

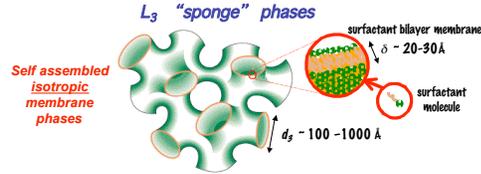
Topological Relaxation of a Shear-induced Lamellar L_α Phase to L_3 Sponge Equilibrium and the Energetics of Bilayer Membrane Fusion

W. A. Hamilton,¹ L. Porcar,^{1→2} P.D. Butler,^{1→2} and G.G. Warr³

¹Center for Neutron Scattering, Oak Ridge National Laboratory, Oak Ridge TN 37831-6393 USA

²National Institute of Standards and Technology, Center for Neutron Research, Gaithersburg, MD20899-8562 USA

³School of Chemistry, University of Sydney, Sydney, Australia

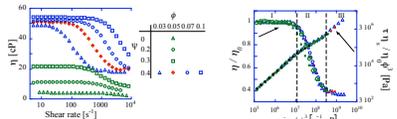


A convoluted solution spanning labyrinth of membrane passages (topologically "handles" in the membrane manifold)
Typically *very* fluid - no response to applied shear - Newtonian creation/destruction & rapid realignment of passages relieves stress

A stronger rheological response: the "sweetened" sponges

Strategy: add inert thickener to membrane solvent - viscosity η_s
Slows membrane dynamics - strengthens response to applied shear

Rheology of Cetylpyridinium(CPCl)-Hexanol L_3 in dextrose-brine solvent



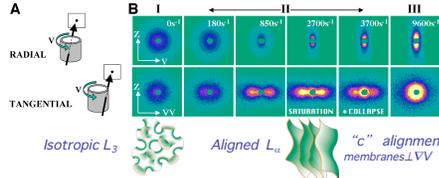
Up to 40vol% dextrose in brine solvent η_s from 1 to 16.3cP

Shear thins at high values of rescaled shear rate parameter: $\dot{\gamma}\eta_s/\phi^3$

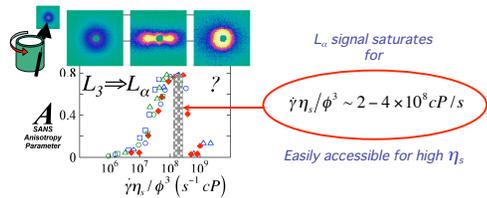
Structural response of the "sweetened" sponges

Small Angle Neutron Scattering (SANS) from $\phi=5\text{vol}\%$ CPCl-hexanol in 40vol% dextrose-brine ($\eta_s=16.3\text{cP}$)

Equilibrium L_3 to Couette Shear-induced L_α state transformation



What we have so far: A "passage free" non-equilibrium state



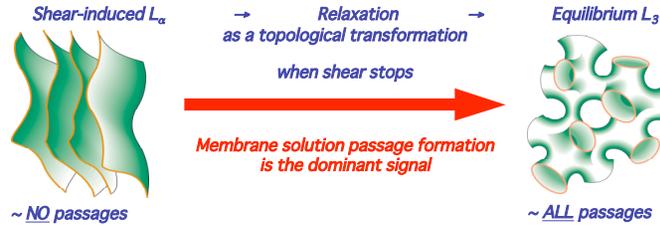
A tunable shear-induced L_3 to L_α transformation

Well characterized:

L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, Physical Review Letters **88**:168301 (2002) & Langmuir **19**:10179 (2003)

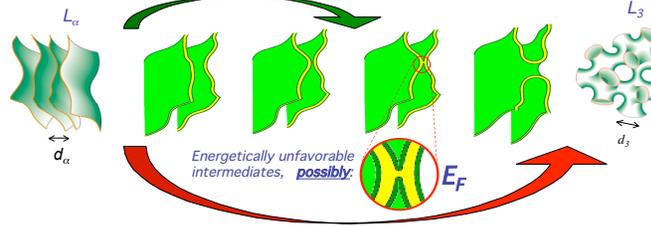
So what can we do with it?

While the fusion of membranes to create a solution passage is important in surfactant chemistry and crucial in cell biology, it also generally occurs relatively infrequently or against a confusing background of other phenomena or responses, but ...



