Structure, Dynamics, and Phase Behavior of Lecithin-Based Microemulsions

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ASSOCIATIONS IN SOLUTION: FUNCTION, PERFORMANCE, AND SYNTHESIS
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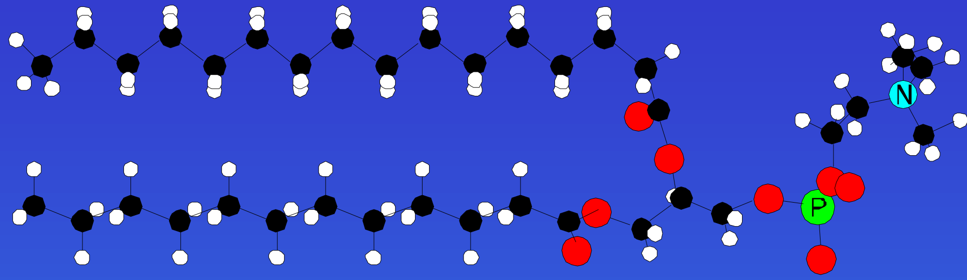
Lecithin = 1,2-diacyl-*sn*-glycero-3-phosphocholine

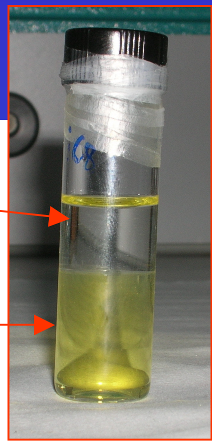


LS & SANS investigations*

water addition induces the formation of giant cylindrical reverse micelles

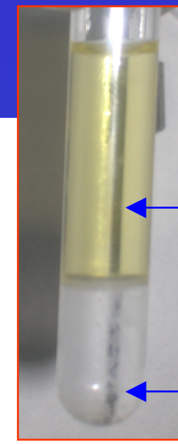
Organogel: transparent, isotropic, highly viscous

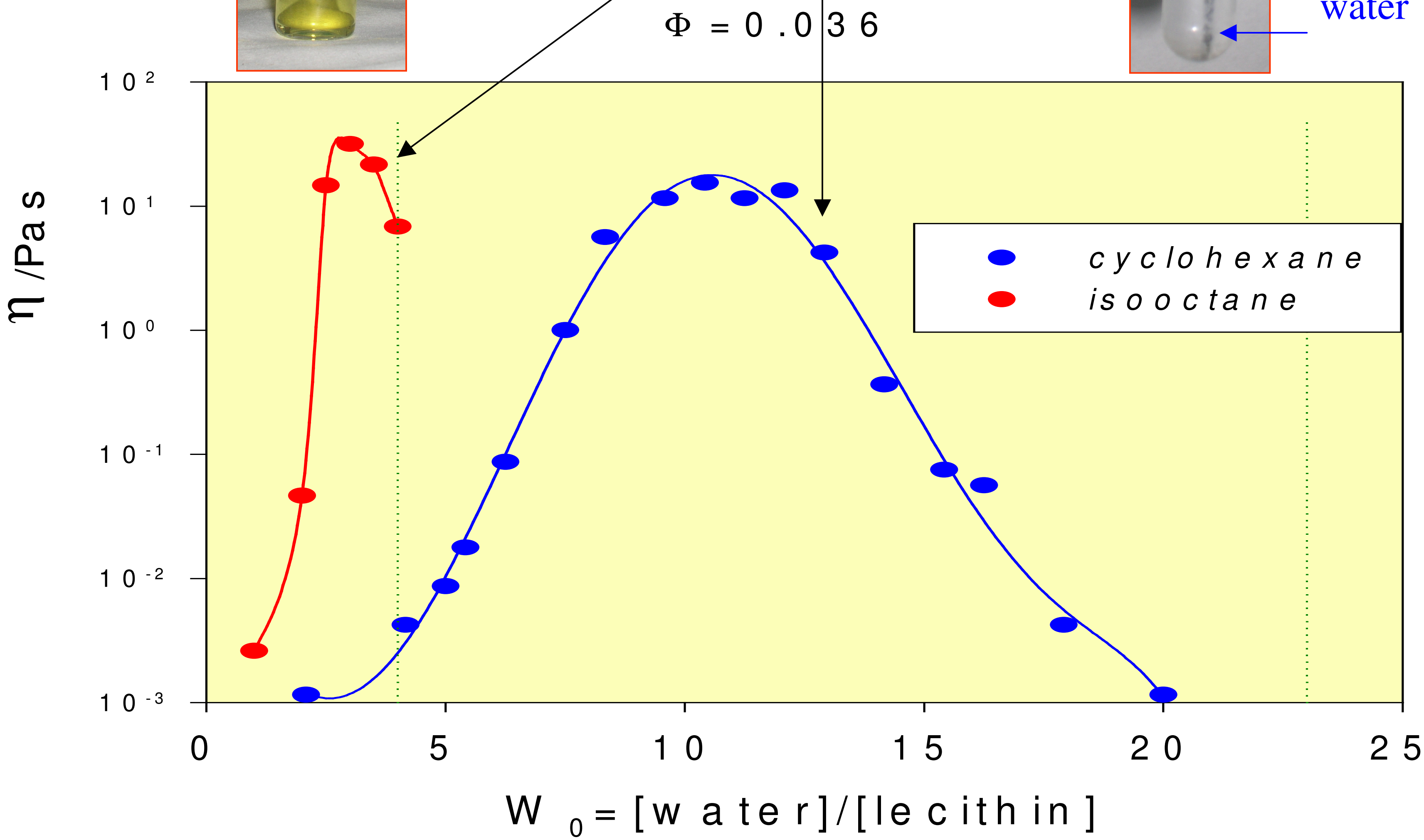
* Schurtenberger et al. *J. Phys. Chem.* **1990**, *94*, 3695
Schurtenberger & Cavaco *Langmuir* **1994**, *10*, 100.
Schurtenberger et al. *Langmuir* **1996**, *12*, 2433.



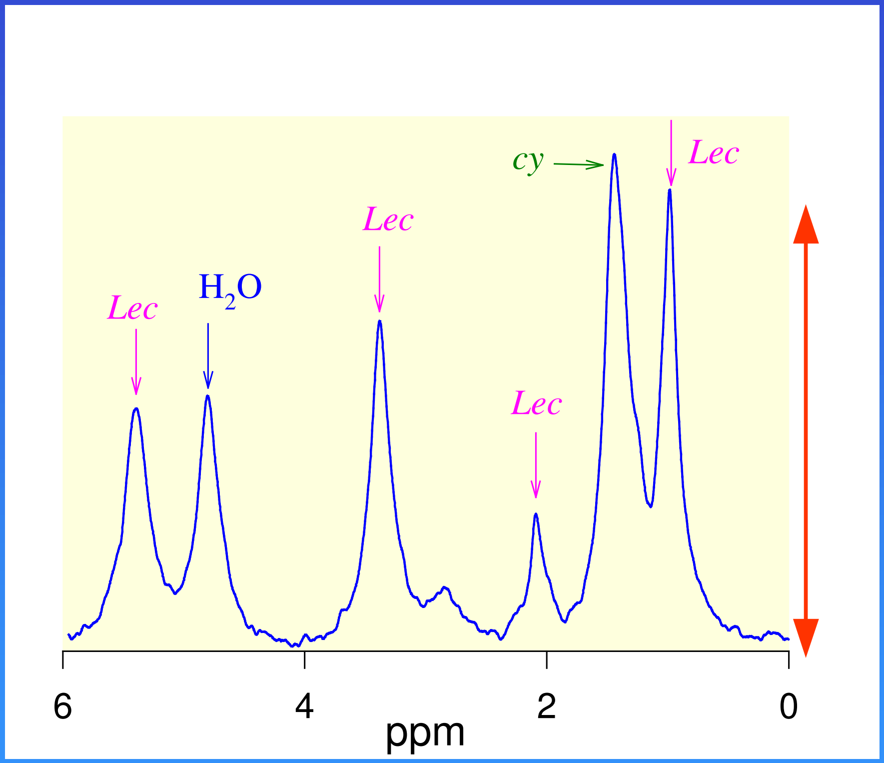
• different phase separation upon water dilution: Winsor II (C_6) or liquid-gas (iC_8)

• drop in viscosity



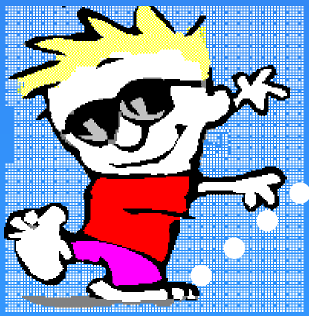


The Measurement of Molecular *Motion* Using PGSE-NMR



Echo attenuation E(q,t)

q & t : instrumental parameters



$$E(q,t) = \int P(Z,t)e^{iqZ}dZ$$

P(Z,t) Gaussian

Simple liquid

$$P(Z,t) = \frac{\exp\left(-\frac{Z^2}{4Dt}\right)}{\sqrt{4\pi Dt}}$$

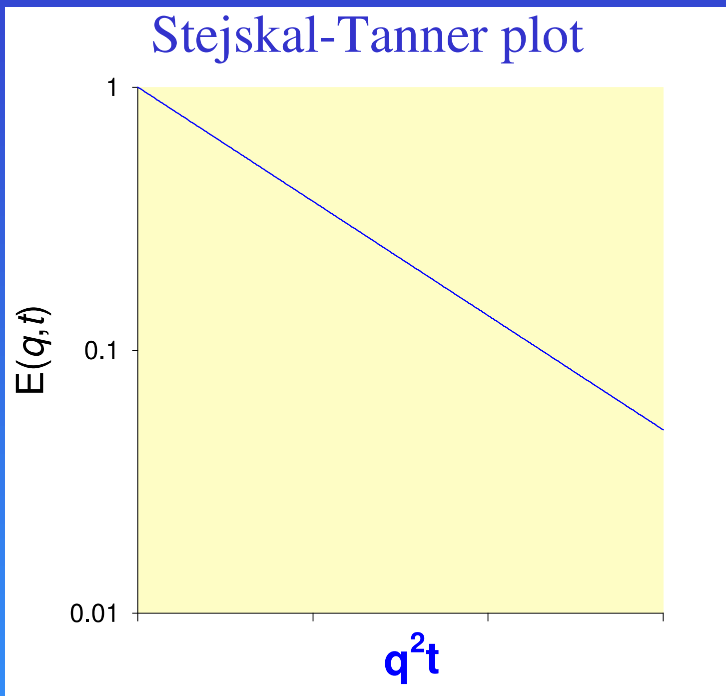
$$E(q,t) = \exp(-\mathbf{D}tq^2)$$

Unknown P(Z,t)

$$\lim_{q^2 \to 0} E(q,t) = 1 - \frac{\langle Z^2 \rangle q^2}{2}$$

Gaussian diffusion:

