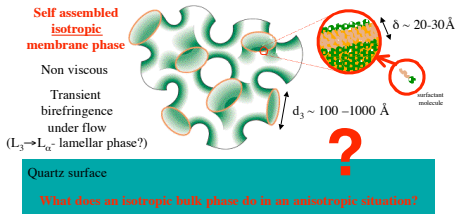
Surface conformation of surfactant sponge phases

W. A. Hamilton, L. Porcar and P. D. Butler, Center for Neutron Scattering, Oak Ridge National Laboratory
and
G. G. Warr, School of Chemistry, University of Sydney, Australia

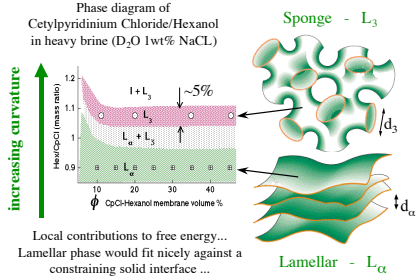
1. A question about the surfactant "sponge" phase - L_3



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

2. A probable answer is nearby in the phase diagram ...

Phase diagram of Cetylpyridinium Chloride/Hexanol in heavy brine (D_2O 1wt% NaCL)



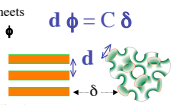
Local contributions to free energy...
Lamellar phase would fit nicely against a constraining solid interface ...

3. Scaling of membrane structures: The sheet equation and dilution "laws"

Correlation length **d** for structure of sheets of thickness **δ** with volume fraction **ϕ**

$$d\,\phi = C\,\delta$$

Inflexible **scaled** structures C constant
e.g. stiff flat lamellae C=1 ⇒ **ϕ=δ/d**
stiff sponge C~1.2-1.4



But, real systems are fluctuation stabilized
⇒ sheets ripple ⇒ more curvature
"excess area" increases C by some factor

e.g. "Real" L_α
C_α>1, $d_\alpha\phi$>δ

Fluctuations are thermodynamic – number of modes increases with available volume i.e. inversely with **ϕ** – so: **C=C[ϕ]≥C[ϕ=1]**

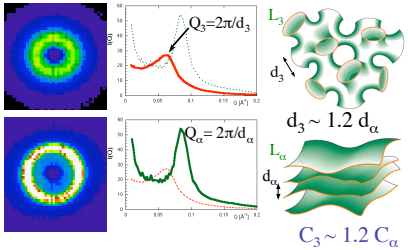
Quick take home lessons:

- More curvature: static (structure) **or** dynamic (fluctuations) ⇒ larger dϕ
- "Ideal" behavior if fluctuations are suppressed => dϕ=const ⇒ **scaling**

Not so fast (exercises for the reader): G. Porte *et al., J. Phys. (France)* **49**, 511 (1988) and **50**, 1335 (1989); W. Helfrich, *Z. Naturforsch* **33a**, 305 (1978) and *J. Phys.: Condens. Matt.* **6**(23A), A79 (1994); Roux *et al., Europhys. Lett.* **17**, 575 (1992); and W.A. Hamilton *et al., J. Chem. Phys.* (May 2002) ...

4. Relation of characteristic lengths d_3 and d_α

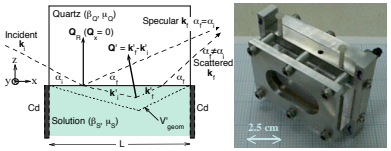
from SANS – ϕ=35vol% sponge and lamellar phases



"12m" SANS instrument - ORNL High Flux Isotope Reactor

5. Neutron Reflectometry and "Near Surface" SANS Reflection geometry Quartz-Solution cell

Surface proximity effects on membrane phase morphology and fluctuations

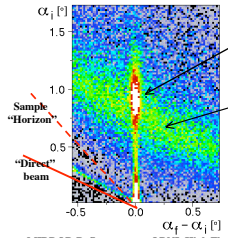


1 mm deep solution trough beneath polished Quartz slab (3Å rms roughness)

Neutron Reflectometer MIRROR - ORNL High Flux Isotope Reactor:
λ=2.59Å
SD=3.4m Ordela PSD detector 100mm x 1mm (0.3mrad) in reflection (k_i,k_f) plane

6. NR and off-specular NS-SANS (in plane)

35vol% CpCl/Hexanol sponge Quartz-Solution cell



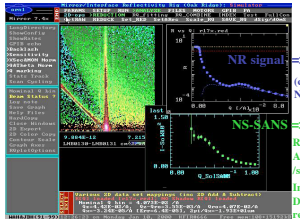
Specular NR signal ($\alpha_i = \alpha_f$) peak at higher Q than and at noticeable offset to …

