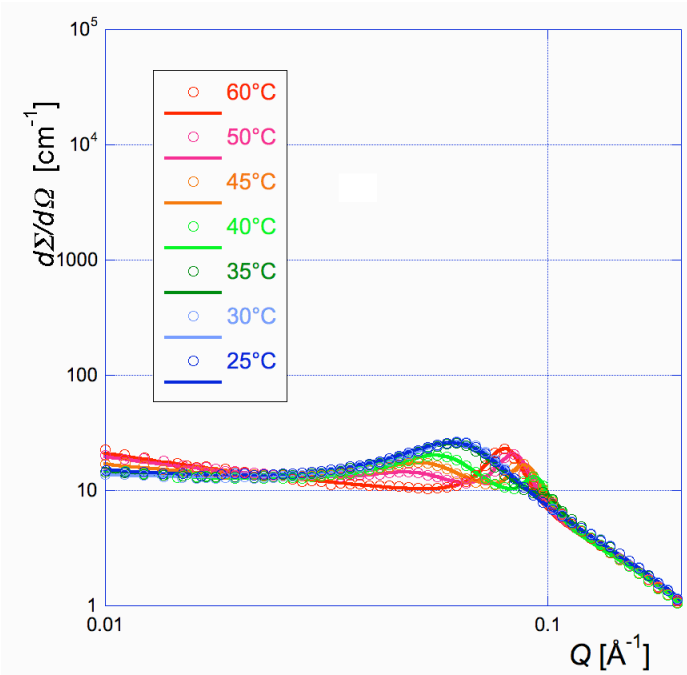
Above and below L_3 to L_3+L_α transition (T_X=31.45°C)

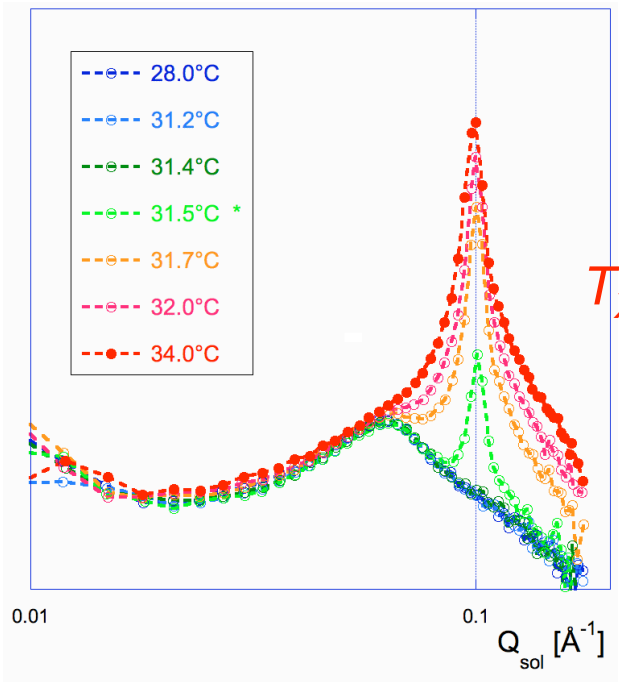


SPEAR/Lujan data imported into MIRROR/ORNL

NS-SANS near miscibility gap boundary (2)

SANS 25%Aerosol-OT in 1.5vol% heavy brine vs T (28-34°C)
SPEAR/Lujan (Raw/Spectrum/Vsol θ_R=0.62°)