Random Walk

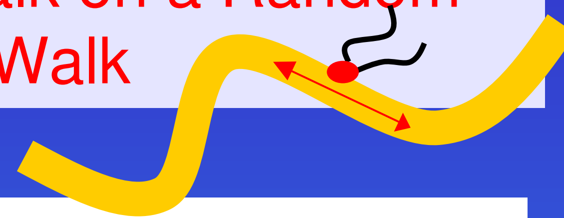


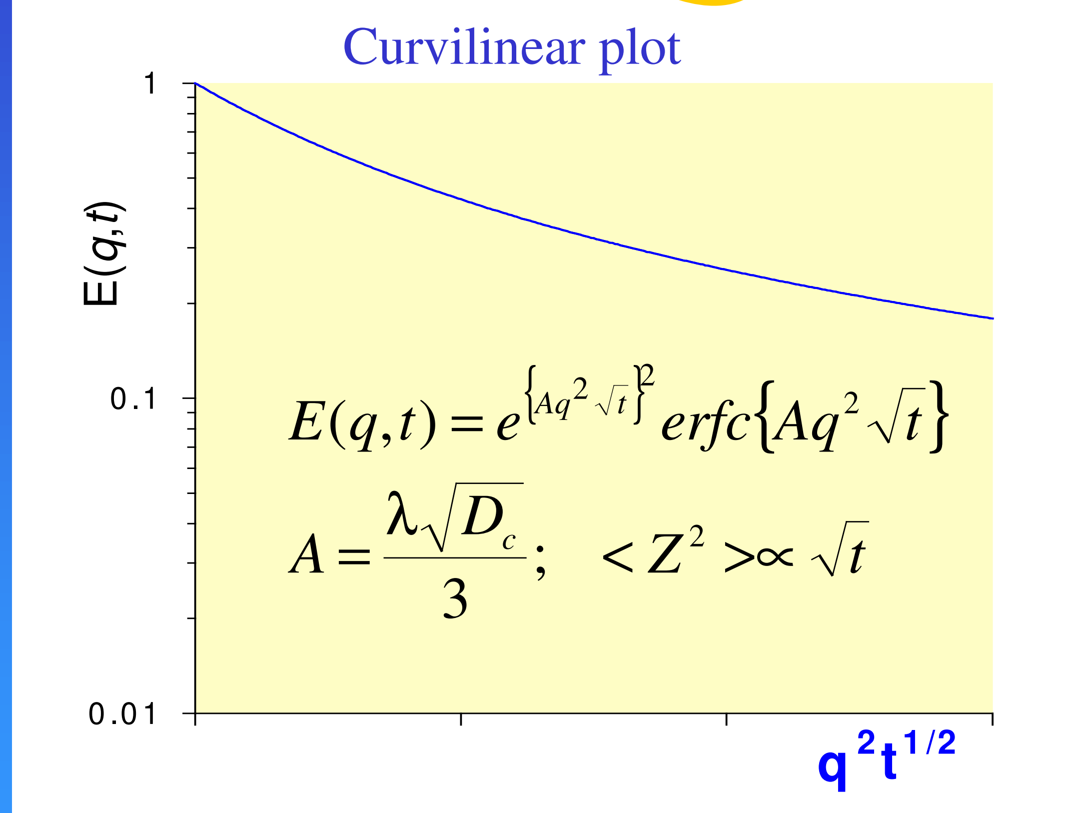
$$E(q,t) = e^{-Dq^2 t}$$

$$< Z^2 >= 2Dt$$

Curvilinear diffusion:

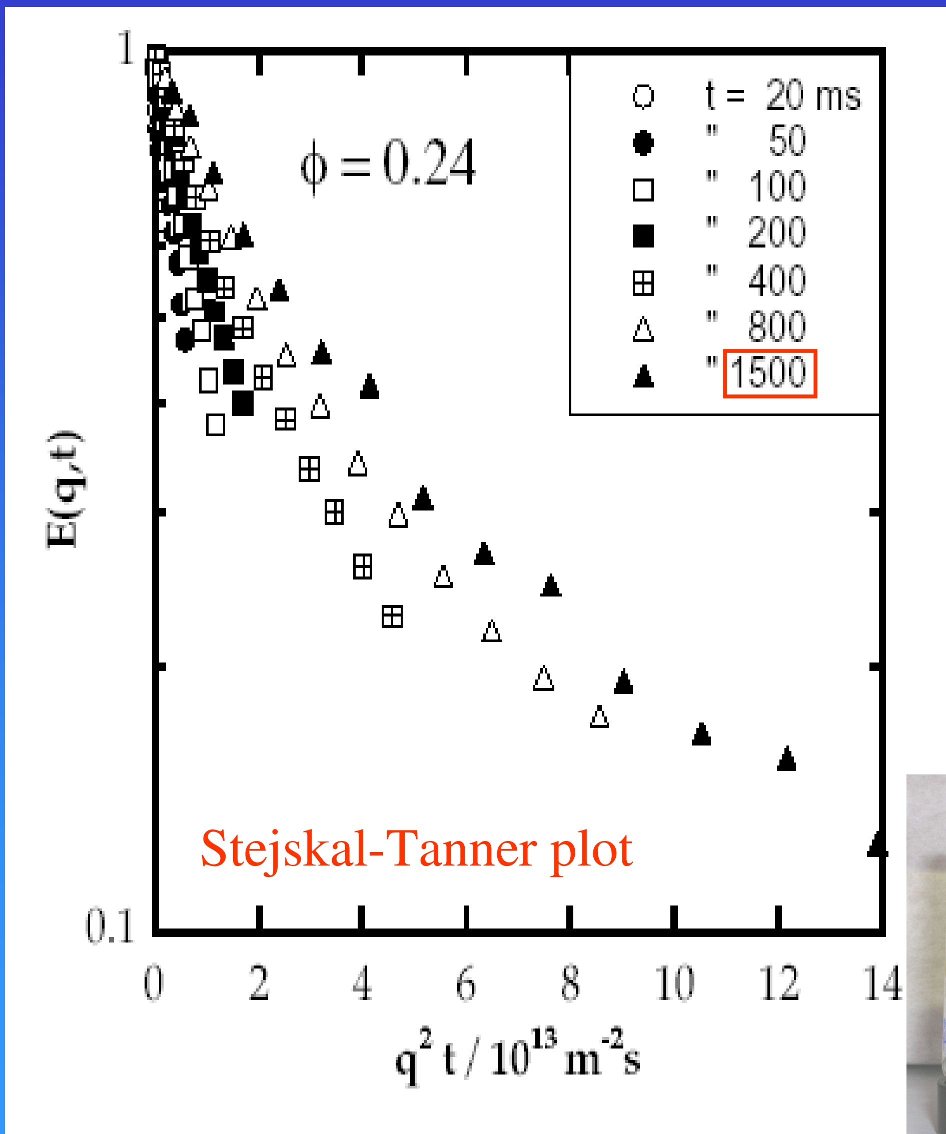
Random Walk on a Random Walk

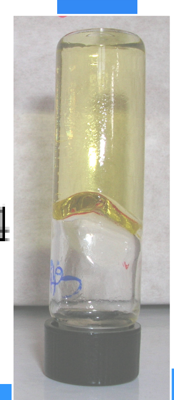


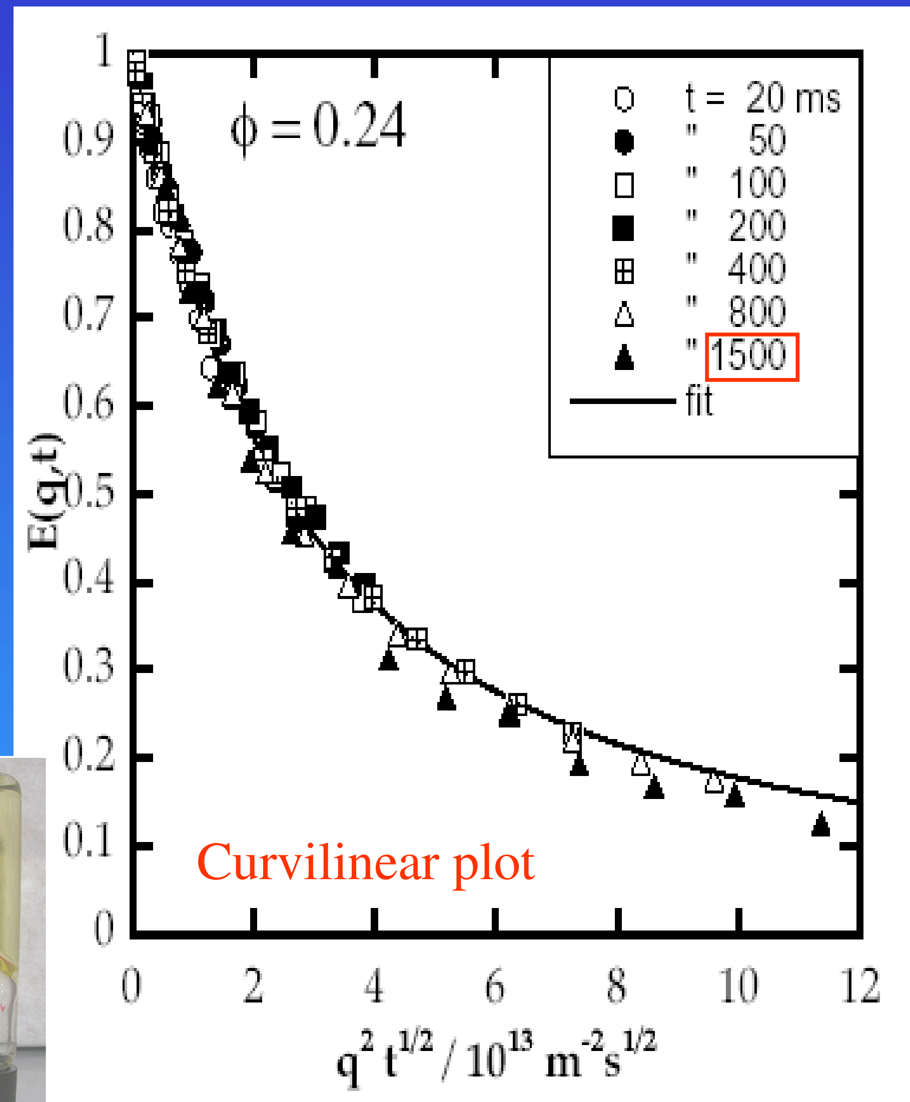


Cyclohexane W_0=10

Angelico, Olsson, Palazzo, Ceglie *Phys. Rev. Letters* **1998**, *81*, 2823







In *cC6* lecithin experiences pure curvilinear diffusion
up to an observation time of 1.5 s

very long micelles (in 1.5 s lecithin explore about 2 μm)

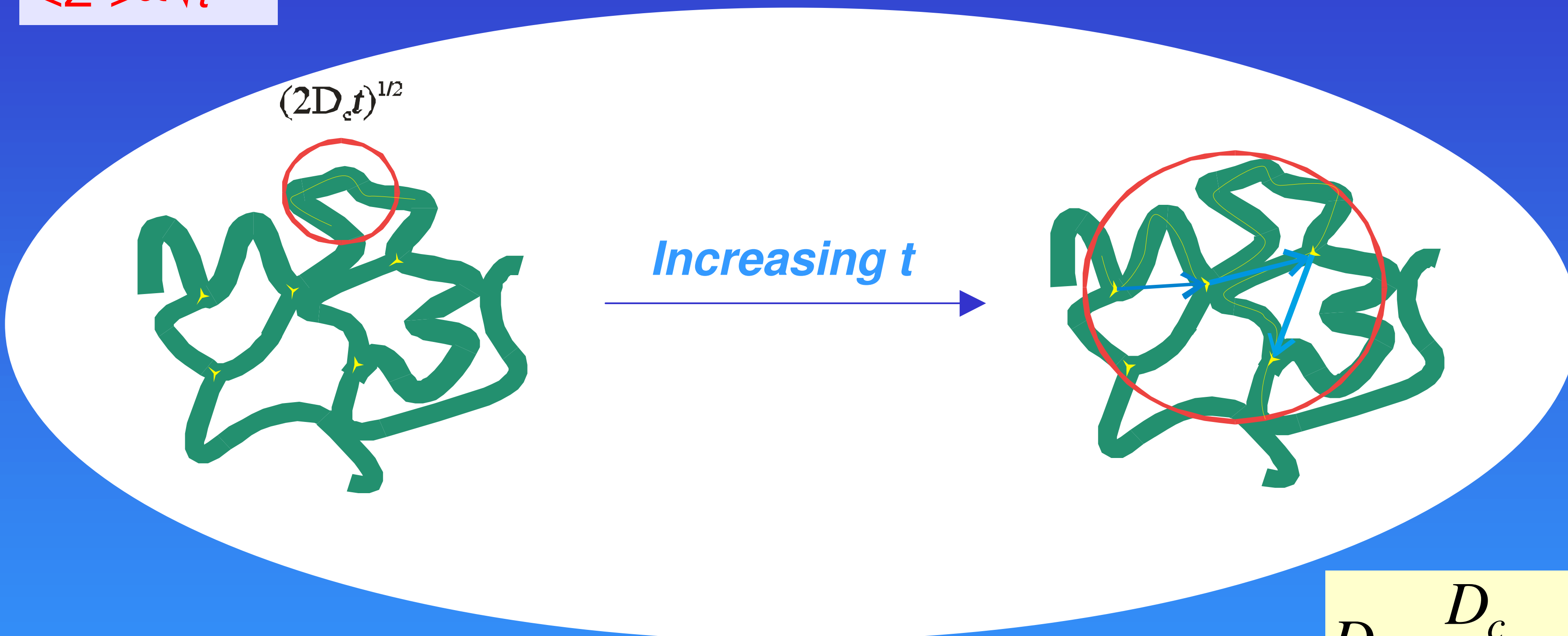
micellar lifetime and the lecithin residence time > 1.5 s

disconnected micelles (not branched)

diffusion experiment in a branched network ?

