Relaxation of shear-induced complex fluid states using time resolved SANS ....

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Greg Warr - U Sydney
B. Hammouda - NIST

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.

SNS/HFIR User Meeting 11-13 October 2005

Two examples

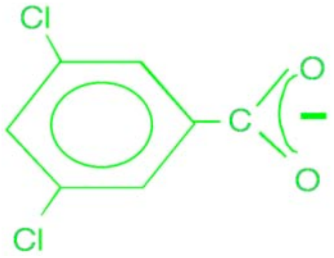
(1) Relaxation of a Poiseuille shear-induced surface state

Melting of a crystalline state
in a threadlike micellar system

(2) Relaxation of a Couette shear-induced bulk state

The kinetics and energetics
of
passage formation in membrane phases

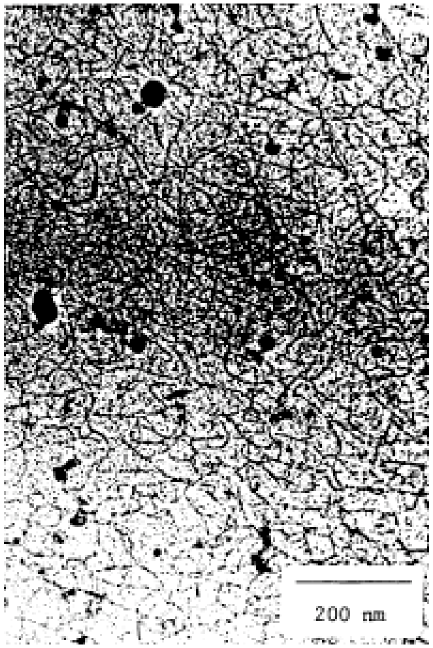
Threadlike micelles (CTA35ClBz)



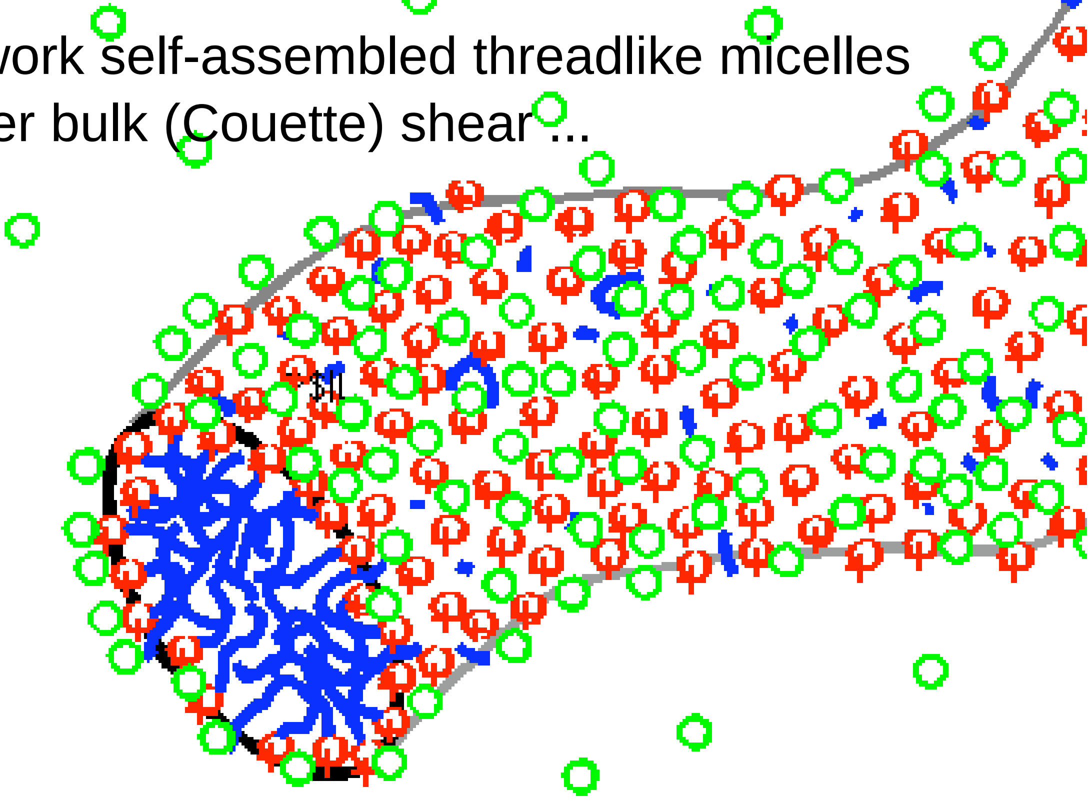
$+N(CH_3)_3 - (CH_2)_{15} - CH_3$

Macroscopically: Even quite dilute solutions are thick, but viscoelastic & shear thinning

Microscopically: Entangled network self-assembled threadlike micelles which SANS shows line up under bulk (Couette) shear ...

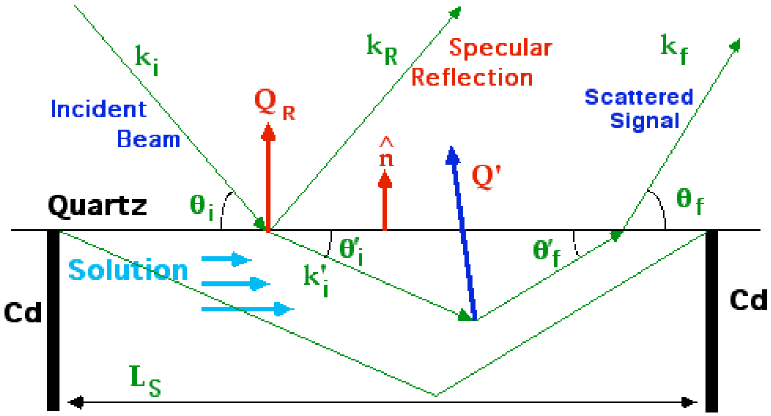


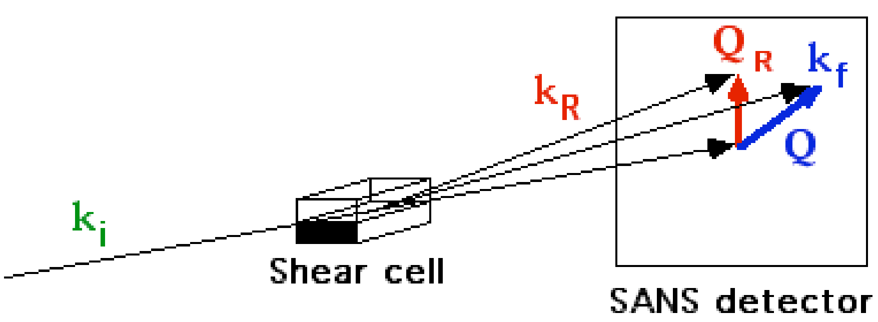
CryoTEM micrograph of pure 3,5diChloroBenzoate micelles
L.J. Magid, J.C. Gee & Y. Talmon, Langmuir **6**, 1609 (1990)



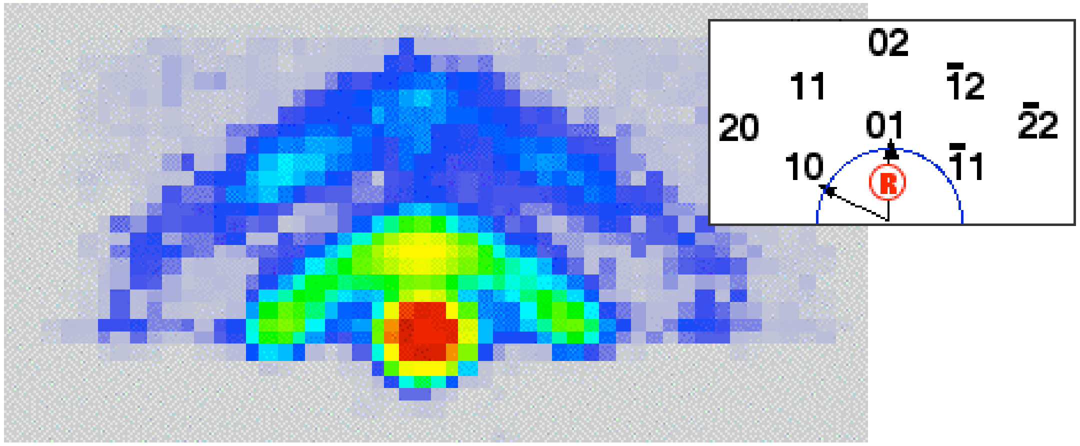
30Å diameter, 1000’s Å long ...