Energetics of passage formation: an activated process

τ_c Diffusive contact interval

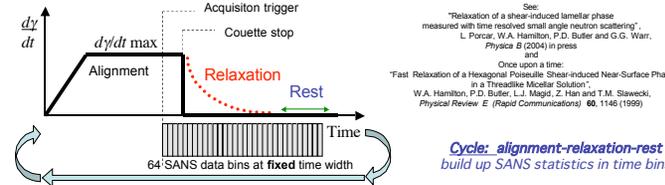


$$\text{Topological relaxation time } \tau_R = \tau_c \exp[-E_F/k_B T]$$

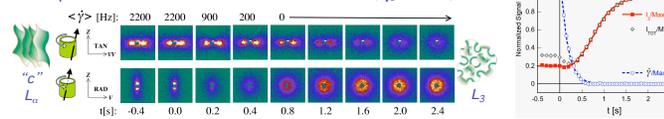
S. T. Milner, M.E. Cates and D. Roux, J. Phys. (Paris) **51**, 2629 (1990)

Determination of τ_R - "t-SANS" (When things are a little too fast for normal SANS)

Even at highest η_s , τ_R ~ seconds \Rightarrow "time sliced" cycled SANS (NIST-NG7)



Example: t-SANS Shear-induced L_α to equilibrium L_3 relaxation $\phi=5\text{vol}\%$ CPCl-hexanol in 40vol% dextrose-brine ($\eta_s=16.3\text{cP}$)



Shear aligned at $\dot{\gamma}\eta_s/\phi^3 \sim 3 \times 10^5 \text{ cP/s}$ ~ center L_α signal plateau

When Couette cell is stopped L_3 signal (passages) re-established $\tau_R = 0.40 \pm 0.08 \text{ s}$

Determination of $\tau_c(1)$ - SANS

We already know: L_α signal saturates for $\dot{\gamma}\eta_s/\phi^3 \sim 2 - 4 \times 10^8 \text{ cP/s}$

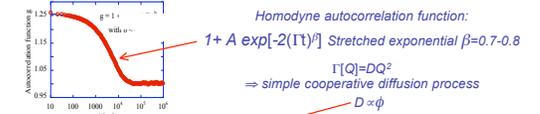
Applied shear rate (s^{-1}) represents 1/time which totally frustrates (re)formation of disrupted membrane passages

$$\text{So expect } \tau_c \sim \frac{1}{\dot{\gamma}_{\text{saturation}}} \sim \frac{\eta_s/\phi^3}{2 - 4 \times 10^8 \text{ cP/s}} \quad (\text{shaded below})$$

Determination of $\tau_c(2)$ - Dynamic Light Scattering

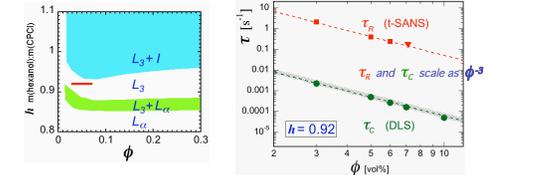
DLS measures membrane diffusion rates

\Rightarrow time to bring membranes separated by a mean separation d_α into contact



Homodyne autocorrelation function:
 $1 + A \exp[-2(\Gamma t)^\beta]$ Stretched exponential $\beta=0.7-0.8$
 $\Gamma[Q]=DQ^2$
 \Rightarrow simple cooperative diffusion process
 $D \propto \phi$
Shear-induced L_α separation $d_\alpha \propto 1/\phi$
 $\Rightarrow \tau_c \approx 1/[Q_\alpha] = 1/DQ_\alpha^2$
where $Q_\alpha = 2\pi/d_\alpha \propto \phi$
 $\Rightarrow \tau_c \propto 1/\phi^3$ (agrees with Shear-induced L_α plateau)

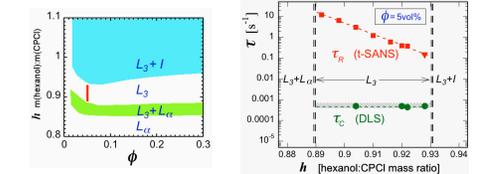
τ_R and τ_c versus membrane volume fraction ϕ



Arrhenius relationship $\tau_R = \tau_c \exp[-E_F/k_B T] \Rightarrow E_F = 6.7 k_B T$ (170 meV)

τ_R and τ_c versus membrane composition hexanol to CPCl mass ratio h

Change membrane composition, i.e. properties, cross L_3 phase region



Increasing $h \Rightarrow$ increasing Gaussian curvature of membrane structures

\Rightarrow Decreasing energy cost of passages (and stalk structures)

4% increase in $h \Rightarrow E_F = 10.3 k_B T$ (260 meV) down to $5.8 k_B T$ (150 meV)

Conclusions

Topological relaxation of shear-induced to equilibrium L_3

t-SANS measurement of membrane passage formation time τ_R

DLS determination and alignment shear rates agreement

on interval between diffusion driven membrane contacts τ_c

\Rightarrow Activation energy for membrane fusion (handle creation) $E_F \sim 5 - 10 k_B T$

E_F constant wrt ϕ (\Rightarrow constant barrier state - stalk/TMC ?)

E_F linear decrease wrt h across L_3 phase region ($=$ Curvature modulus ?)

Future: Application of technique to (quasi-)biological system?

Identify (or engineer) lipid system with suitable relaxation mode