Curvilinear
$\langle Z^2 \rangle \propto \sqrt{t}$

Random walk (Gaussian)
$\langle Z^2 \rangle \propto t$

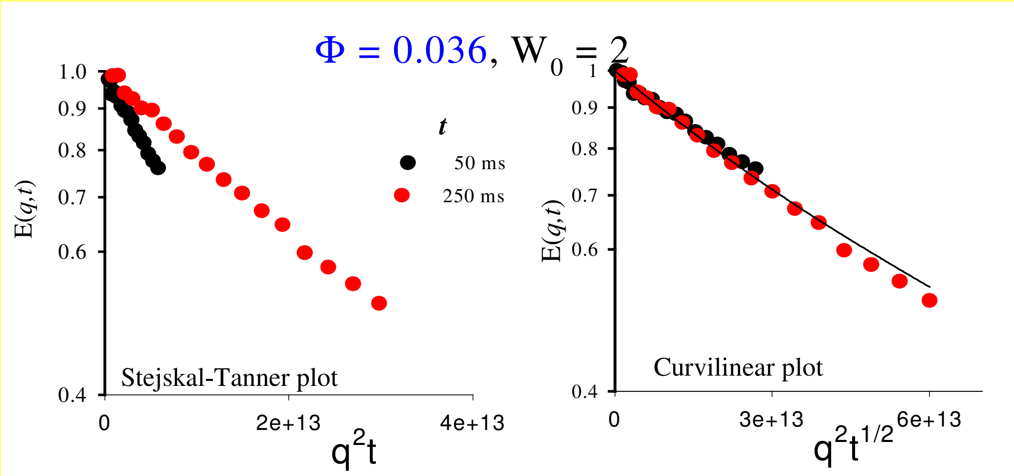


$$D = \frac{D_c}{3N}$$

$$N = \frac{L_{branch}}{2\lambda}$$

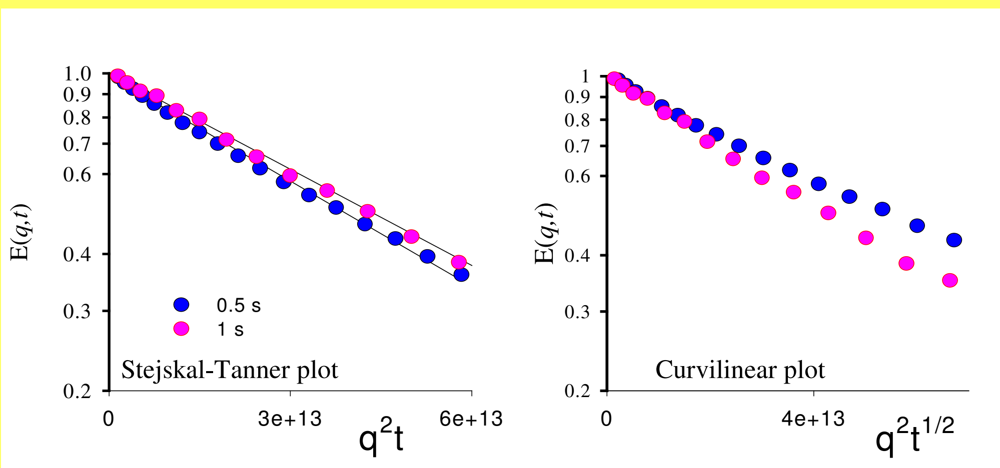
Ambrosone, Angelico, Ceglie, Olsson, Palazzo
Langmuir 2001, *22, 6822*

Isooctane, W_0=2 low concentration



Low Φ, short times

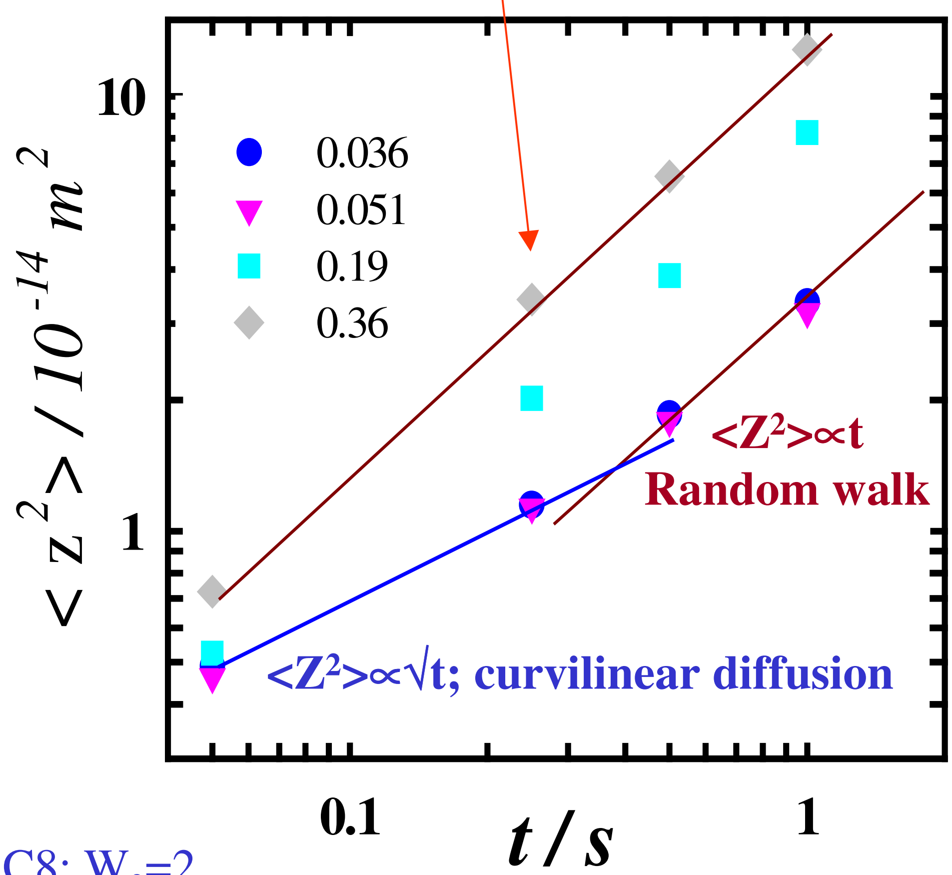
curvilinear diffusion
λ=150 Å



Low Φ, long times

almost Gaussian

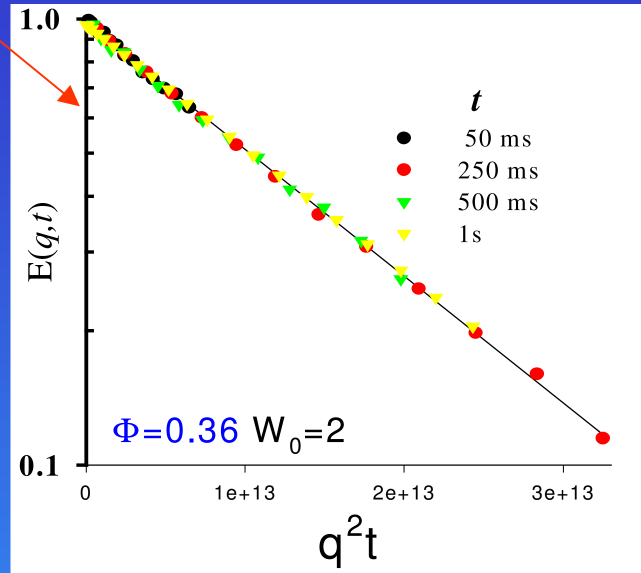
higher concentration: Gaussian diffusion in the whole timescale range



Gels in iC8; W_0=2

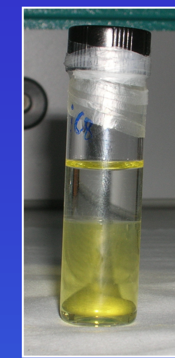
Lecithin mean squared displacement as a function of observation time

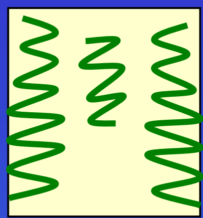
More connections



Increasing the W_0: Gaussian diffusion also at very low volume fraction

Phase separation

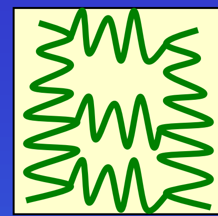




branches

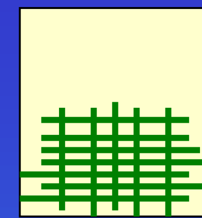
W_0

η **decreases**



more branches

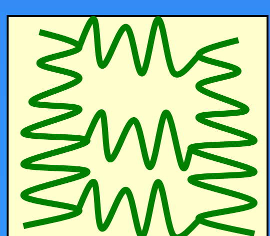
W_0



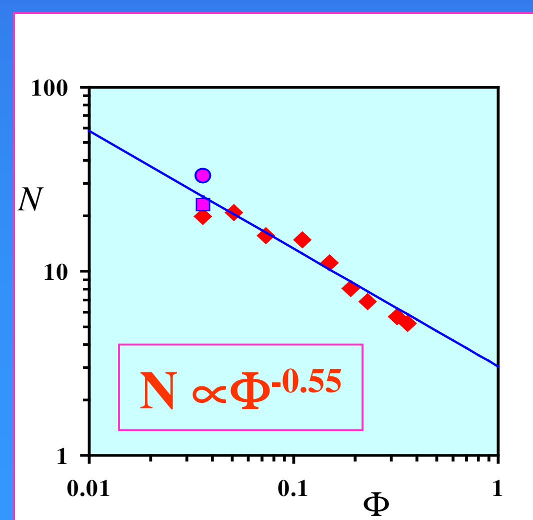
Theory

Drye & Cates *J.Chem. Phys*. **1992**, 96,1367
Tlusty & Safran *Phys. Rev. Lett*. **2000**, 84,1244
Zilman & Safran *Phys. Rev. E* **2002**, *66*, art. N. 051107

Φ **more branches**



$$D = \frac{D_c}{3N}$$



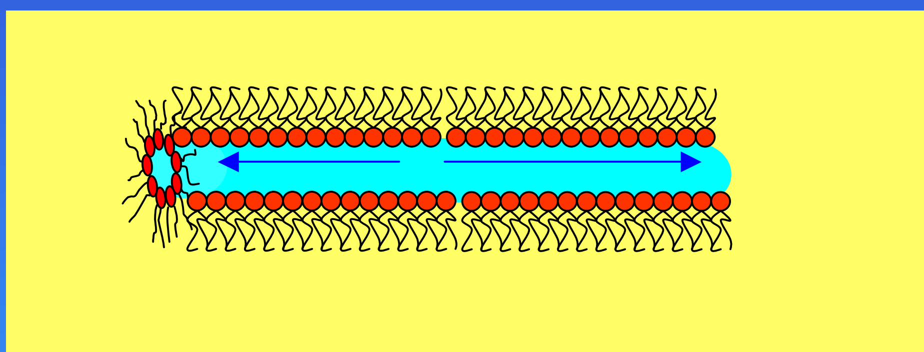
$$N \propto L_{branch} \propto \Phi^{-1/2}$$

Cyclohexane: water diffusion

For water the residence time is ~ 1µs (Gaussian diffusion)

Water self-diffusion coefficient D_w

giant slow moving micelles
D_w reflects the water motion inside the micelle



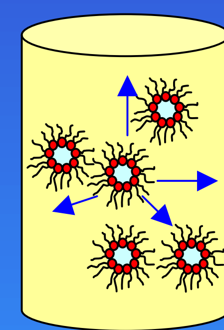
the motion of water parallel to oriented lipid bilayers was previously studied*

for lamellae D_w increases upon increase in W_0

$D_W(\text{cylinders}) = \frac{1}{3} D_w$

* Wassel *Biophys. J.* **1996**, *71*, 2724.

