# Topological Relaxation of a Shear-induced Lamellar $L_\alpha$ Phase to $L_3$ Sponge Equilibrium and the Energetics of Bilayer Membrane Fusion*

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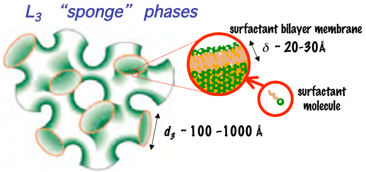
## $L_3$ "sponge" phases

Self assembled *isotropic* membrane phases




A convoluted solution spanning labyrinth of membrane passages (topologically "handles" in the membrane manifold)

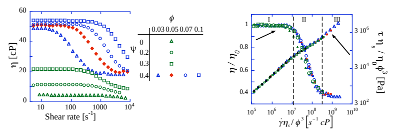
Typically *very* fluid - no response to applied shear ~ Newtonian creation/destruction & rapid realignment of passages relieves stress

## A stronger rheological response: the "sweetened" sponges

Strategy: add inert thickener to membrane solvent - viscosity $\eta_s$

Slows membrane dynamics - strengthens response to applied shear

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



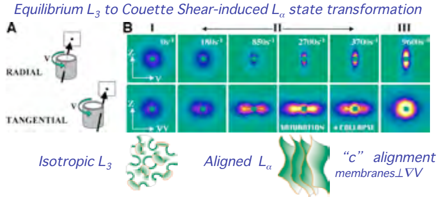

Up to 40vol% dextrose in brine solvent $\eta_s$ from 1 to 16.3cP

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

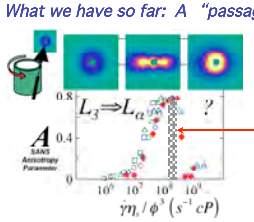
## Structural response of the "sweetened" sponges

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

Equilibrium $L_3$ to Couette Shear-induced $L_\alpha$ state transformation




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




$L_\alpha$ signal saturates for

$\dot{\gamma}\eta_s/\phi^3 \sim 2-4\times10^8 cP/s$

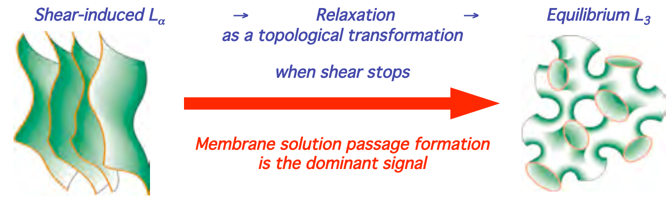
Easily accessible for high $\eta_s$

A tunable shear-induced $L_3$ to $L_\alpha$ transformation

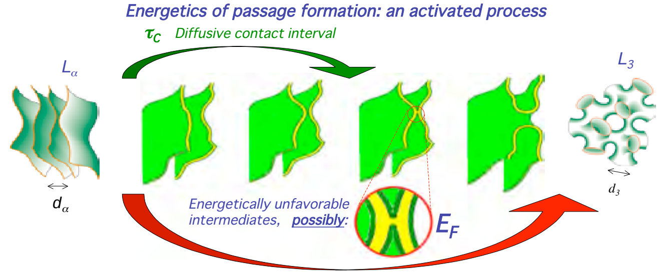
Well characterized:
L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, *Physical Review Letters* **89**,168301 (2002) & *Langmuir* **19**, 10779 (2003)

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

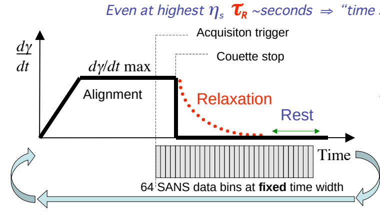



Topological relaxation time $\tau_R = \tau_C\ \exp[-E_F/k_BT]$

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

## Determination of $\tau_R$ - "t-SANS" (When things are a little too fast for normal SANS)

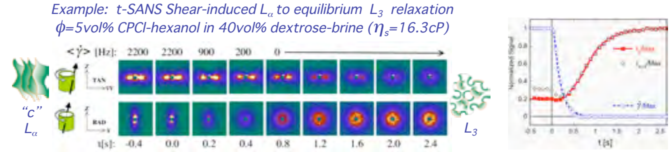
Even at highest $\eta_s$ $\tau_R$ ~seconds ⇒ "time sliced" cycled SANS (NIST-NG7)