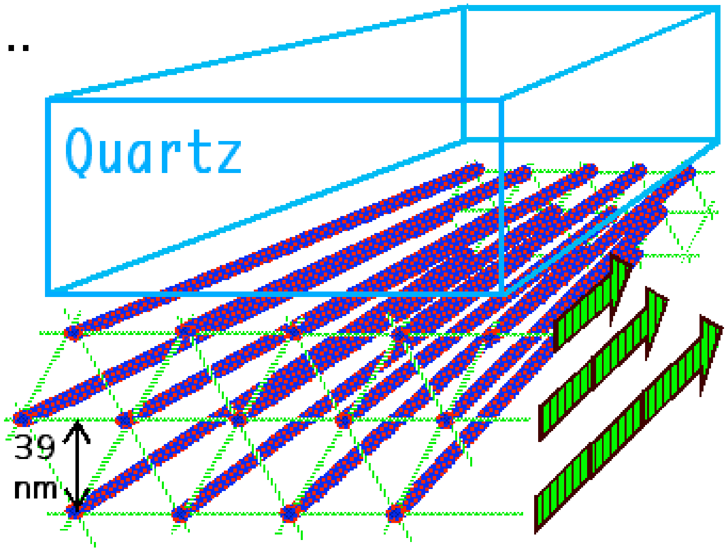
Poiseuille shear response of mixed counterion 20mM 70% CTA35ClBz & 30% CTABr threadlike micelles





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





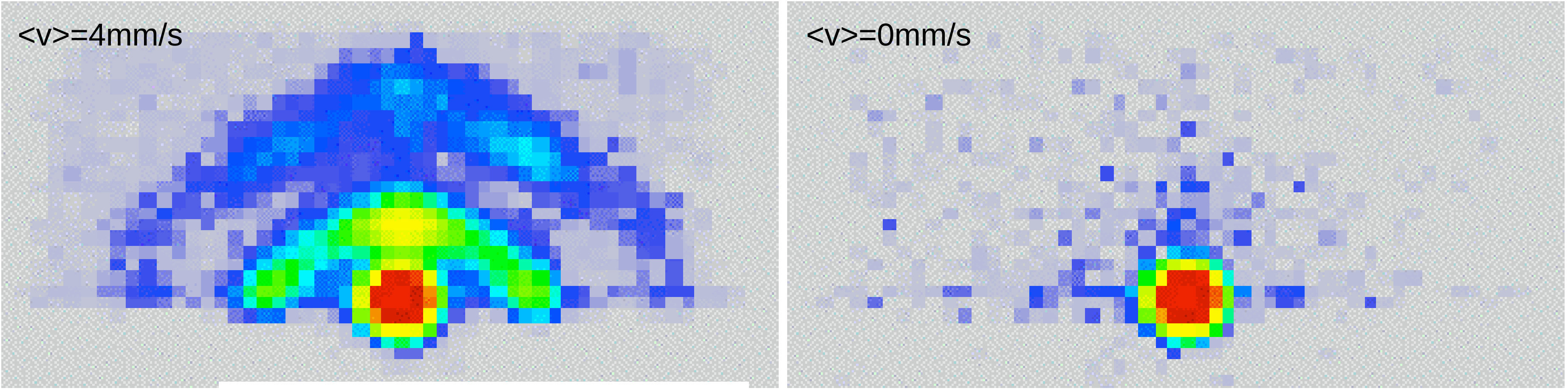
Grazing incidence “Near Surface” SANS data (<~100micron) from surface

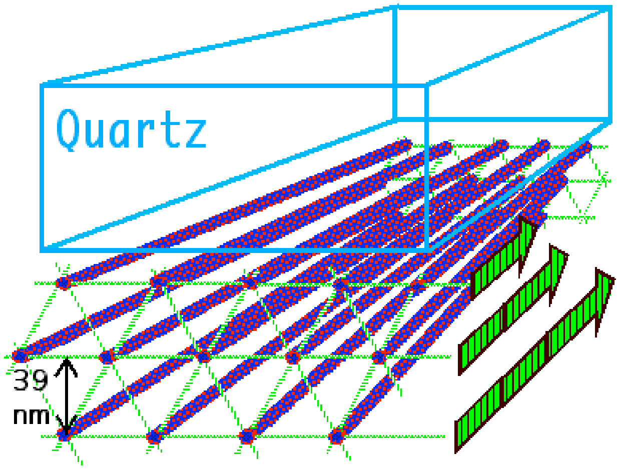
W.A. Hamilton, P.D. Butler, S.M. Baker, G.S. Smith, J.B. Hayter, L.J. Magid and R. Pynn, *Physical Review Letters* **72**, 2219 (1994)
W.A. Hamilton, P. D. Butler, John B. Hayter, L. J. Magid and P. J. Kreke, *Physica B* **221**, 309 (1996)

A question of relaxation when shearing flow stopped:

Couette measurements => slow bulk micellar rentanglement ~30min

But surface Xtal state apparently disappeared “immediately” ~seconds



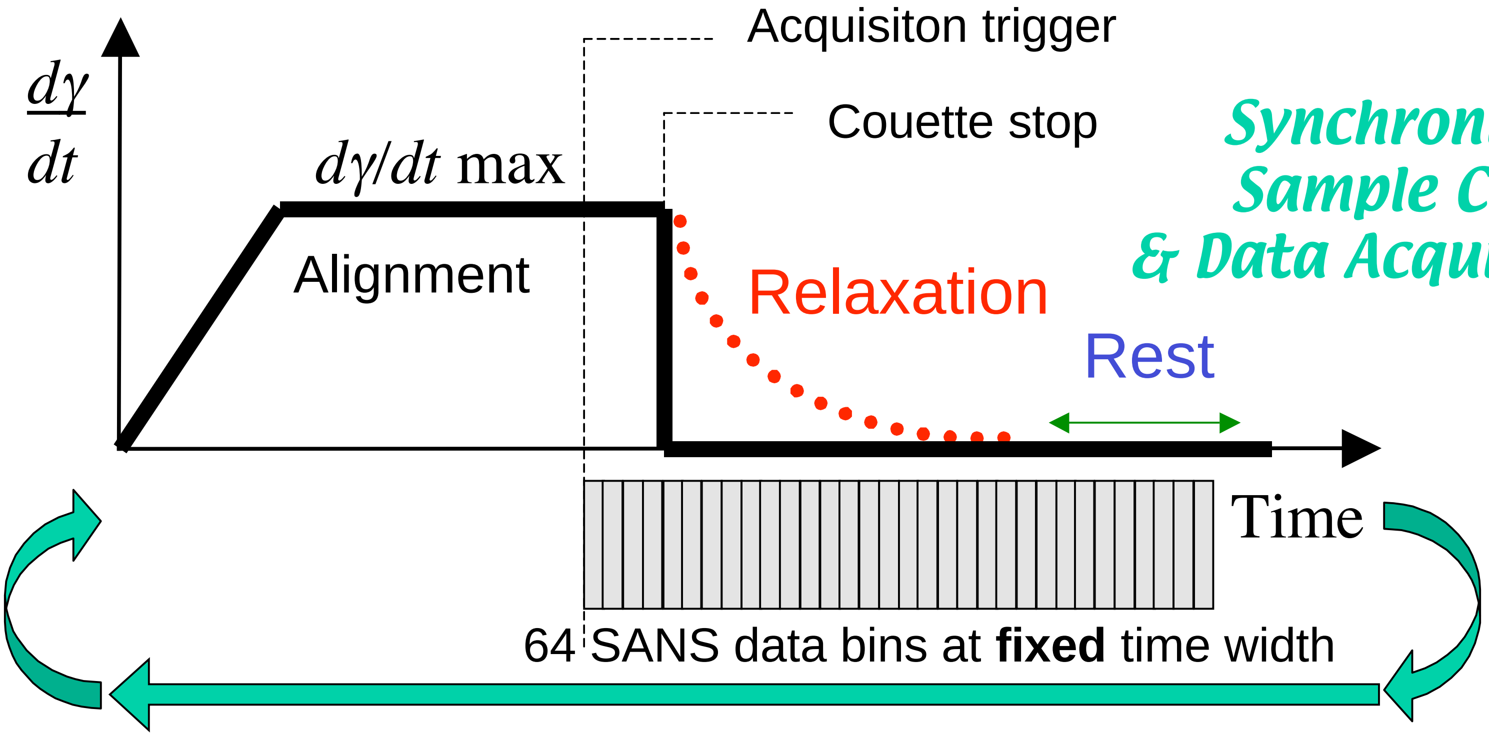


Where does it go ...
how does it relax ?

When things are (a little) too fast for SANS - "t-SANS"

Cycled multiplexed synchronized data collection

*Very fast (for SANS) ⇒ "time sliced" cycled **SANS (NIST-NG7)***



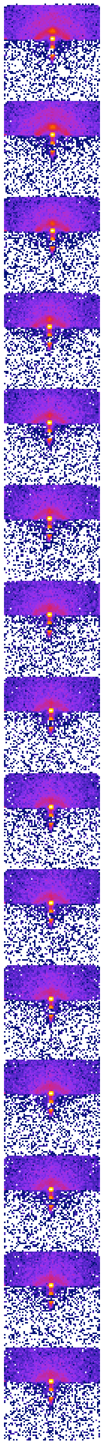
64 SANS data bins at **fixed** time width