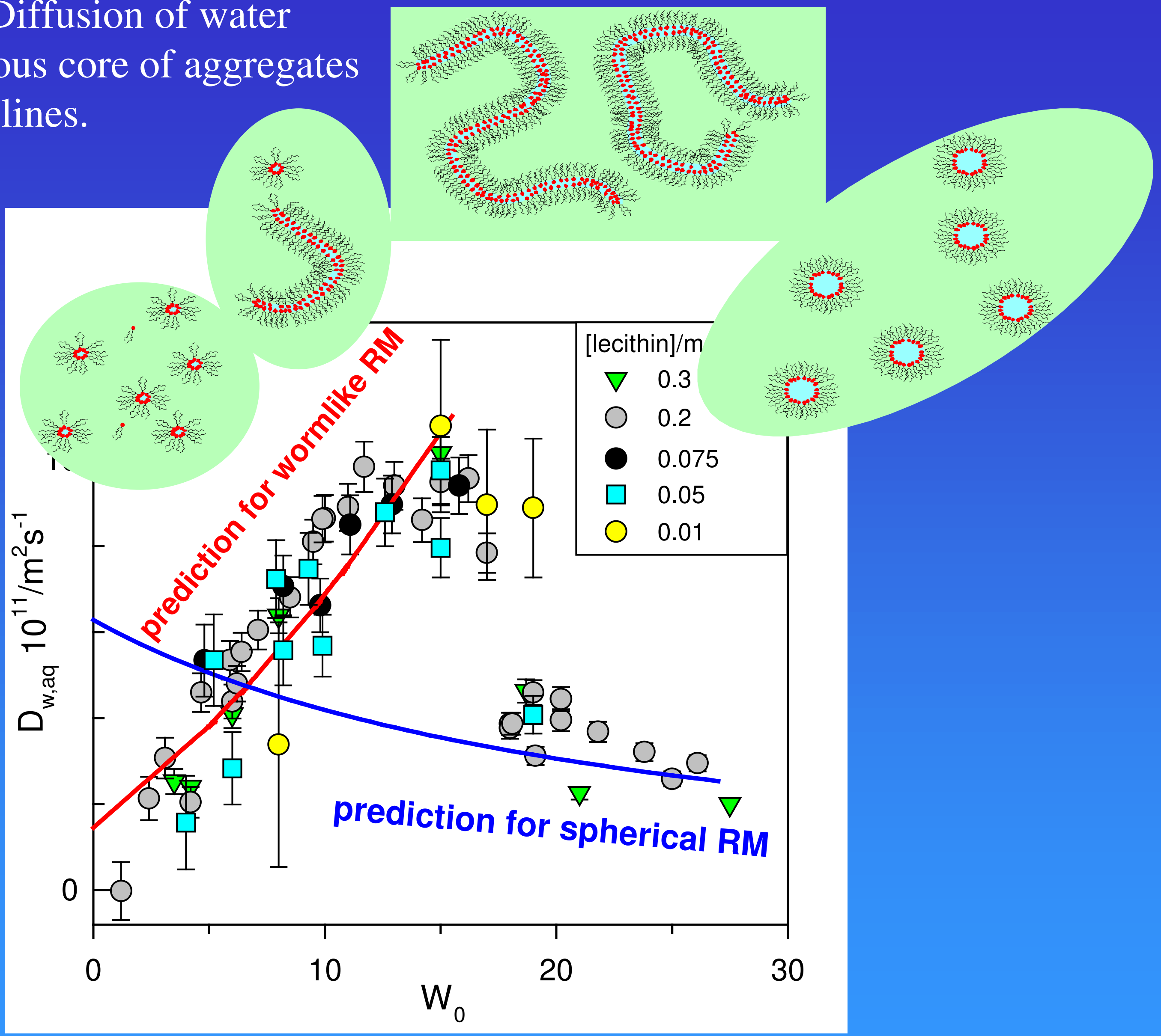
Small fast moving micelles
D_w reflects the overal micelle motion



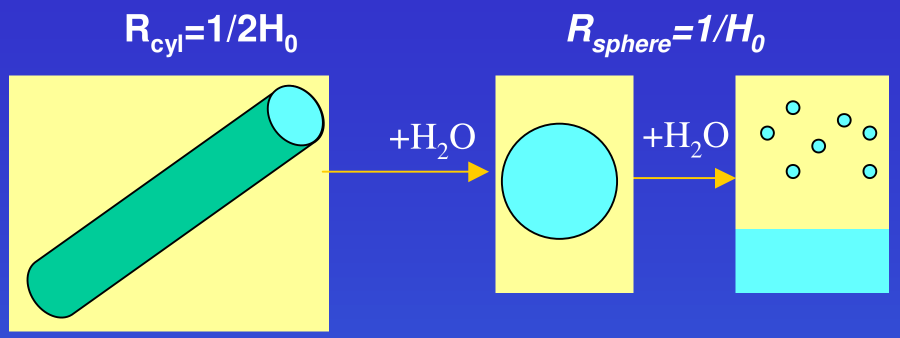
D_w can be calculated for spherical RM

D_w decreases upon increase in W_0

Organogels in cC6: Diffusion of water confined in the aqueous core of aggregates along water-dilution lines.



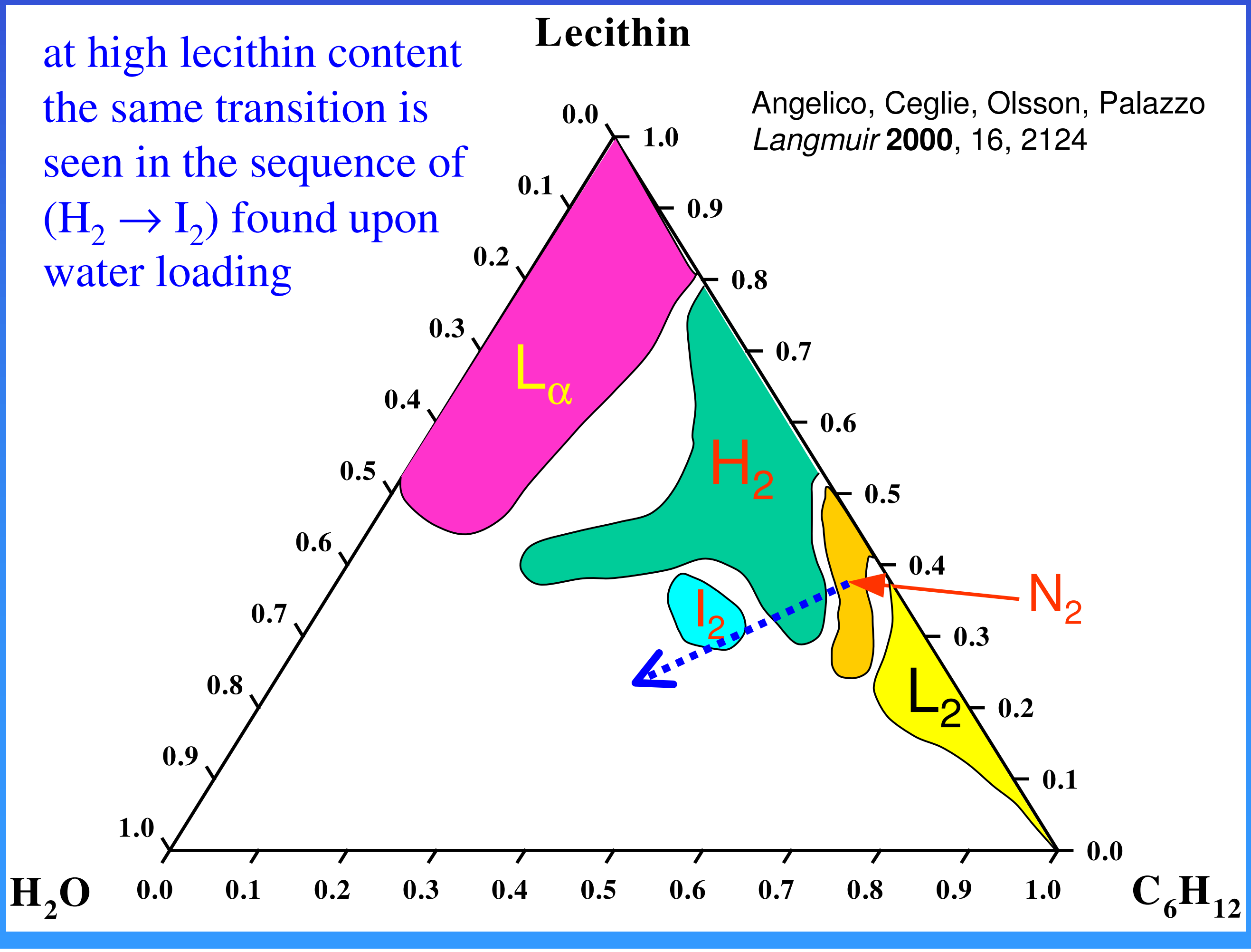
Angelico, Palazzo, Colafemmina, Cirkel, Giustini, Ceglie *J. Phys. Chem. B* ***1998****, 102, 2883*
Angelico, Balinov, Ceglie, Olsson, Palazzo, Soderman *Langmuir,* ***1999****, 15,* 1679



The rod-to-spheres transition accommodates a larger amount of water, leaving constant the mean curvature at the optimal value H_0.

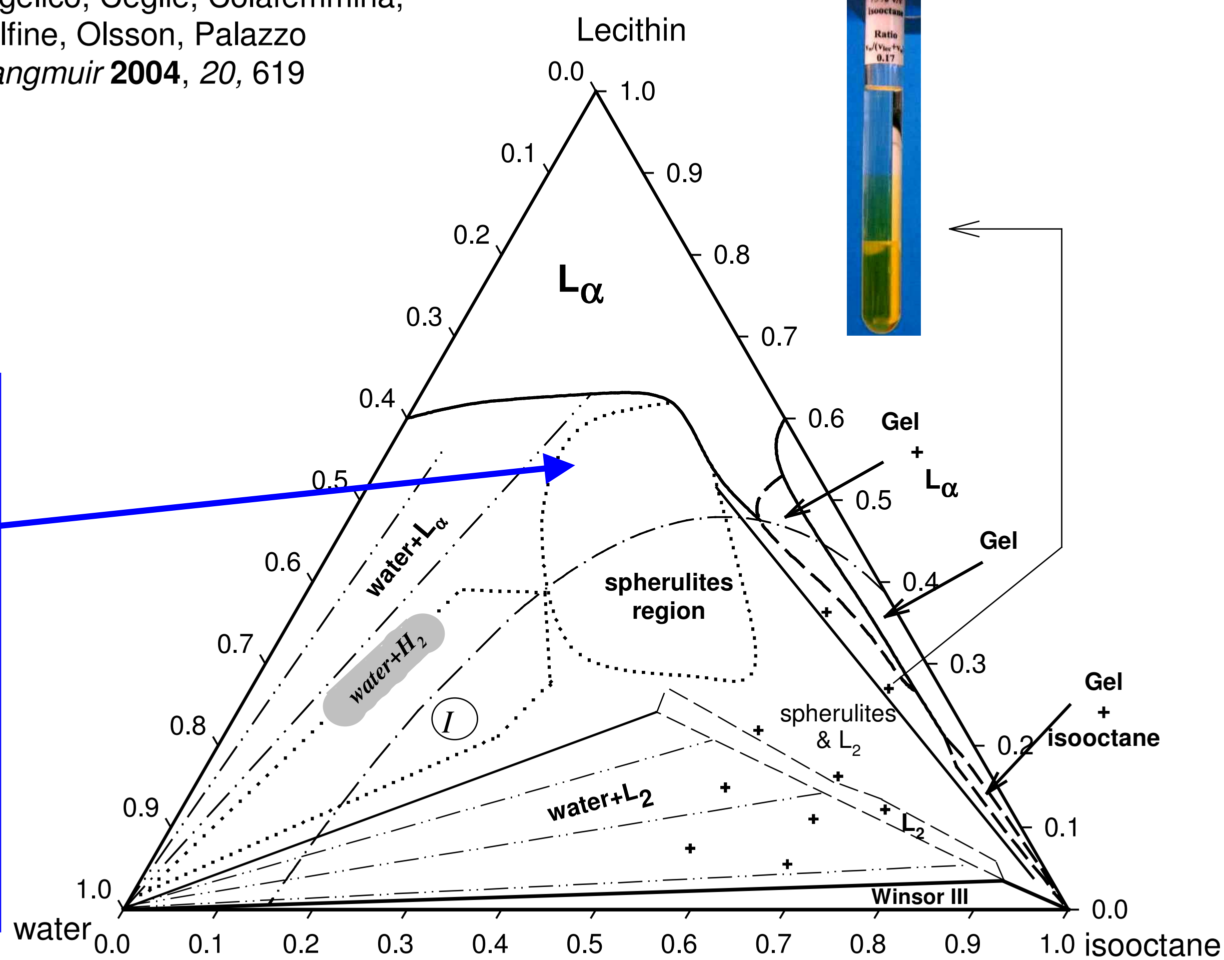
Upon further water addition the system expels excess water

at high lecithin content the same transition is seen in the sequence of ($H_2 \rightarrow I_2$) found upon water loading