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

7. MIRROR data collection and reduction program



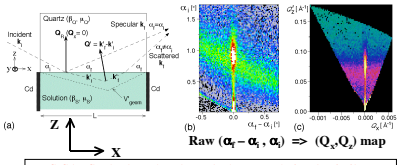
⇒ $R[Q_R]$ vs Q_R
(correctly) subtracts NS-SANS background

⇒ $d\Sigma/d\Omega$ vs Q_S
Refraction, Absorption /sample volume, Interface Transmissions, Detector/instrument resolution …

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)

8. Partial NS-SANS reduction:

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



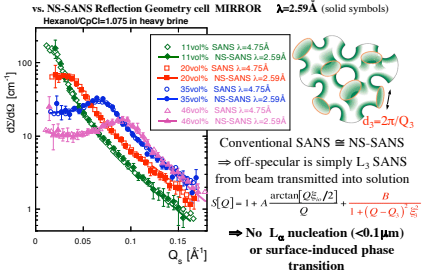
Raw ($\alpha_f - \alpha_i$, α_i) ⇒ (Q_x,Q_z) map

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

Correct for transverse (y) resolution: $Q_S \approx \sqrt{Q_x^2 + (\delta Q_x)^2 + Q_z^2}$ …

9. SANS versus NS-SANS ("All SANS patterns look the same")

Conventional bulk SANS "12m" SANS instrument λ=4.75Å (open symbols)
vs. NS-SANS Reflection Geometry cell MIRROR λ=2.59Å (solid symbols)
Hexanol/CpCl=1.075 in heavy brine



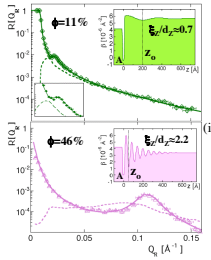
Conventional SANS ≅ NS-SANS
⇒ off-specular is simply L_3 SANS from beam transmitted into solution

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

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

Quick take home corollary: Interesting looking off-specular scattering isn't necessarily. Analyze your data & be wary of picture shows.

10. Specular Neutron Reflectivity Analysis



Scattering length density β[z] profile normal to interface:

(i) Quartz (β_Q=4.17x10^{-6} Å^{-6})

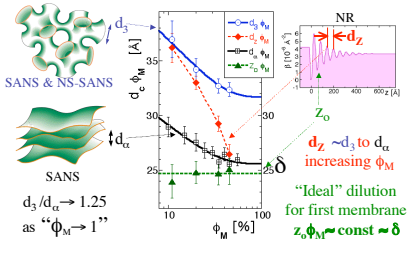
(ii) Adsorbed bilayer
(expected: since CpCl is a cationic surfactant and quartz a negatively charged surface)

(iii) Symmetric decaying oscillation to bulk solution membrane concentration (β_s)

Periodicity d_Z
Exponential decay ξ_Z
z_o offset ⇔ "1st" in-solution membrane

ξ_Z / d_Z increases with ϕ_M

11. Dilution law behavior of length scales



d_Z ~d_3 to d_α increasing ϕ_M

"Ideal" dilution for first membrane
$z_o\phi_M$ ≈ const ≈ δ

12. Conclusions

- SANS/NS-SANS: No surface-induced phase change or nucleation of L_α phase
- NR: (i) Adsorbed surface layer. Near full bilayer coverage (>94% for all ϕ)
- NR: (ii) At low ϕ_M d_Z≈d_3, but proximate surface region becomes "quasi-lamellar" at higher membrane concentrations: $d_Z \rightarrow d_\alpha$ & increasing ξ_Z/d_Z
  Interpret as suppression of fluctuations that stabilize L_3 structure?
  (analogy with shear-induced L_3 to L_α transformations)
- NR: (iii) "Ideal" scaling/dilution behavior of z_o. Surface constraint supresses fluctuations of solution membrane nearest to surface for all ϕ ?
  (Caveat: Our 1° model is single mode in oscillation. z_o is not necessarily a very good measurement of this separation.)
- **Need a theory of surface constrained membrane morphology**

W.A. Hamilton, L. Porcar, P.D. Butler and G.G. Warr,
"Local membrane ordering of sponge phases at a solid-solution interface",
***Journal of Chemical Physics* 116, 8533 (2002)**

(• PS: The modification of dilution law behavior presented in the JCP fits bulk SANS data well)

Research supported by the US Department of Energy, Division of Materials Science, under contract DE-AC05-00OR22725 with UT-Batelle LLC which manages the Oak Ridge National Laboratory.