$T_X \approx 31.45°C$

Bulk SANS SAND

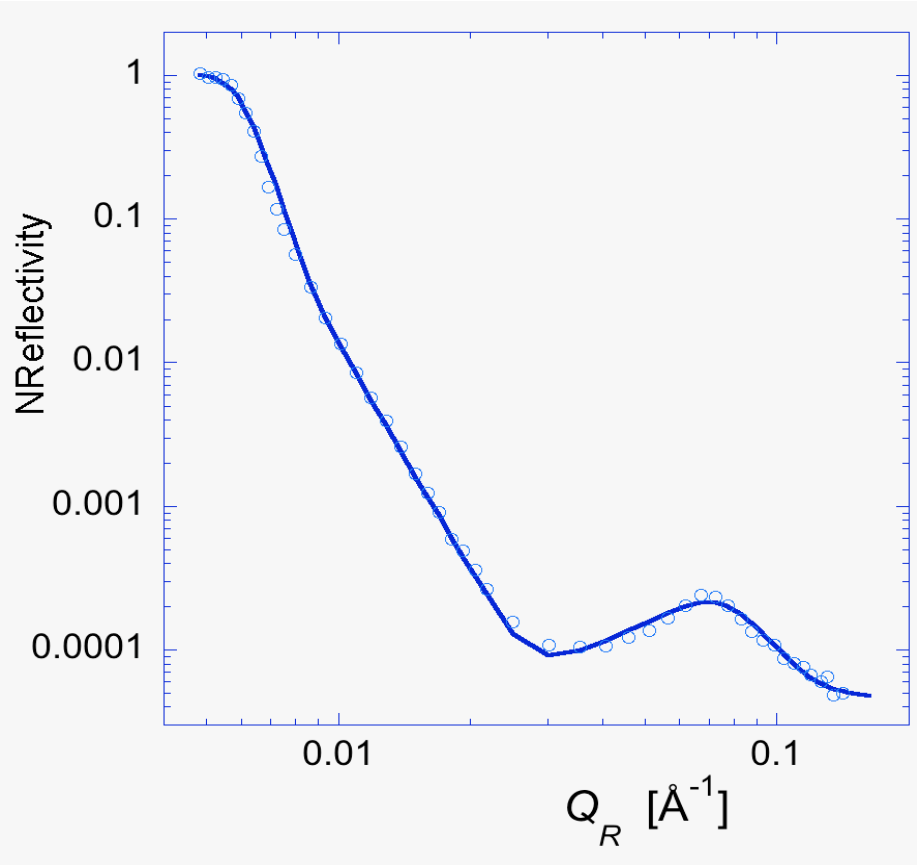
NS-SANS SPEAR√

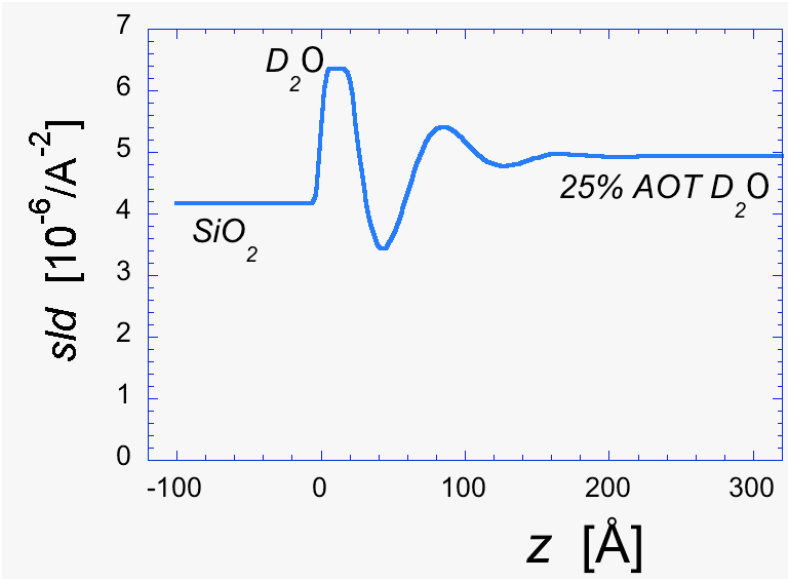
Below transition T<31.45°C NS-SANS constant

T>31.45°C NS-SANS vs bulk => significant L_α at and ~parallel surface
This is not phase coherent with the surface