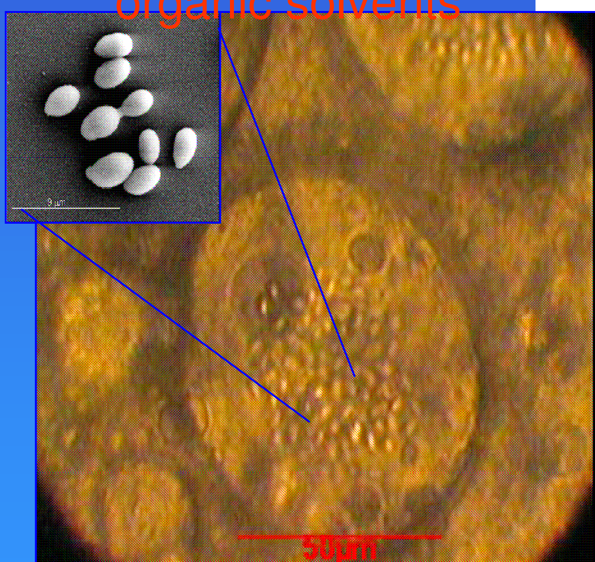


For isooctane and linear alkanes the system is governed by *local* curvature energy and large-scale network fluctuations

Angelico, Ceglie, Colafemmina, Delfine, Olsson, Palazzo
Langmuir **2004**, *20,* 619



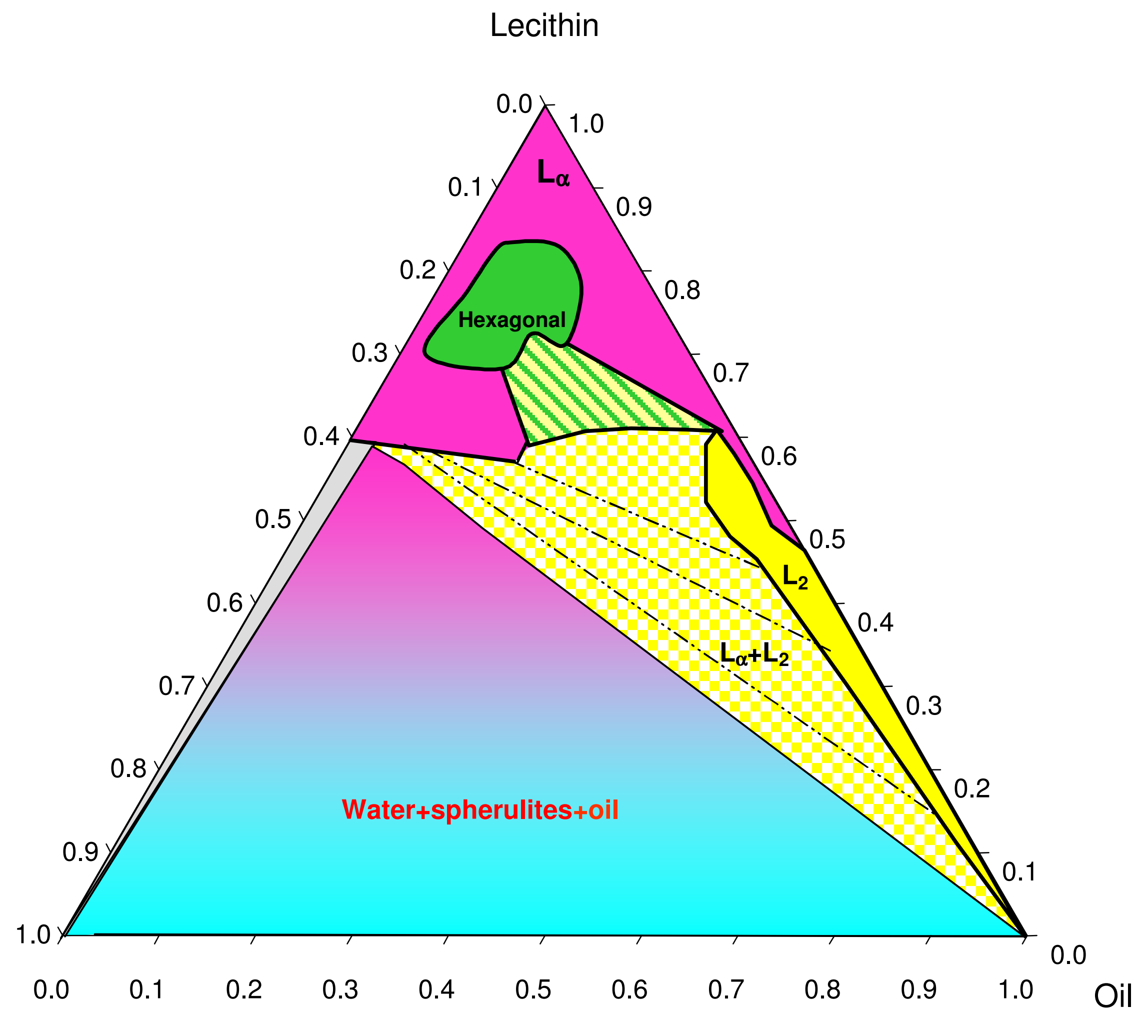
whole-cell biocatalysis in organic solvents



Stefan, Palazzo, Ceglie, Panzavolta, Hochkoeppler
Biotech. Bioeng. **2003,** 81, 323.8

Biocompatible fatty acid esters

Angelico, Ceglie, Colafemmina, Lopez, Olsson, Palazzo
Langmuir **2005**, *21*,140



Use as controlled drug release system

Mackeben, Müller, Müller-Goymann
Colloids Surf. A **2001**, *699*, 183.

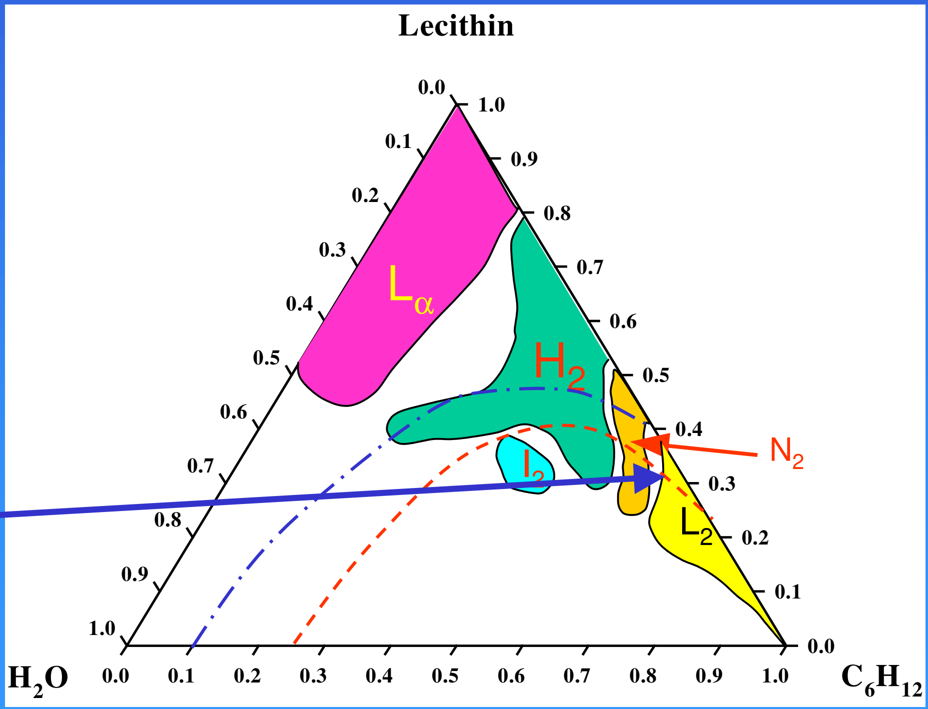
Micellar Dynamics

water residence time of about 1μs

micellar lifetime and lecithin residence time > 1 s

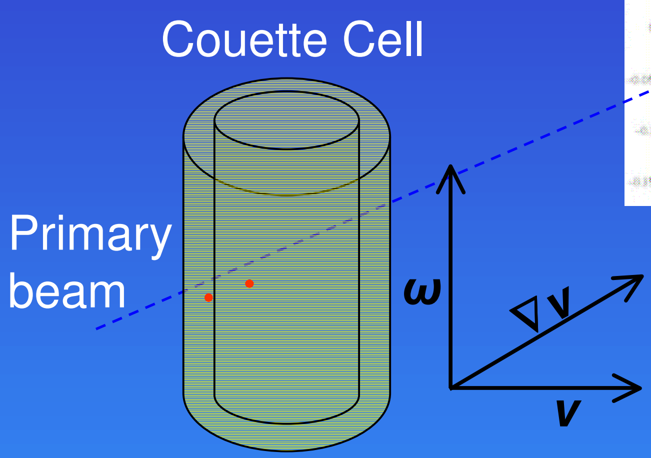
A more precise estimation of upper limit for the micellar lifetime can be obtained in cyclohexane

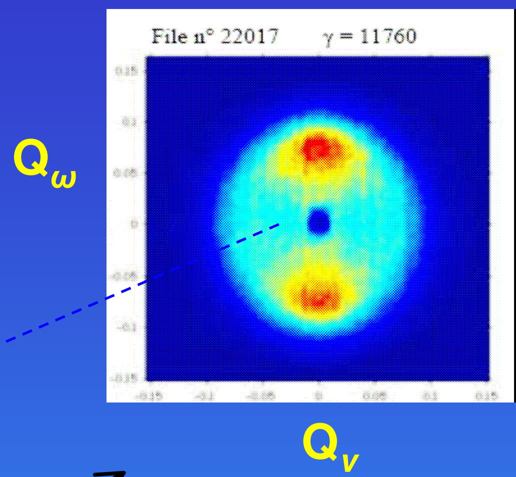
For isotropic samples close to the boundary of L_2 phase a moderate shear is sufficient to induce the alignment of the micelles into a nematic state.



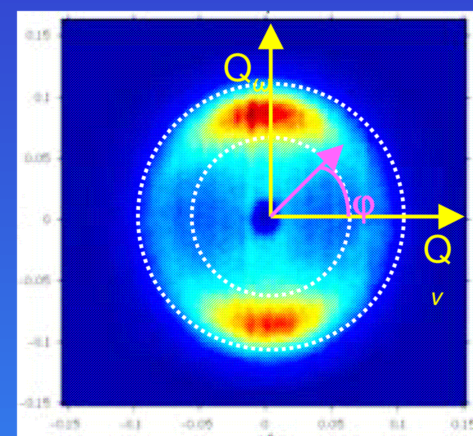
Relaxation of shear-aligned reverse micelles: SANS experiments

Setup:
Hayter, Penfold
J. Phys. Chem. **1984,** 88, 4589





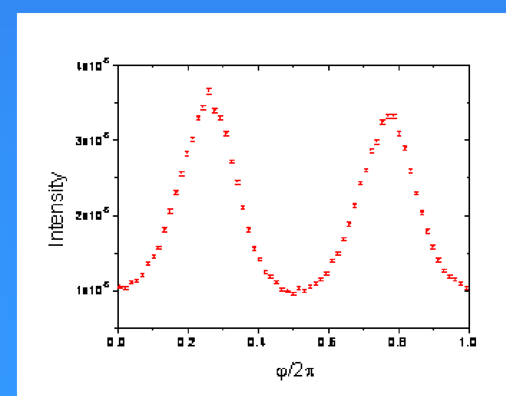
Linear micelles scatter mainly in a direction perpendicular to their long axis.