Synchronize Sample Cell & Data Acquisition

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

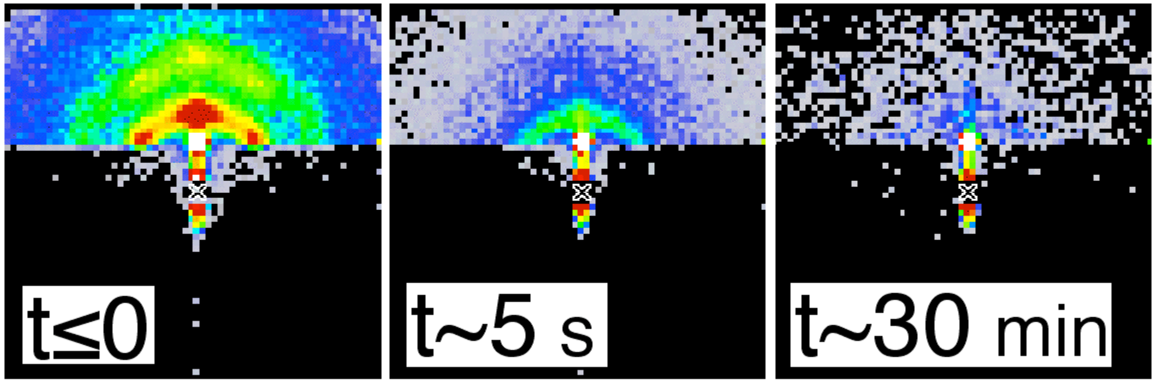
"Relaxation of a shear-induced lamellar phase measured with time resolved small angle neutron scattering", L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, *Physica B* **350**, e963 (2004)

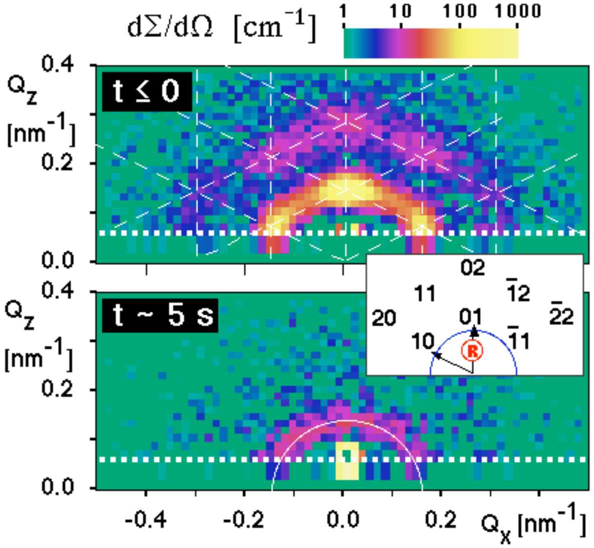
Once upon a time: "Fast Relaxation of a Hexagonal Poiseuille Shear-induced Near-Surface Phase in a Threadlike Micellar Solution", W.A. Hamilton, P.D. Butler, L.J. Magid, Z. Han and T.M. Slawecki, *Physical Review E (Rapid Communications)* **60**, 1146 (1999)

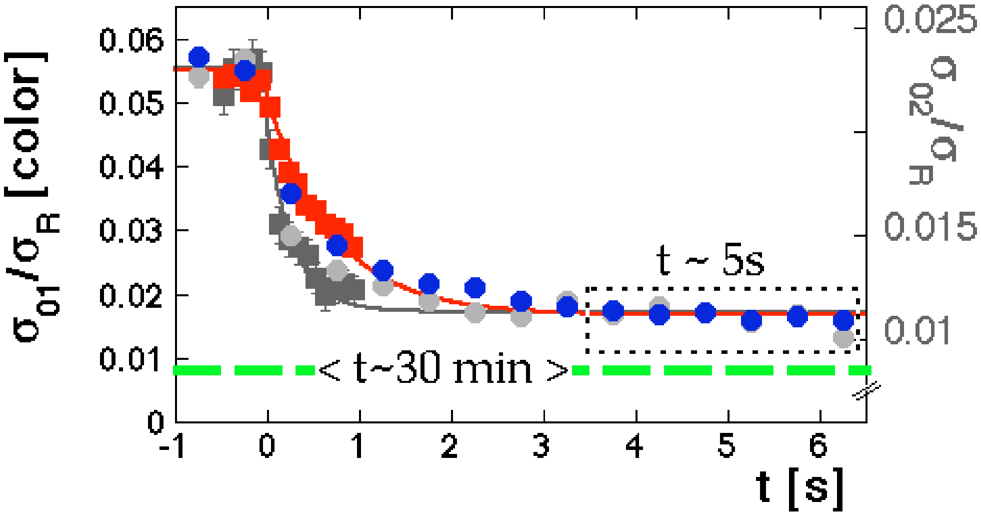


What we saw in threadlike micelle relaxation

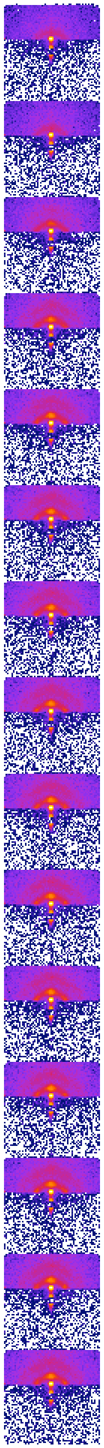
0.1s and 0.5s multiplexed data reveals a two stage process

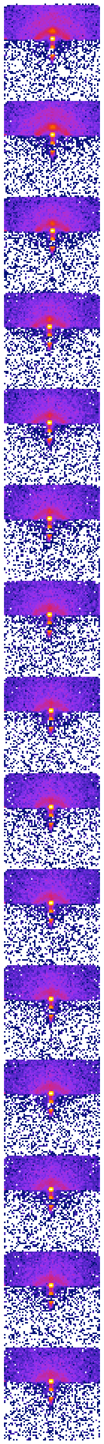






Xtal phase 01 peak fast decay time 0.7±0.2s





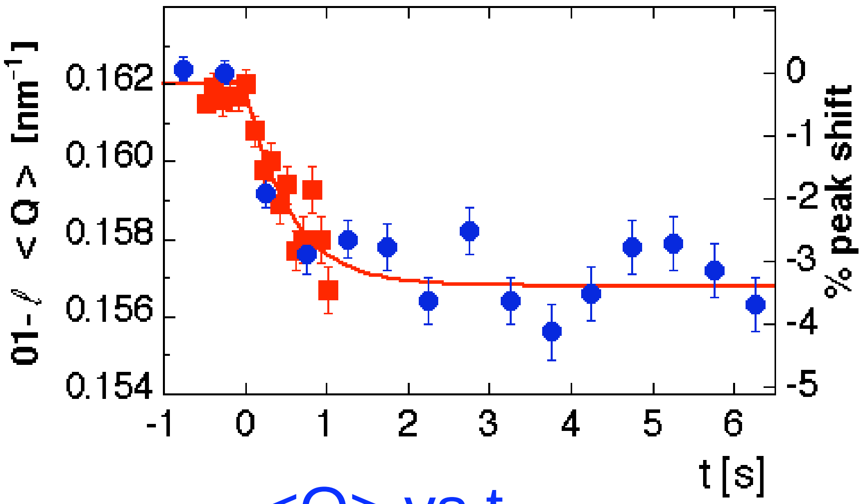
Nature of the relaxation

nearest neighbor <Q>
2D liquid vs hex lattice

$$I[Q_R] = \int_{R=0}^{\infty}\int_{\phi=0}^{2\pi} \left(\beta[R]-\beta_o\right) e^{iQ_R R\cos\phi}\, R\,dR\, d\phi$$

$$= \int_{R=0}^{\infty} R\left(\beta[R]-\beta_o\right) \int_{\phi=0}^{2\pi} e^{iQ_R R\cos\phi}\, d\phi\, dR$$

$$= \int_{R=0}^{\infty} 2\pi R \left(\beta[R]-\beta_o\right) J_0[Q_R R]\, dR$$



<Q> vs t
in 01 peak region

$$\frac{\partial}{\partial Q_R} I = 0 \quad \Rightarrow \quad \frac{\partial}{\partial Q_R} J_0[Q_R R] = 0$$

$$\Rightarrow \quad R\, J_1[Q_R R] = 0$$

$$\Rightarrow \quad Q_R R = \; 0,\; 3.832,\; \mathbf{7.0156},\; 10.173, \ldots$$

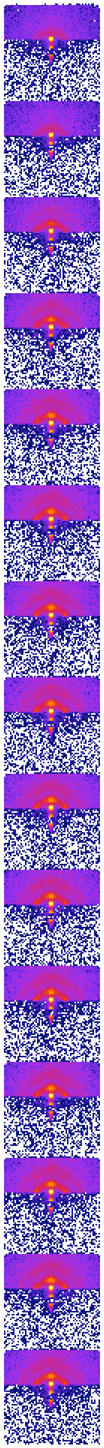
$$Q_{01} = \frac{2\pi}{\sqrt{3}\,R_{nn}/2} = \frac{7.2552}{R_{nn}}$$

$$Q_\ell = \frac{7.0156}{R_{nn}} = (1-3.30\%)\,\frac{7.2552}{R_{nn}}$$

-3.4±0.3% shift between first order diffraction spot Q and that of the arc on same time scale as decay. This is consistent with melting of the hexagonal phase (predicted 2D xtal shift -3.3%) rather than simple loss of crystalline alignment in which case the peak would **not** shift.