See:
"Relaxation of a shear-induced lamellar phase measured with time resolved small angle neutron scattering", L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, *Physica B* **350**, e963 (2004)
and
Once upon a time:
"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)

*Cycle:* alignment-relaxation-rest
build up SANS statistics in time bins

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




Shear aligned at $\dot{\gamma}\eta_s/\phi^3 \sim 3\times10^8 cP/s$ ~ center $L_\alpha$ signal plateau

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

## Determination of $\tau_C$ (1) - SANS

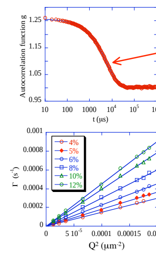
We already know: $L_\alpha$ signal saturates for $\dot{\gamma}\eta_s/\phi^3 \sim 2-4\times10^8 cP/s$

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

So expect $\tau_C \sim \frac{1}{\dot{\gamma}_{Saturation}} \sim \frac{\eta_s/\phi^3}{2-4\times10^8 cP/s}$ (shaded below)

## Determination of $\tau_C$ (2) - Dynamic Light Scattering

DLS measures membrane diffusion rates
⇒ time to bring membranes separated by a mean separation $d_\alpha$ into contact




Homodyne autocorrelation function:
1+ A exp[-2(Γt)$^\beta$] Stretched exponential $\beta$=0.7-0.8

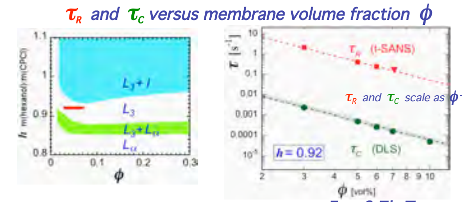
Γ[Q]=DQ²
⇒ simple cooperative diffusion process
$D\propto\phi$

Shear-induced $L_\alpha$ separation $d_\alpha \propto 1/\phi$

⇒ $\tau_C \approx 1/\Gamma[Q_\alpha]=1/DQ_\alpha^2$
where $Q_\alpha=2\pi/d_\alpha \propto \phi$

⇒ $\tau_C \propto 1/\phi^3$ (agrees with Shear-induced $L_\alpha$ plateau)

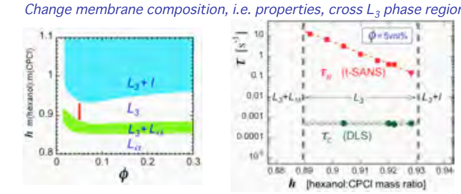
## $\tau_R$ and $\tau_C$ versus membrane volume fraction $\phi$




Arrhenius relationship $\tau_R = \tau_C\ \exp[-E_F/k_BT]$ ⇒ $E_F$ = 6.7$k_BT$ (170 meV)

## $\tau_R$ and $\tau_C$ versus membrane composition hexanol to CPCl mass ratio $h$

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




Increasing $h$ ⇒ increasing Gaussian curvature of membrane structures
⇒ *Decreasing* energy cost of passages (and stalk structures)
4% increase in $h$ $E_F$= 10.3$k_BT$ (260 meV) down to 5.8$k_BT$ (150 meV)

## Conclusions

Topological relaxation of shear-induced to $L_\alpha$ to equilibrium $L_3$
t-SANS measurement of membrane passage formation time $\tau_R$
DLS determination and alignment shear rates agreement
on interval between diffusion driven membrane contacts $\tau_C$
⇒ Activation energy for membrane fusion (handle creation) $E_F$ ~ 5 - 10 $k_BT$
$E_F$ constant wrt $\phi$ (⇒ *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

*"Topological relaxation of a shear-induced lamellar phase to sponge equilibrium and the energetics of membrane fusion", L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, *Physical Review Letters* **93**, 198301 (2004)
This Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC for the U. S. Department of Energy under Contract DE-AC05-00OR22725.
The NG7 SANS instrument is operated by the NIST, U.S. Department of Commerce, with funding from the U.S. National Science Foundation under Agreement No. DMR-9986442.
G.G.W. acknowledges Australian Nuclear Science and Technology Organization and Australian Research Council support.