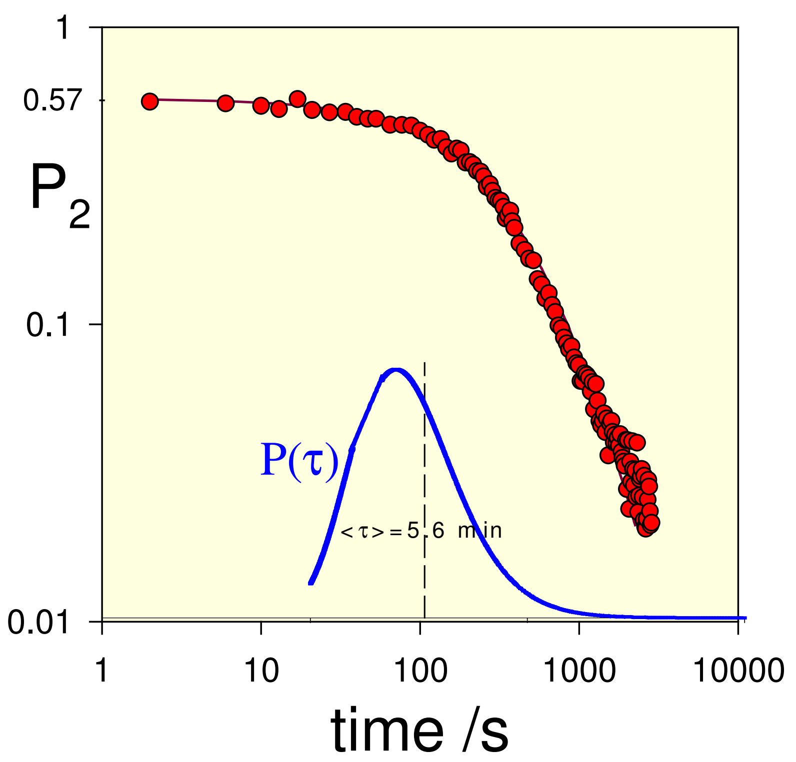
The anisotropy can be analyzed by plotting the scattered intensity as a function of the azimuthal angle, φ

from this azimutal representation, the orientational order can be quantified in terms of the second rank order parameter P_2

Deutsch, . *Phys. Rev. A* **1991**, *44*, 8264

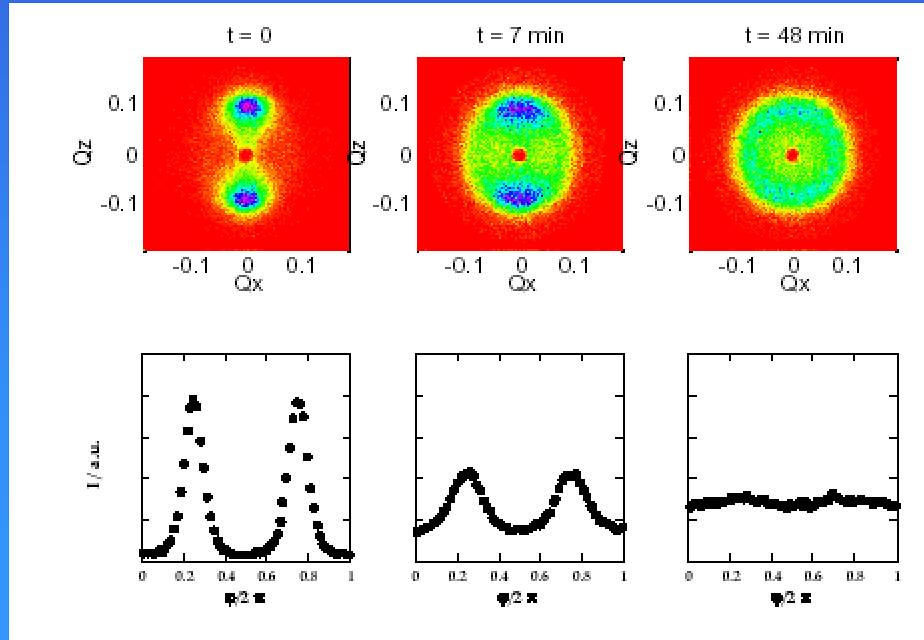


Variation of the second rank order parameter with time after cessation of shear ($d\gamma/dt$= 10 s^{-1}). A fit to $P_2=P_2(0)(1+t/<\tau>)^{-n}$ is shown as solid line.



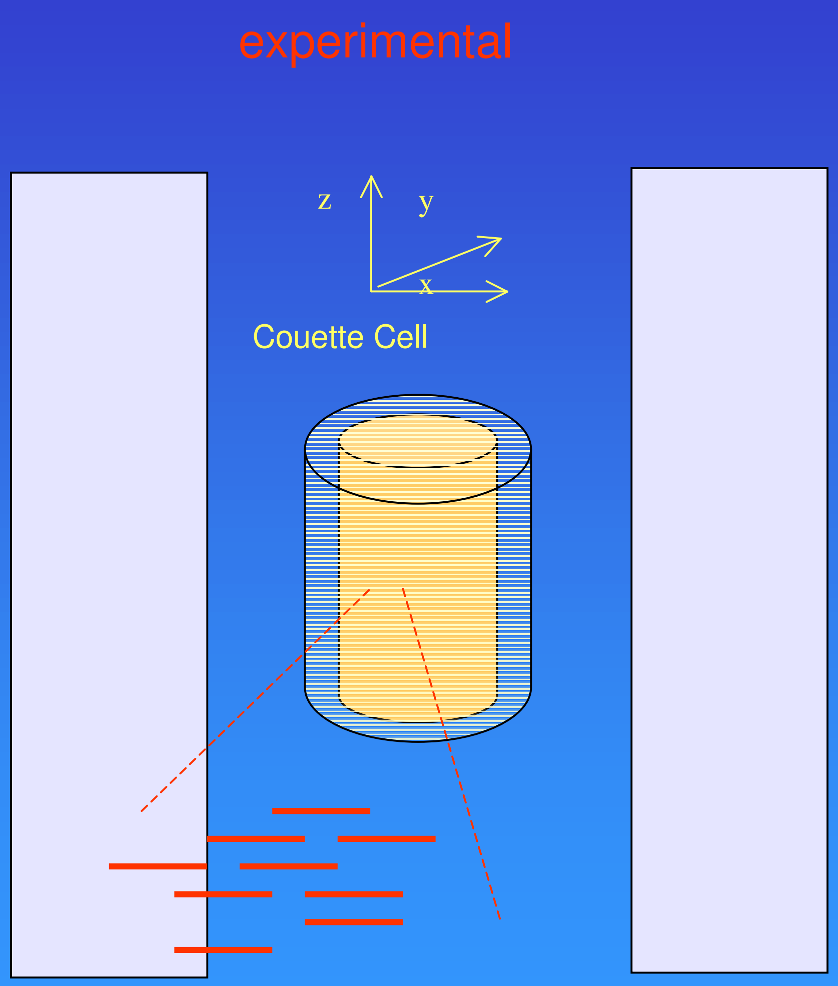
By SANS one can follows the decay of P_2 The time scale of the order parameter decay is of the order of minutes

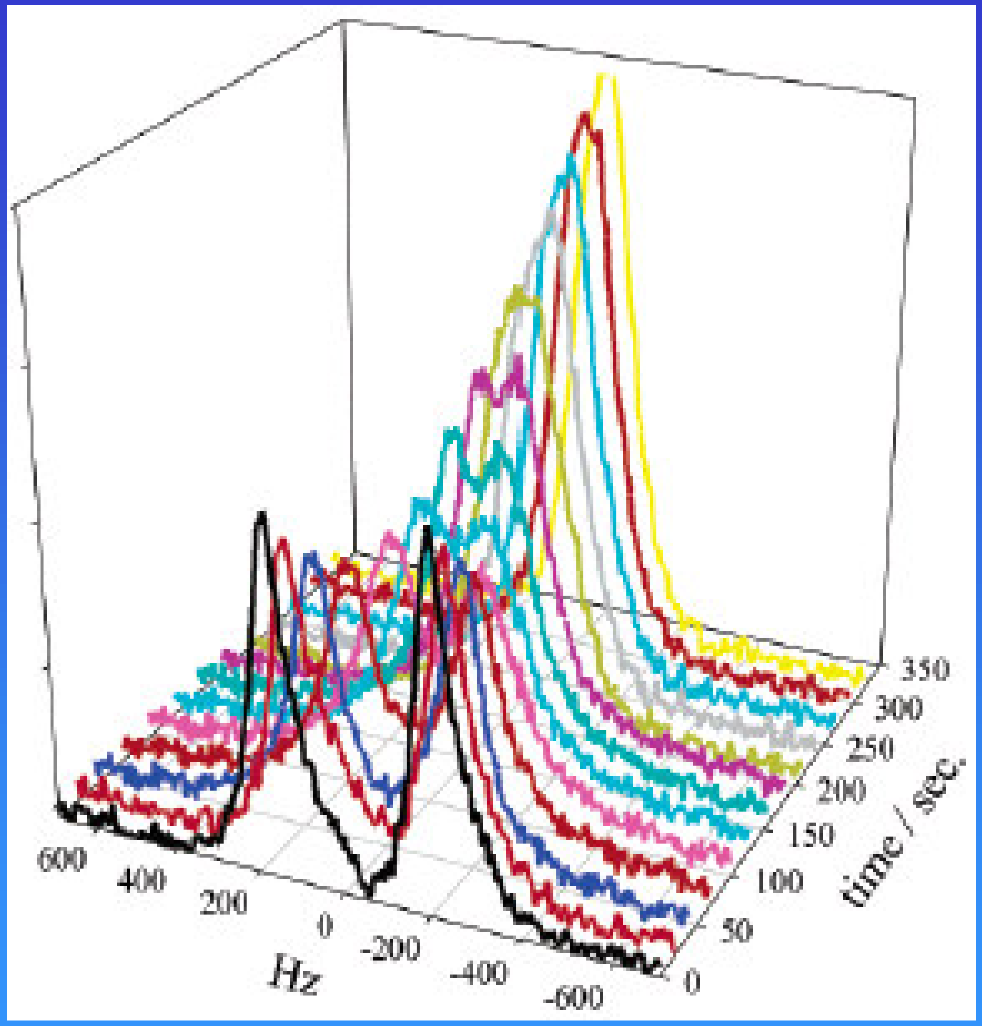
The relaxation from N_2 to L_2 is characterized by a gradual decay of orientational order (no nucleation and growth)



Angelico , Olsson , Mortensen , Ambrosone, Palazzo, Ceglie
J. Phys. Chem. B **2002**, 106, 2426