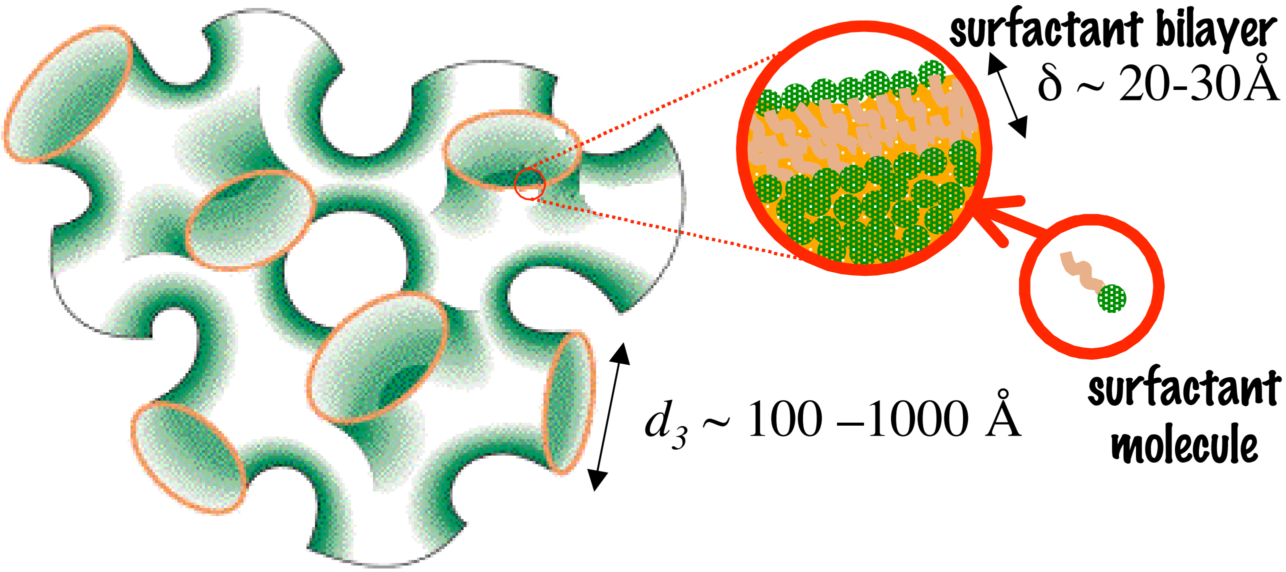
The crystal is melting before micellar rentanglement

W.A. Hamilton, P.D. Butler, L.J. Magid, Z. Han & T.M. Slawecki, Phys. Rev. E (Rapid Comm.) **60**, R1146 (1999)



L_3 "sponge" phases

Self assembled
<u>isotropic</u>
membrane
phases



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

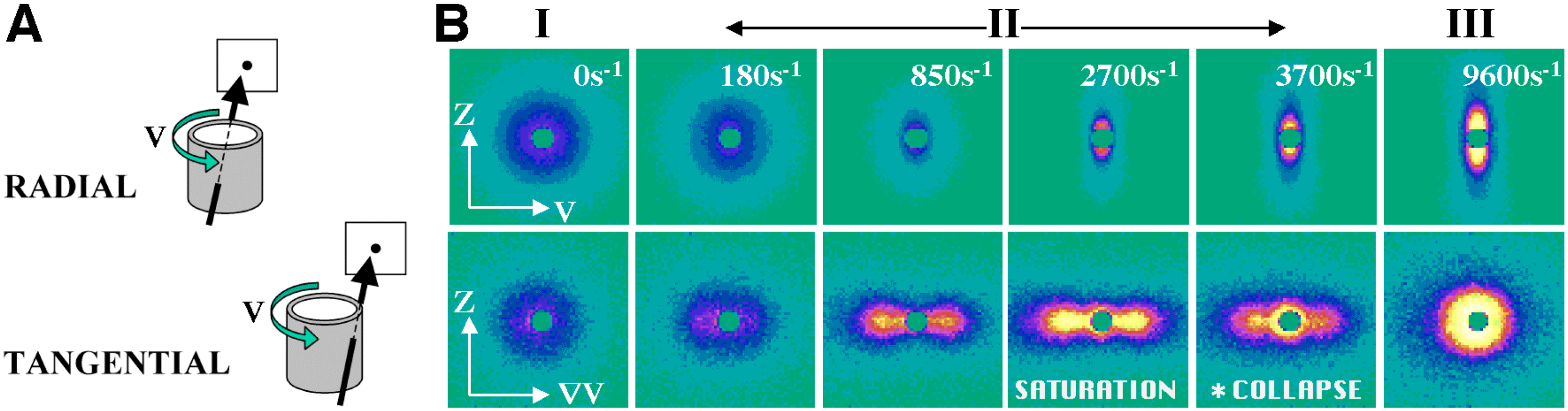
Scaling of dilution $d_3\phi \sim$ const, volume fraction $\phi \sim$ 40% ... <1%

Typically <u>very</u> fluid
Not much of a response to applied shear ~ Newtonian
rapid realignment of passages relieves stress
but:
Stir ⇒ <u>Transient</u> birefringence for dilute samples d_3>500Å

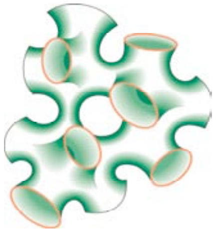
Structural response of the "sweetened" sponges

Small Angle Neutron Scattering from
ϕ=5vol% CPCl-hexanol in 40vol% dextrose-brine (η_s=16.3cP)

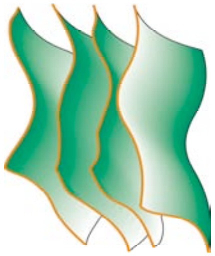
Equilibrium L_3 to Couette Shear-induced L_α transformation



Isotropic L_3



Aligned L_α



"c" alignment
membranes$\perp\nabla V$

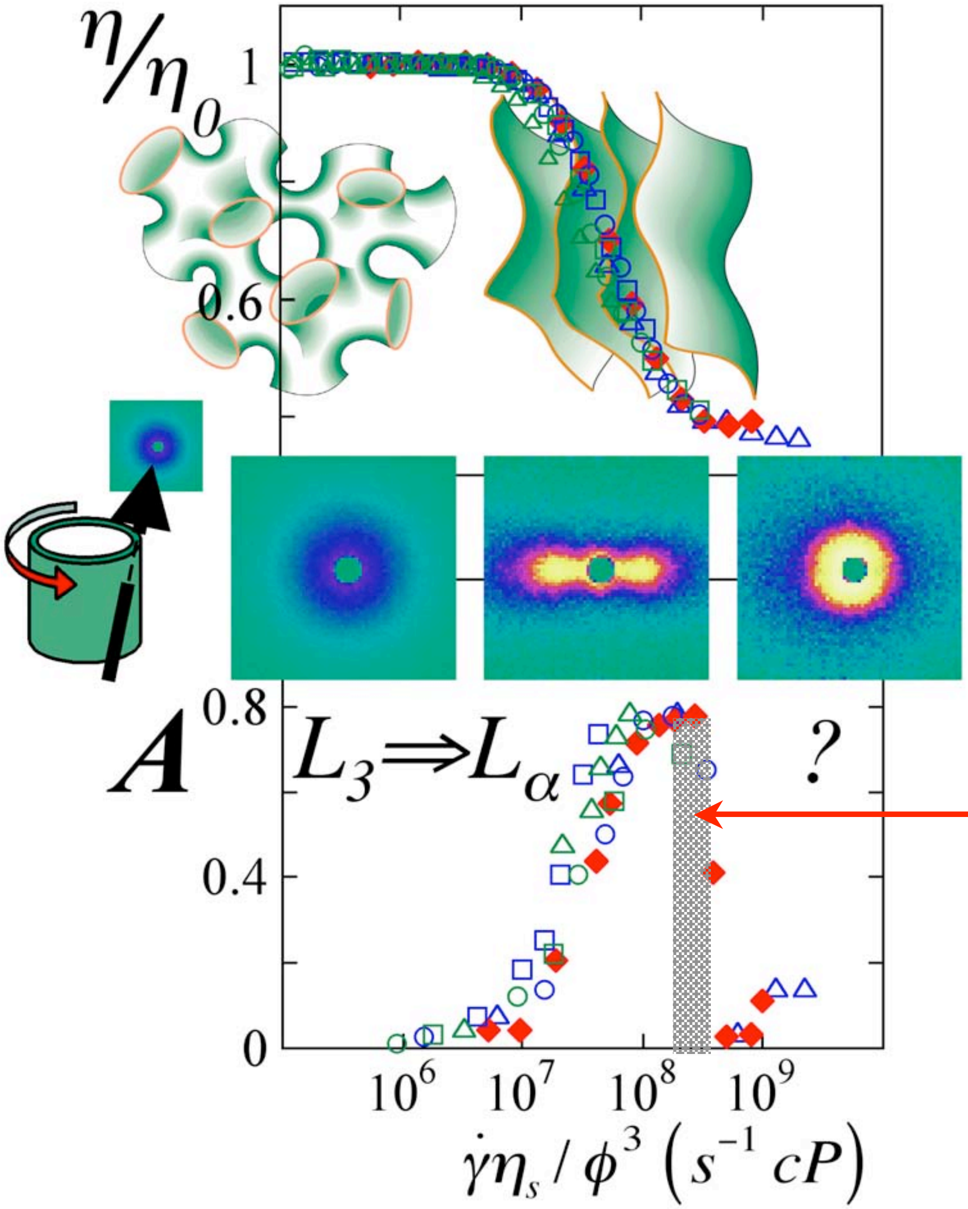
Correlation peak $Q_3 = 0.008\,Å^{-1}$ Bragg peak $Q_\alpha = 0.010\,Å^{-1}$

passage size $d_3 = 780\,Å^{-1}$ separation $d_\alpha = 630\,Å^{-1}$

$d_\alpha / d_3 \sim 80\%$ - same ratio as for equilibrium L_α & L_3 at same ϕ

1st shear $L_3 \rightarrow L_\alpha$ J. Yamamoto and H. Tanaka, PRL **77**, 4390(1996) $C_{12}E_5$ ϕ<2%, our system ϕ<3-7%