Beginnings of NR analysis

Surface ordering 25% AOT in D2O brine at 28°C



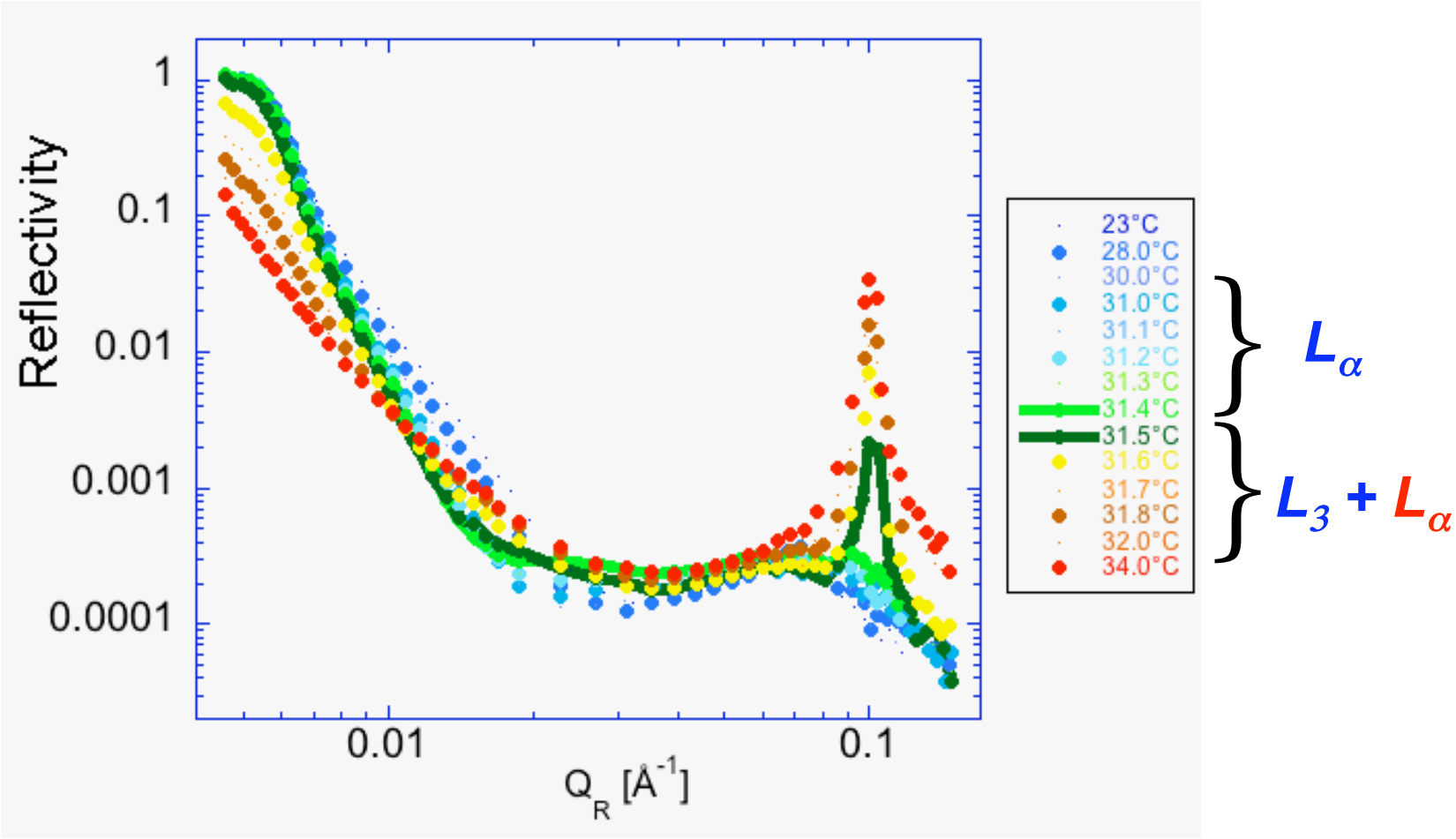


d_z= 84 Å τ/d_z = 0.44

(monophase d_3 = 101Å, $d\alpha$ = 80Å)

AOT is stiffer than CPCL/Hexanol => fewer oscillations
smaller range of surface ordering
~25Å pure D2O brine layer at SiO_2 surface (AOT anionic)

NR across miscibility gap boundary



Unlike NS-SANS precursor effects ... smaller d_z

Critical edge falloff above 31.45°C is consistent with bulk

$\phi_\alpha > \phi > \phi_3$ => as per bulk L_α more hydrogenous lowers sld

Concluding Questions

Why is $d_3 / d_\alpha \sim 1.7 > 1.5 > 1.25$ in biphasic region ?
What are the structural implications?

Shift in surface ordering peak (lower d_z)
as $L_3 / L_3 + L_\alpha$ phase boundary is approached?

Actual nature of near surface structures near boundary ?
(fits above 28°C are not very good)

The end