Relaxation of shear-aligned reverse micelles: Rheo-NMR experiments

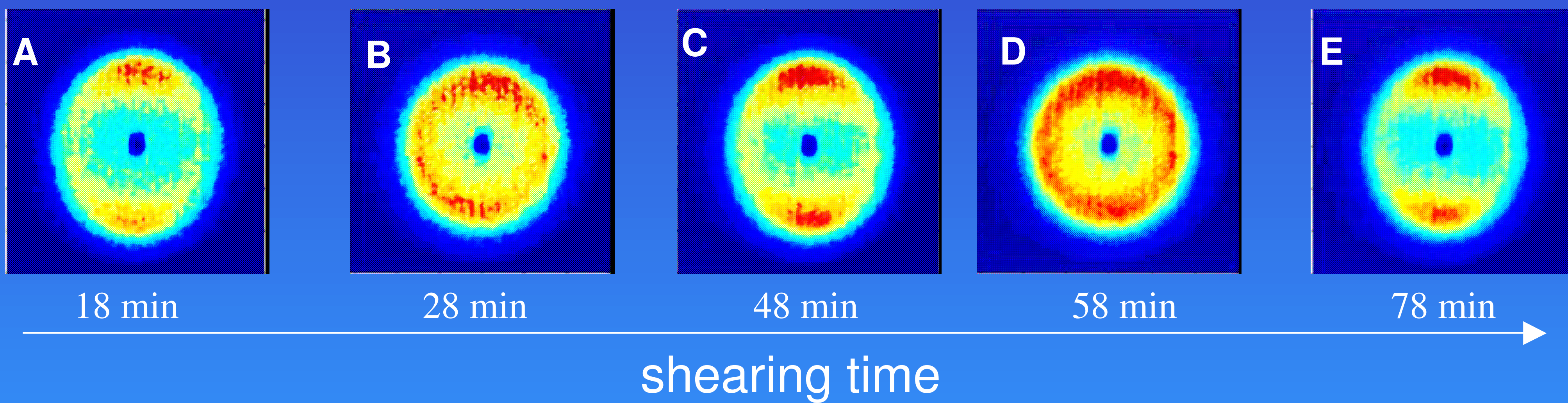




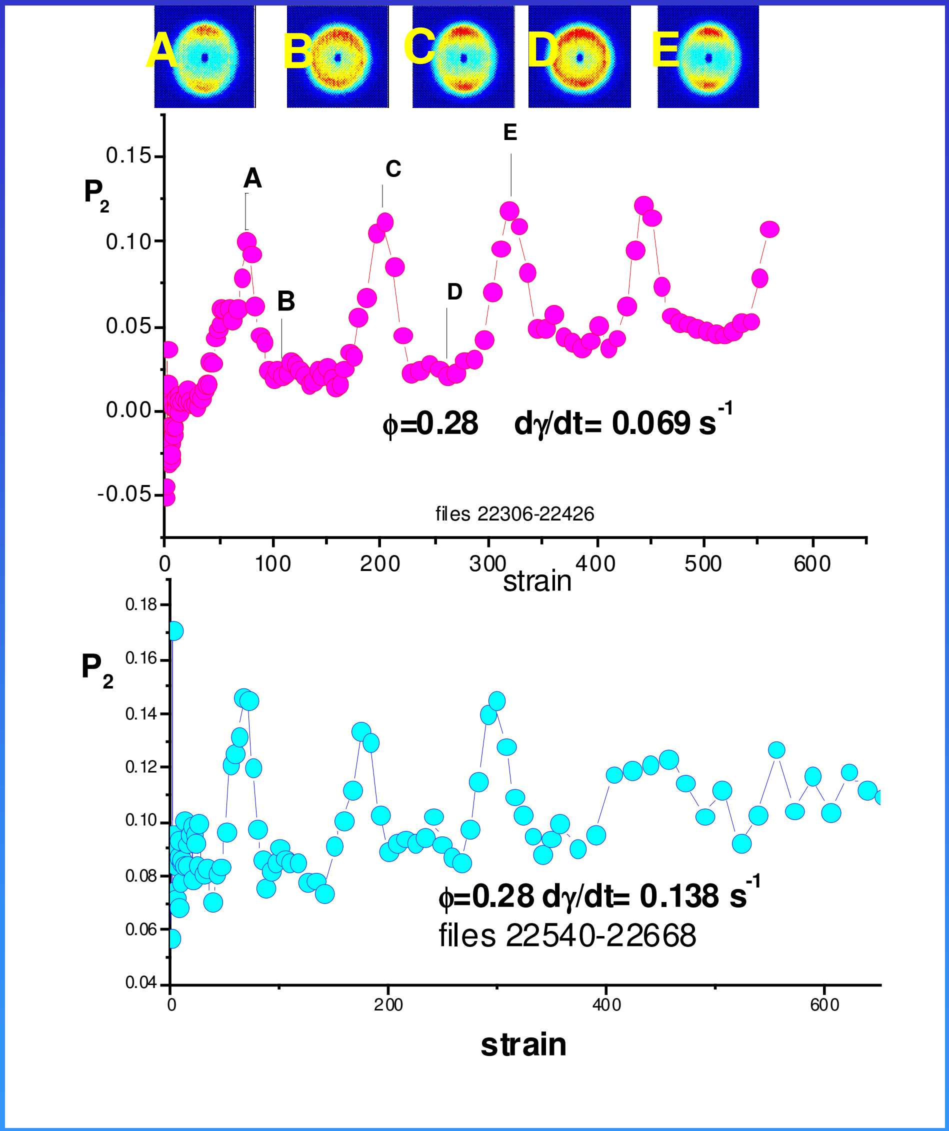
Angelico, Burgemeister, Ceglie, Olsson, Palazzo, Schmidt
J. Phys. Chem. B **2003**, *107*, 10325

Rheo-SANS start-up experiments at very low shear rate

$\phi=0.28 \quad d\gamma/dt = 0.069\ s^{-1}$



Angelico, Mortensen, Olsson, Palazzo *Unpublished*



P_2 exhibits damped oscillations scaling with the strain

Working hypothesis:

oscillations reflect the tumbling dynamics of nematic polydomains during the shear-induced isotropic-nematic transition

Caveat:
more measurements are required

acknowledgements

Ruggero ANGELICO & Andrea CEGLIE – Campobasso, Italy ***grazie!!!***

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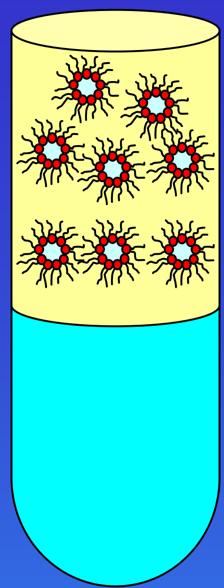
Claudia SCHMIDT - Padeborn, Germany ***danke!!!***

Ulf OLSSON – Lund, Sweden ***tack!!!***



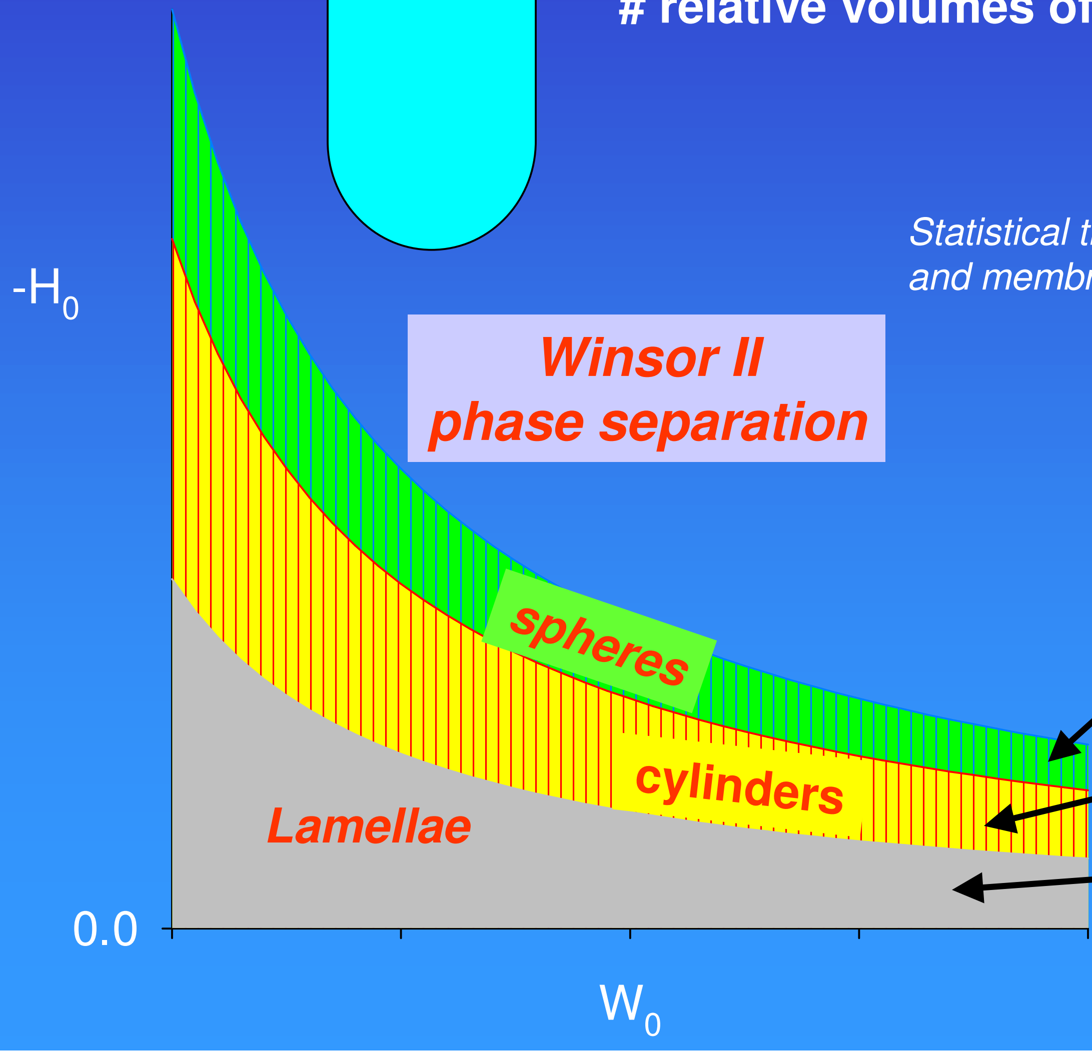
Effect of oil

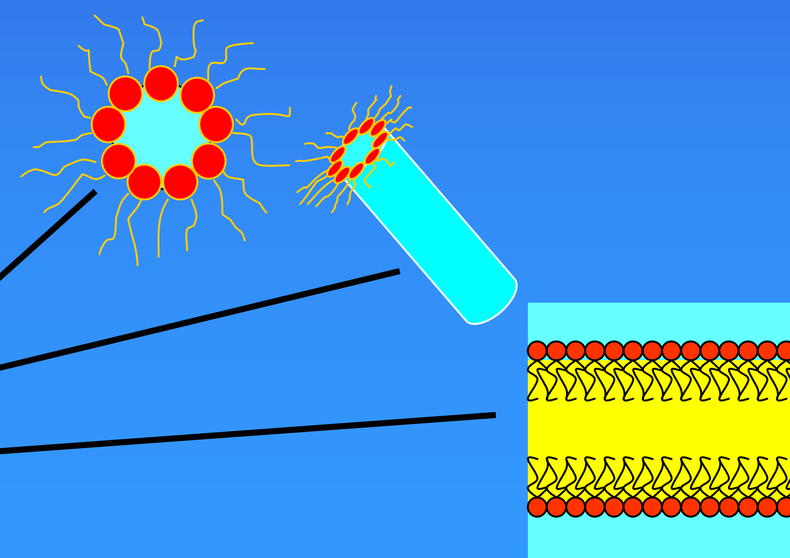
Aggregates shapes is dictated by:

 # H_0 function of polar head hydration and oil penetration

 # relative volumes of water and oil (W_0)

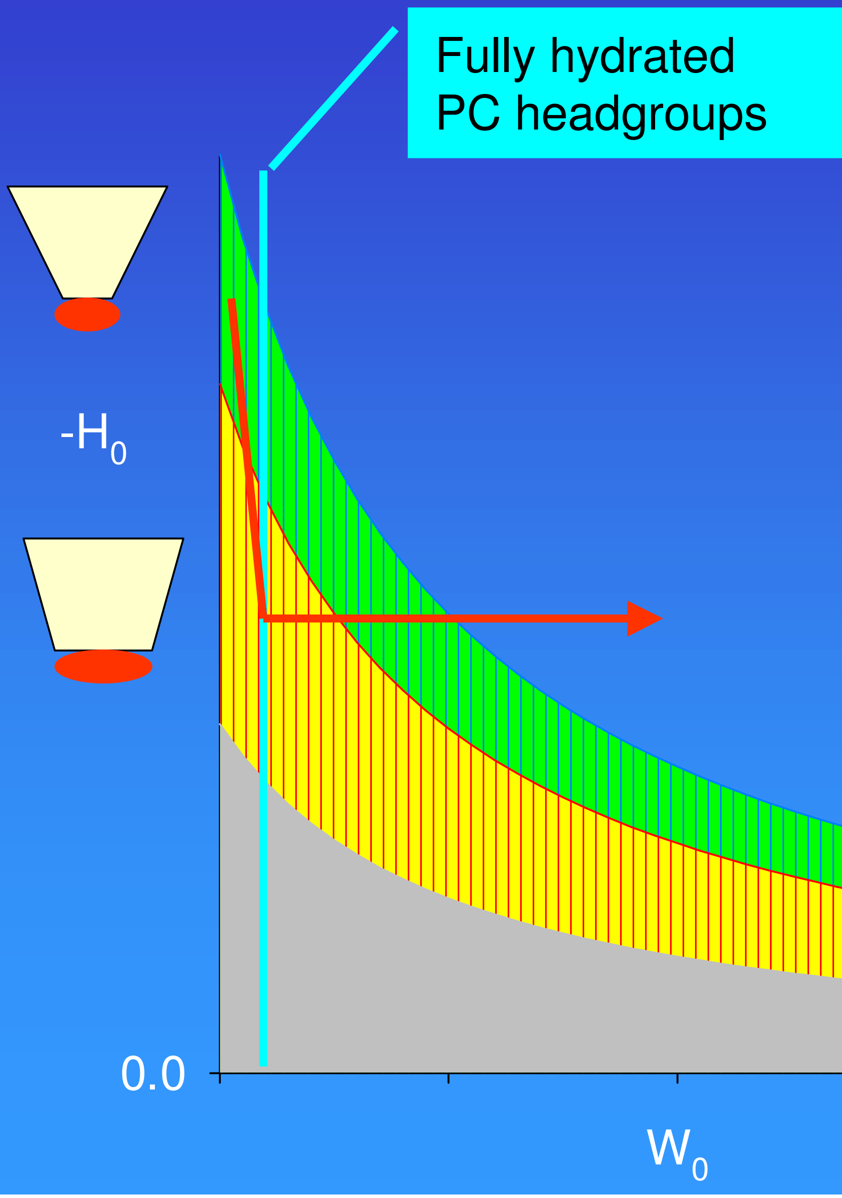
S.A. Safran
Statistical thermodynamics of surfaces, interfaces and membranes