Well defined scaling of shear-induced $L_3 \rightarrow L_\alpha$



Tunable
shear-induced
L_3 to L_α
transformation

A well characterized system

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

L_α anisotropy saturates for

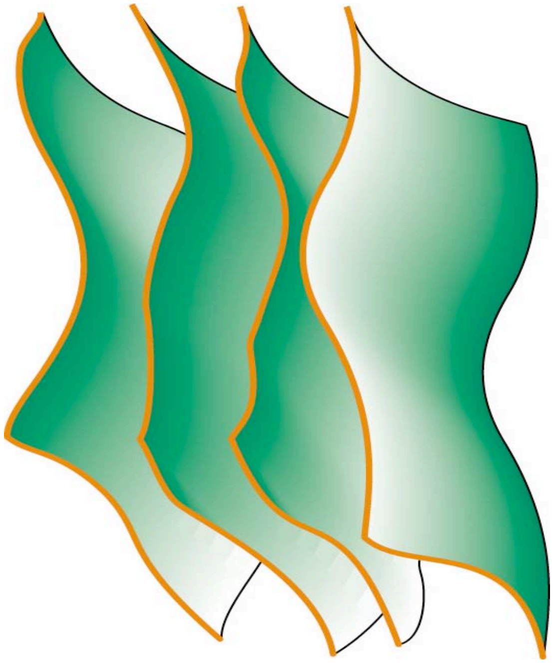
$$\dot{\gamma}\eta_s / \phi^3 \sim 2 - 4 \times 10^8 cP/s$$

Easily accessible for high η_s

So what can we do with it?

Relaxation is now a topological transformation

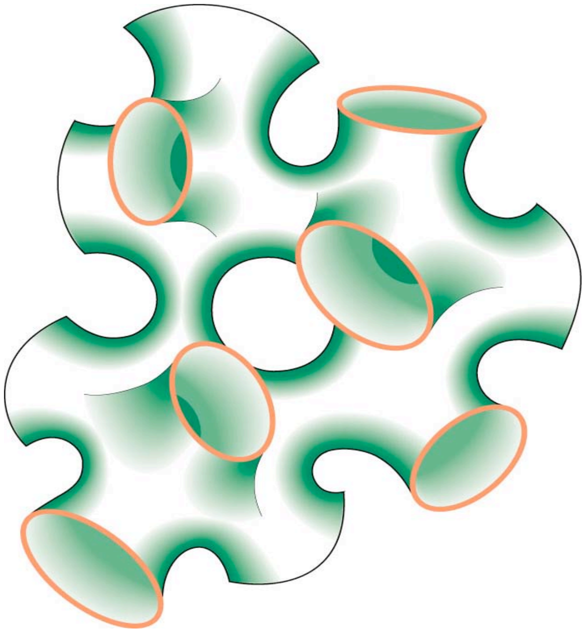
Shear-induced L_α



~ NO passages

stop shear

Equilibrium L_3

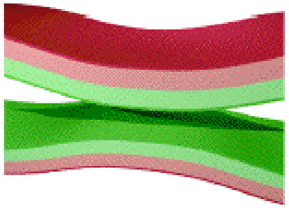


~ ALL passages
(“handles” in membrane manifold)

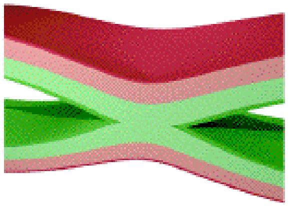
Offers a strong clear signal
of membrane solution passage creation. So ... ?

Solution passage/pore formation … an important chemical and (especially) biological process

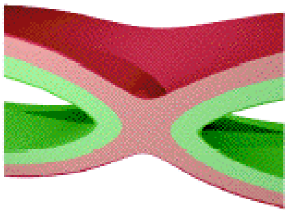
The “stalk” hypothesis of membrane fusion



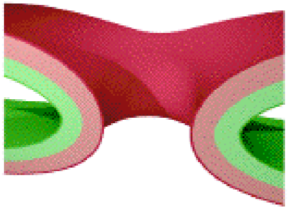
(a) Approach to small distances



(b) Merger of proximal monolayers
“Stalk” formation



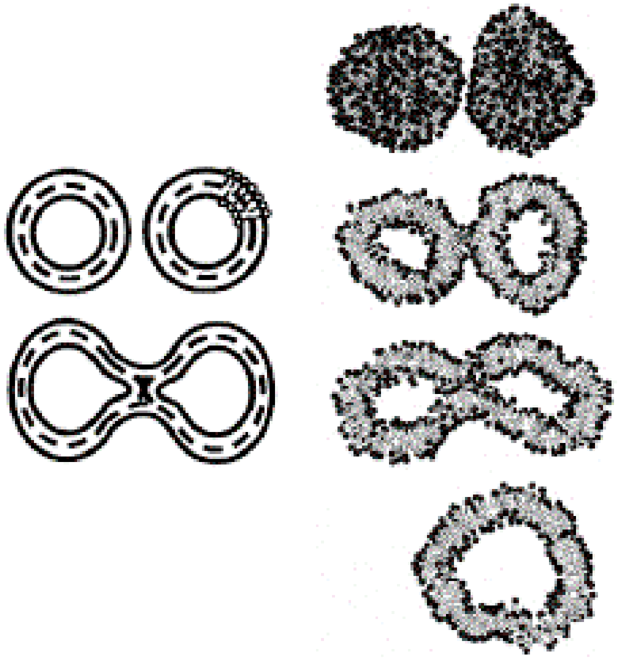
(c) Merger of distal monolayers
Stalk to TMC evolution



(d) Expansion to pore formation

from R. Jahn and H. Grubmüller,
Current Opinion in Cell Biology **14**, 488 (2002)

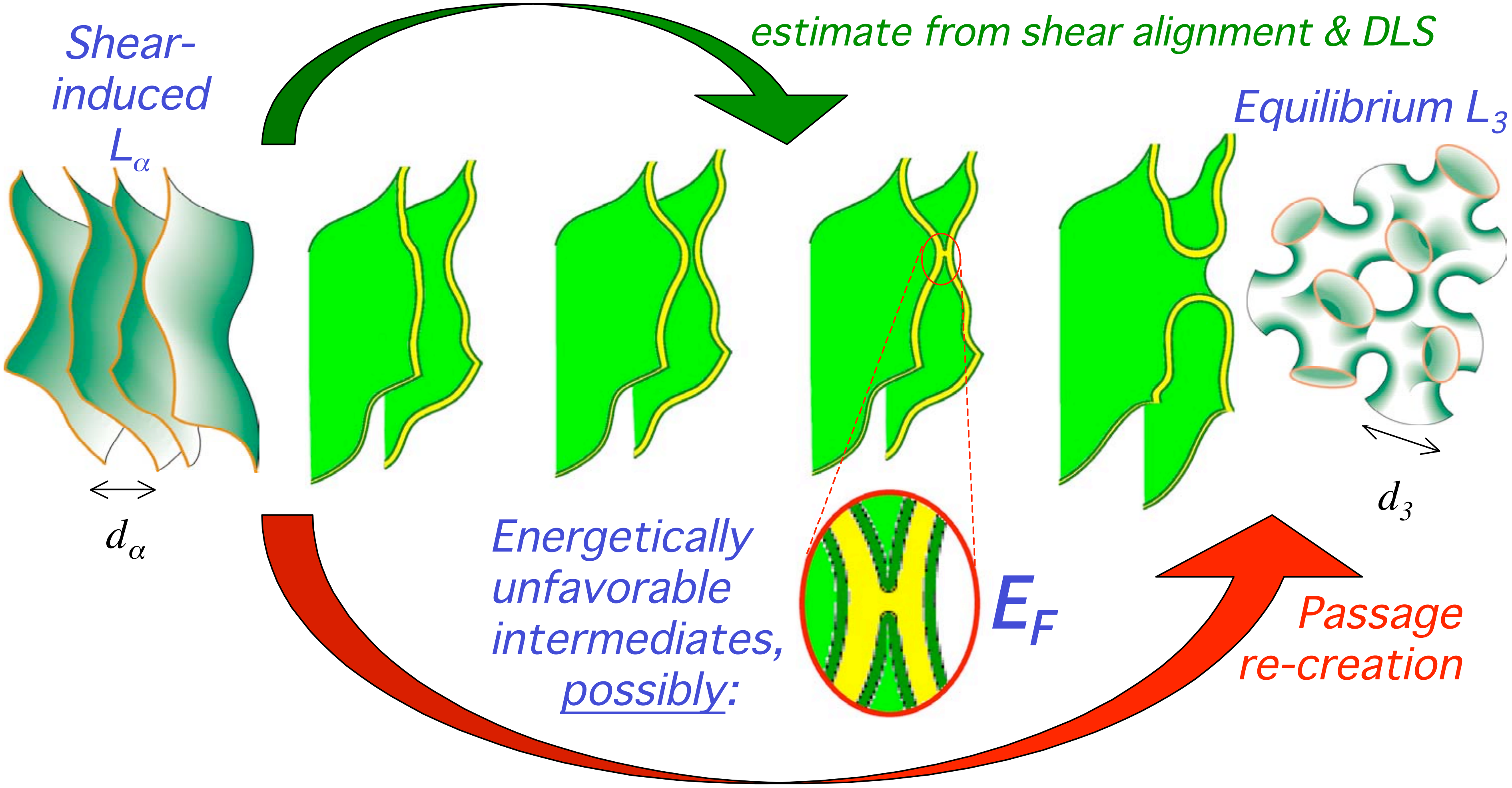
MD simultations



from H. Noguchi and M. Takasu,
J. Chem. Phys. **115**, 9547 (2001)

Stalk, TMC, or some ***other*** *intermediate structure*
⇒energy barrier to solution passage formation
(NB Our results can benchmark biophysical theories)

Energetics of passage formation



τ_C Diffusive __contact__ interval

estimate from shear alignment & DLS

Shear-induced L_α

Equilibrium L_3

Energetically unfavorable intermediates, __possibly__:

Passage re-creation

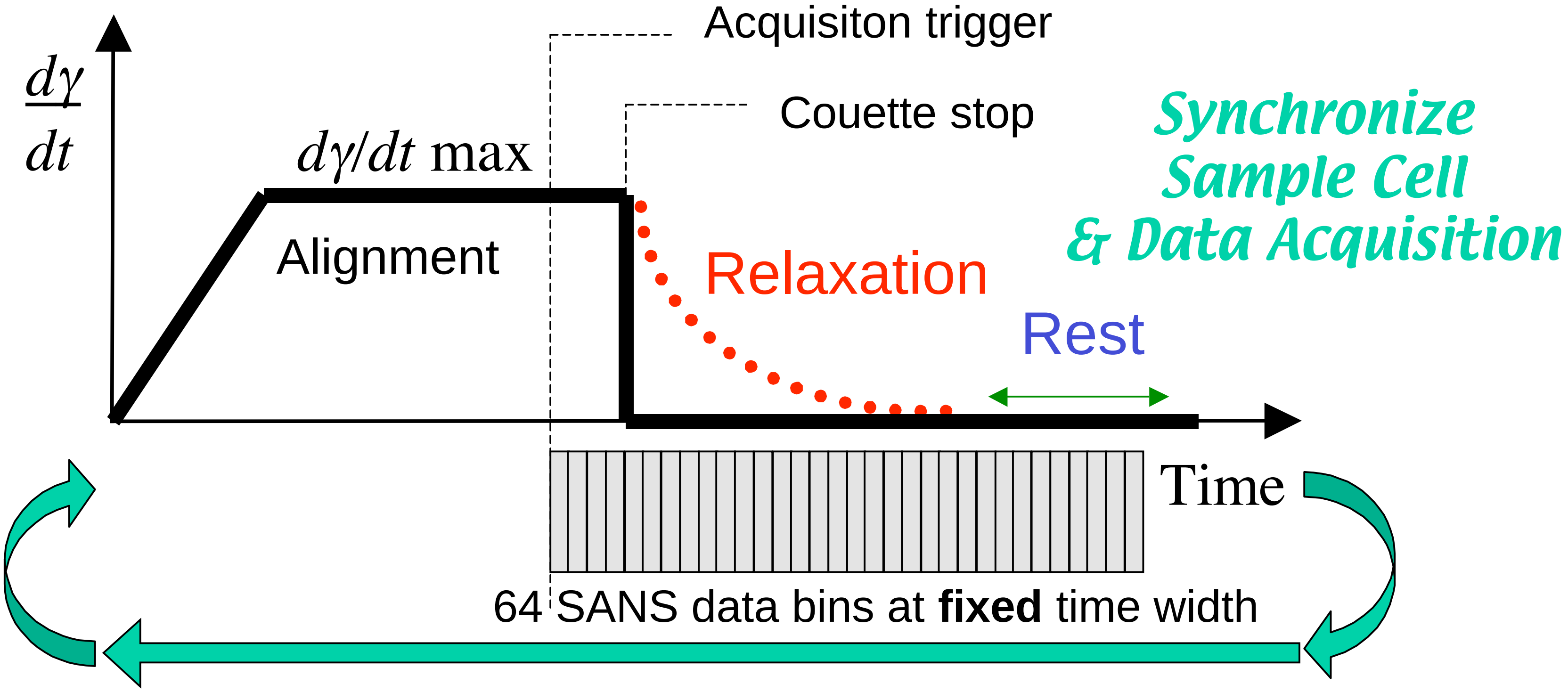
Topological relaxation time $\tau_R = \tau_C \exp[-E_F/k_BT]$

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

When things are (a little) too fast for SANS - "t-SANS"

Even at highest viscosity full topological relaxation τ_R *~seconds*

Very fast (for SANS) ⇒ "time sliced" cycled SANS (NIST-NG7)



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

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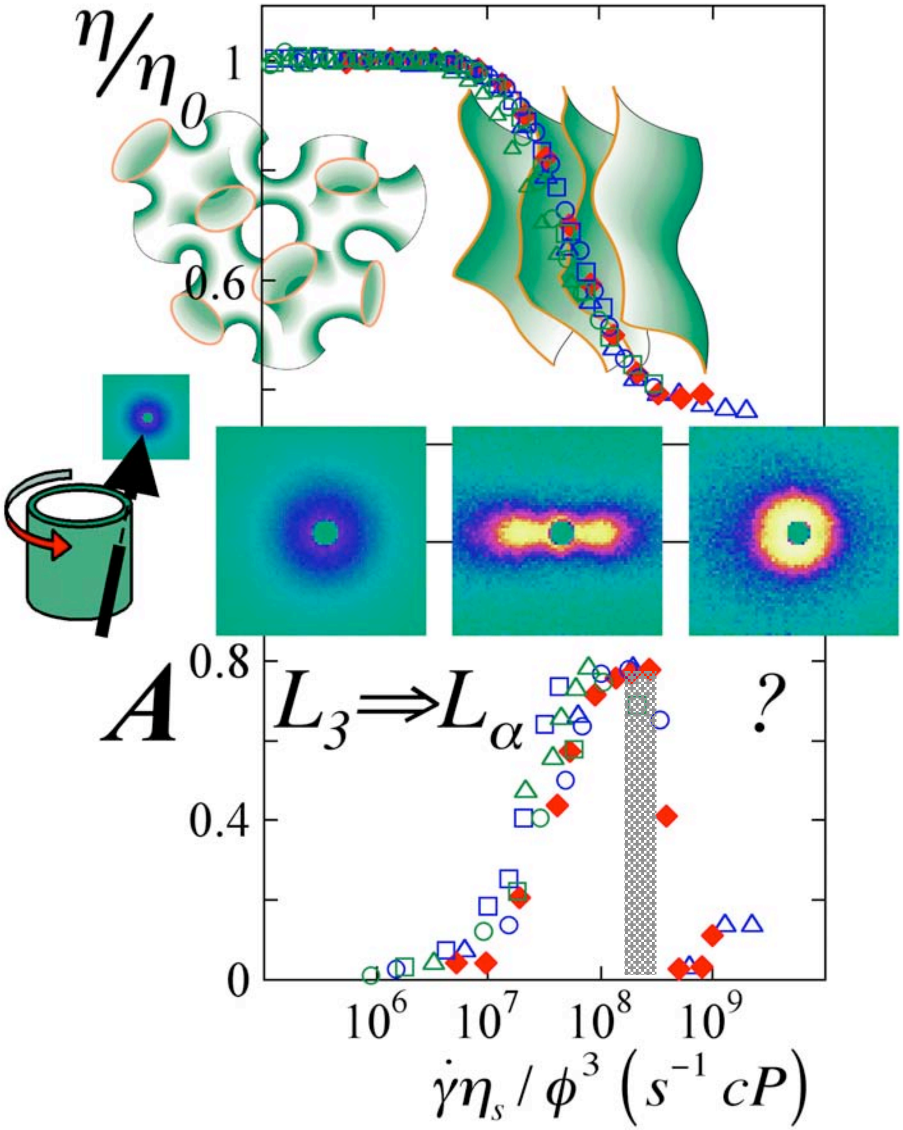
Can estimate τ_C from earlier SANS vs shear



We already know:
L_α signal saturates for

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

(shaded)

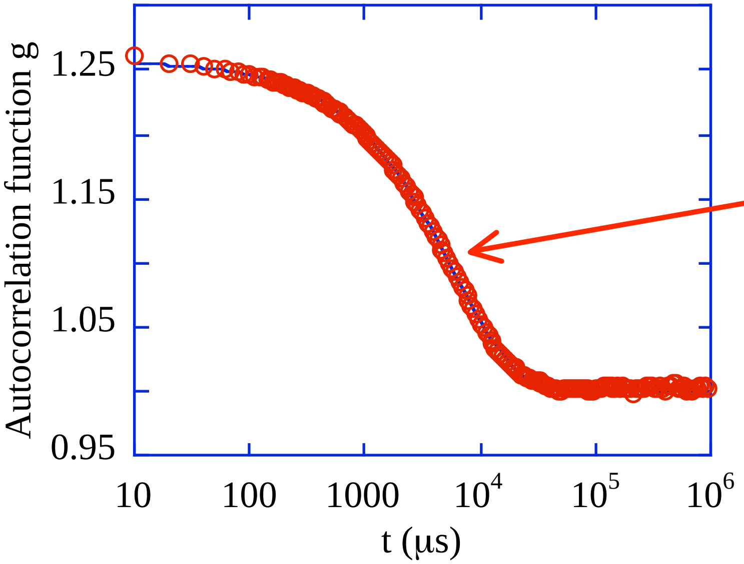
Applied shear rate (s^{-1}) represents
1/time which totally frustrates
(re)formation of disrupted
membrane passage ...
because they never meet

So can expect

$$\tau_C \sim \frac{1}{\dot{\gamma}_{Saturation}} \sim \frac{\eta_s/\phi^3}{2-4\times10^8\,cP/s}$$

Or ... we can use Dynamic Light Scattering (DLS) to measure membrane diffusion rates
$\tau_C \Rightarrow$ time to bring membranes separated by an average separation d_α into contact

Determination of contact time τ_c (#2) - DLS



Homodyne autocorrelation function:

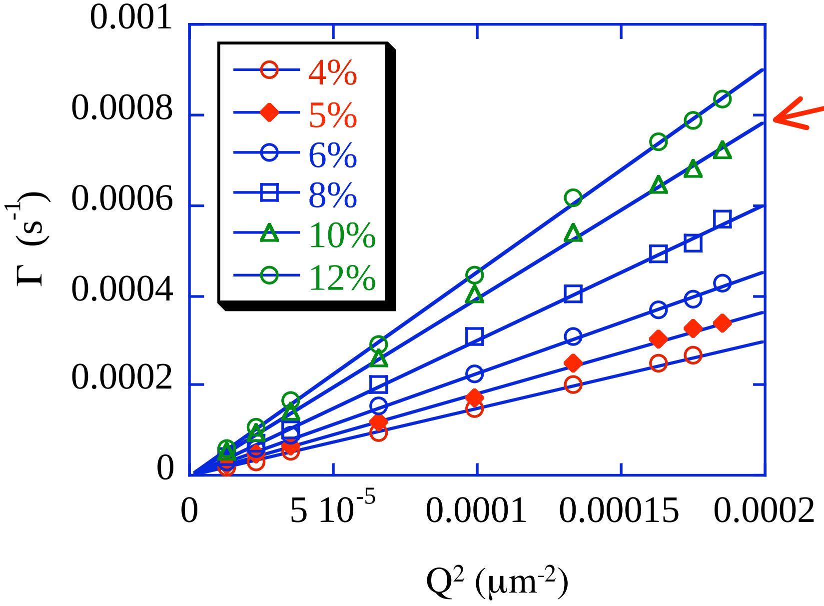
$1+ A \exp[-2(\Gamma t)^{\beta}]$

Stretched exponential β=0.7-0.8

$\Gamma[Q]=DQ^2$

⇒ *simple cooperative diffusion process*

$D \propto \phi$



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

$\Rightarrow \tau_c \approx 1/\Gamma[Q_\alpha]=1/DQ_\alpha^{2}$

where $Q_\alpha=2\pi/d_\alpha \propto \phi$

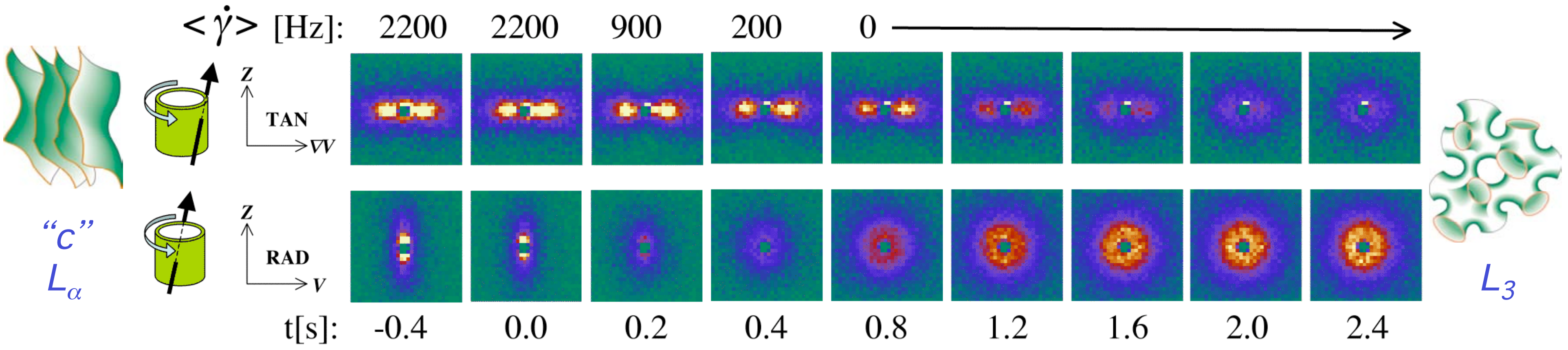
$\Rightarrow \tau_c \propto 1/\phi^3$

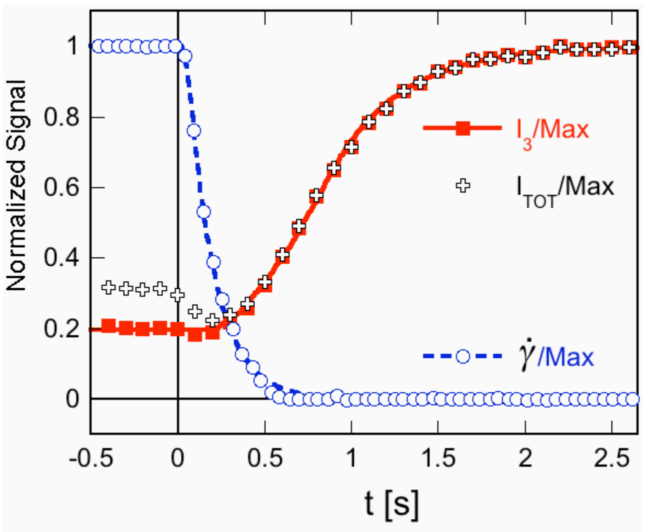
agrees with Shear-induced L_α plateau estimate

Determination of topological relaxation time τ_R - t-SANS

t-SANS Shear-induced L_α to equilibrium L_3 relaxation

ϕ=5vol% CPCl-hexanol in 40vol% dextrose-brine (η_s=16.3cP)





Shear aligned at

$$\dot\gamma \eta_s / \phi^3 \sim 3\times10^8 cP/s$$

~center L_α signal plateau

When Couette cell is stopped

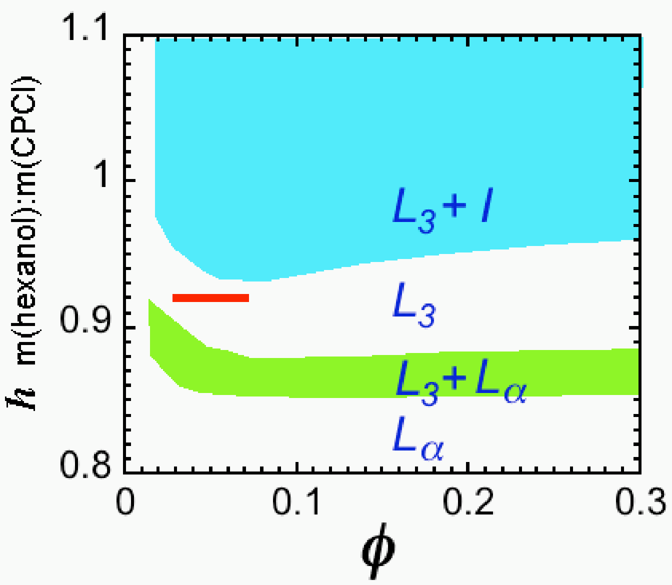
L_3 signal (passages) re-established

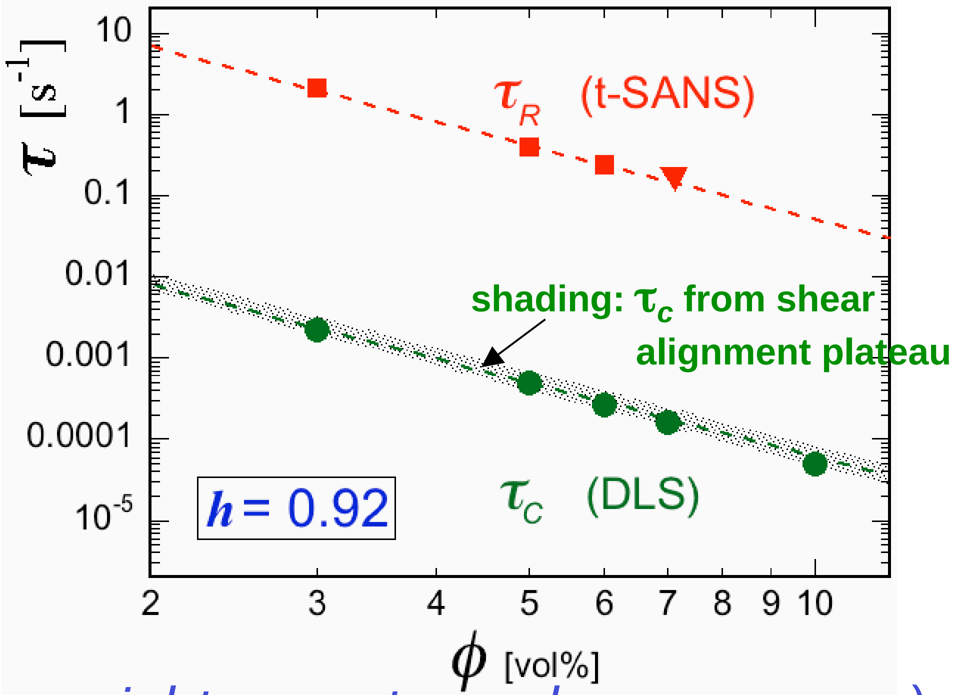
τ_R=0.40±0.08 s

τ_R and τ_C versus membrane volume fraction ϕ

Constant membrane composition, i.e. properties

Dilution series: $d_3\phi \approx const$, $d_\alpha\phi \approx const$





τ_R and τ_C scale as ϕ^{-3} (as you might expect per shear response)

Constant Arrhenius relationship (despite >2X scaling)

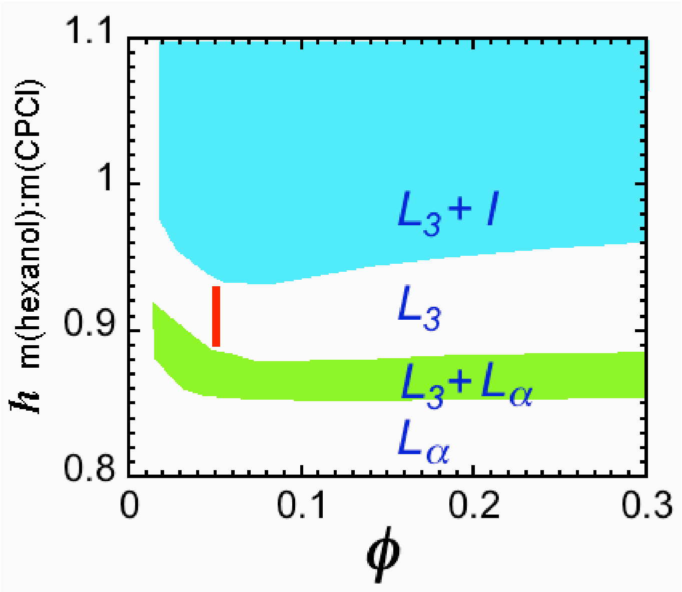
$$\tau_R = \tau_C \exp[-E_F/k_BT] \Rightarrow E_F = 6.7k_BT \quad (170\ \text{meV})$$

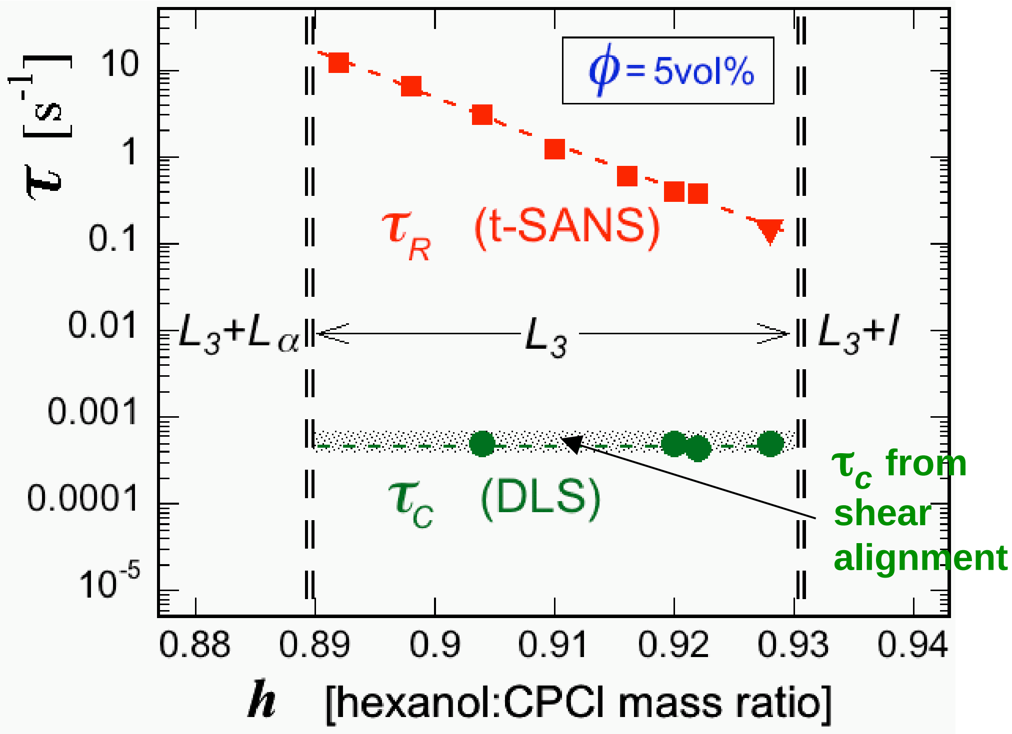
Topological relaxation of a shear-induced lamellar phase to sponge equilibrium and the energetics of membrane fusion",

L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, *Physical Review Letters* **93**, 198301(2004)

τ_R and τ_C versus membrane composition h

Change membrane composition, i.e. properties
across L_3 phase region for constant ϕ





Increasing hexanol to CPCl mass ratio h

⇒ *Increasing Gaussian curvature modulus of membranes*

⇒ *<u>Decreasing</u> energy cost of passages (and stalk structures)*

4% increase in h $E_F = 10.3k_BT$ (260 meV) down to $5.8k_BT$ (150 meV)

Summary/Conclusions/Future

Nice information from relatively simple multiplexed time-resolved SANS

(1) Threadlike micellar system

Second order peaks decay 4 times faster 0.1-0.2 s than first order peaks

$\Rightarrow$ Debye-Waller factor ~ $\exp[-Q^2<\Delta r2(t)>/2]$

2D translational diffusion constant: $<\Delta r^2(t)>=<\Delta r^2(0)>+Dt$

τ =0.7±0.2s for Q01=0.16nm^{-1} $D=2/(Q^2\ \tau)=110\pm30 nm^2/s$

Fast relaxation of the hexagonal threadlike lattice <u>is</u> melting

(2) "Sweetened" Cetylpyridinium-Hexanol/dextrose-brine L_3 sponges

Viscosity tuning $\Rightarrow$ accessible shear-induced L_3 to L_α transition

Activation energy for membrane fusion (handle creation)

$\tau_R = \tau_C \exp[-E_F/k_BT] \Rightarrow E_F \sim 5 - 10\ k_BT$

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

E_F linear decrease wrt h across L_3 phase region $\Leftrightarrow$ Gaussian curvature modulus

Relaxation measurements to "0.01s" easy enough to do in data acquisition hardware/software ...

we will do this on new HFIR SANS in 2006 ...

with a little more synchronization possible for SNS SANS

So start thinking about measurements ...

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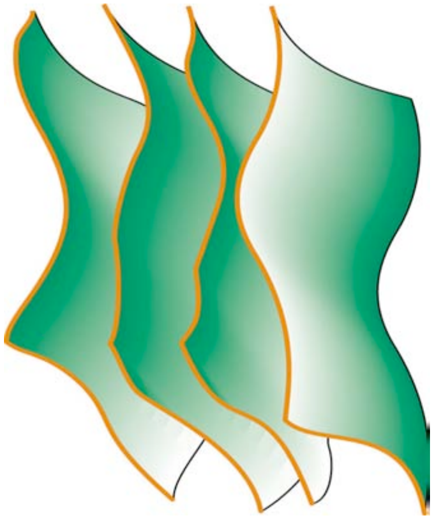
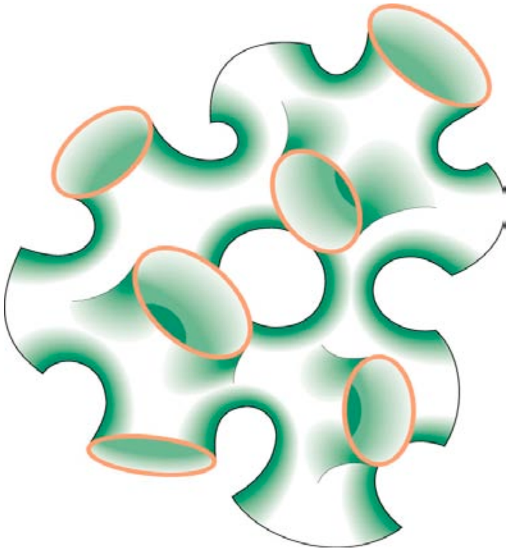
Bonus: Membrane phase energetics

L_α

~NO
passages





L_3

ALL
passages
("handles"
in membrane
manifold)

Helfrich membrane Hamiltonian: $dE = \kappa\left(1/r_1 + 1/r_2\right)/2 + \bar{\kappa}(1/r_1 r_2)$

$1/r_1, 1/r_2$ curvatures κ bending modulus $\bar{\kappa}$ Gaussian curvature modulus

Gauss-Bonnet Theorem: $\iint dA(1/r_1 r_2) = 4\pi\left(n_p - n_h\right)$

$\Rightarrow$ Gaussian Curvature Energy per passage: $-4\pi\bar{\kappa}$

$\Rightarrow$ $\bar{\kappa} > 0$ Favors passage formation i.e. $\Rightarrow L_3$