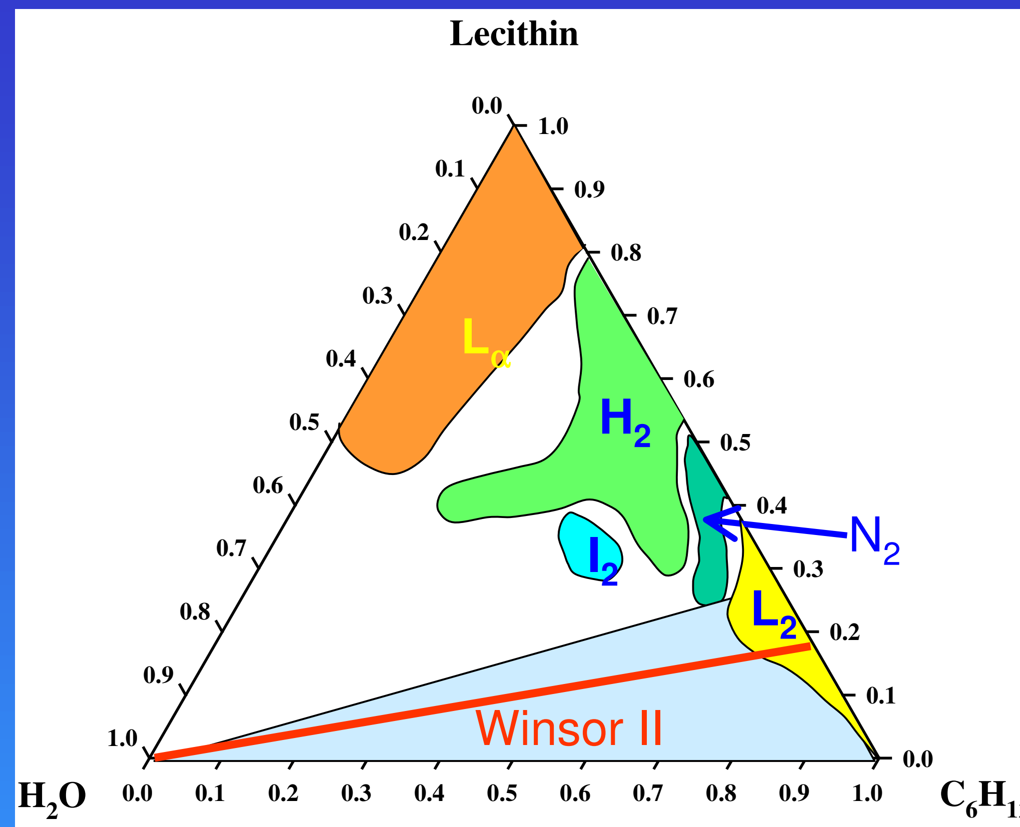




Angelico, Ceglie, Olsson, Palazzo
Langmuir **2000**, 16, 2124

Highly penetrable oil:cyclohexane



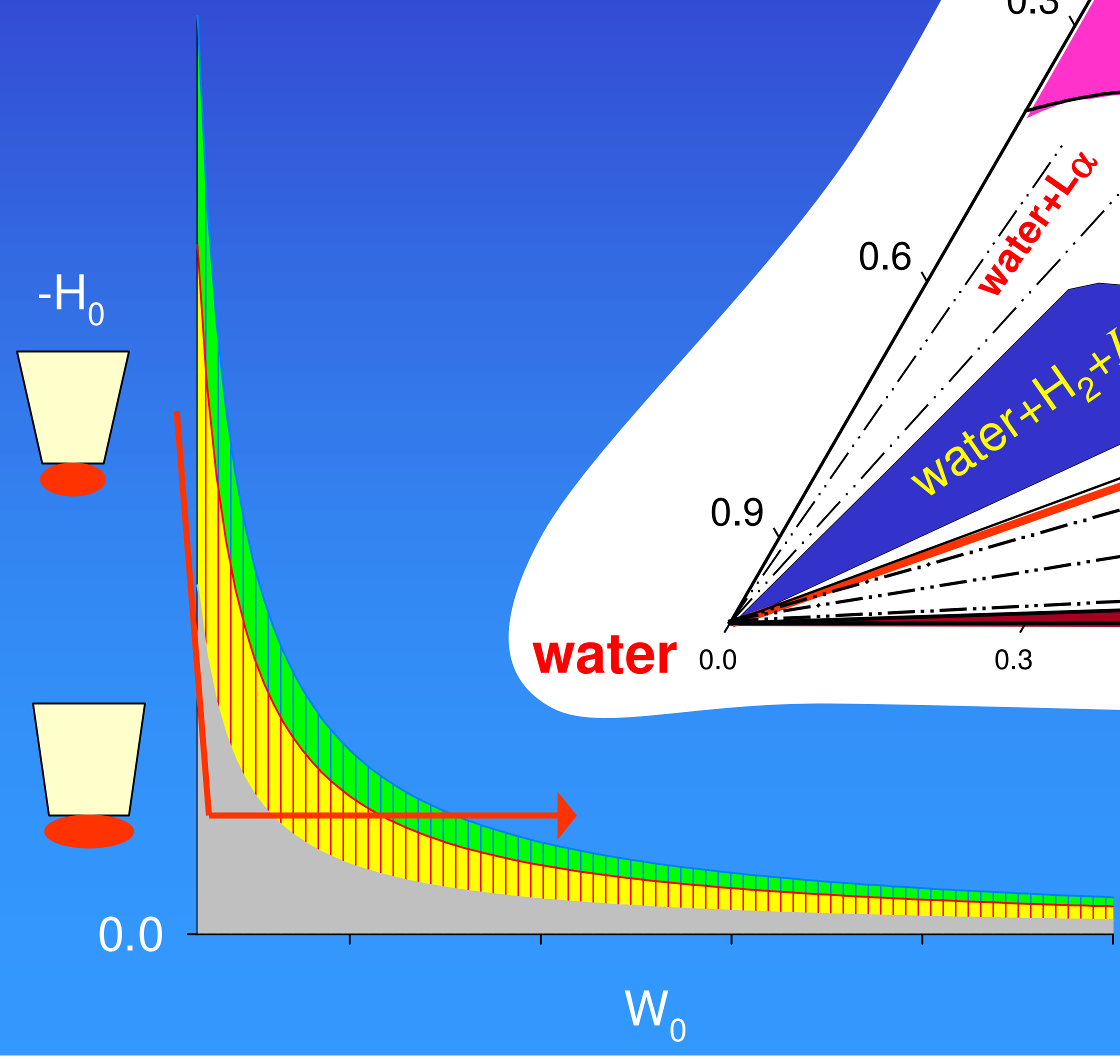


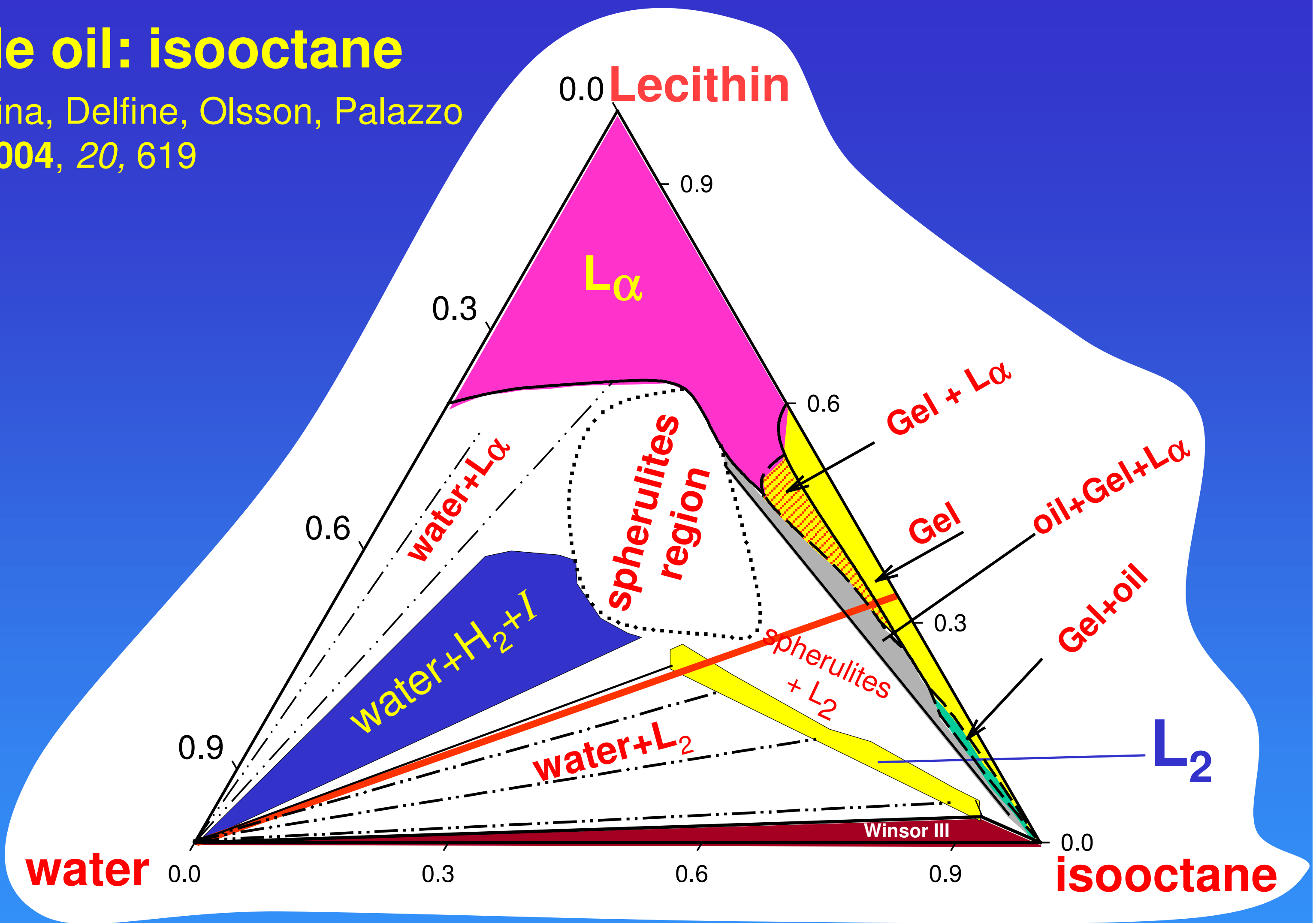
Small RM→gel →Winsor II

W_0

Less penetrable oil: isooctane

Angelico, Ceglie, Colafemmina, Delfine, Olsson, Palazzo
Langmuir **2004**, *20,* 619



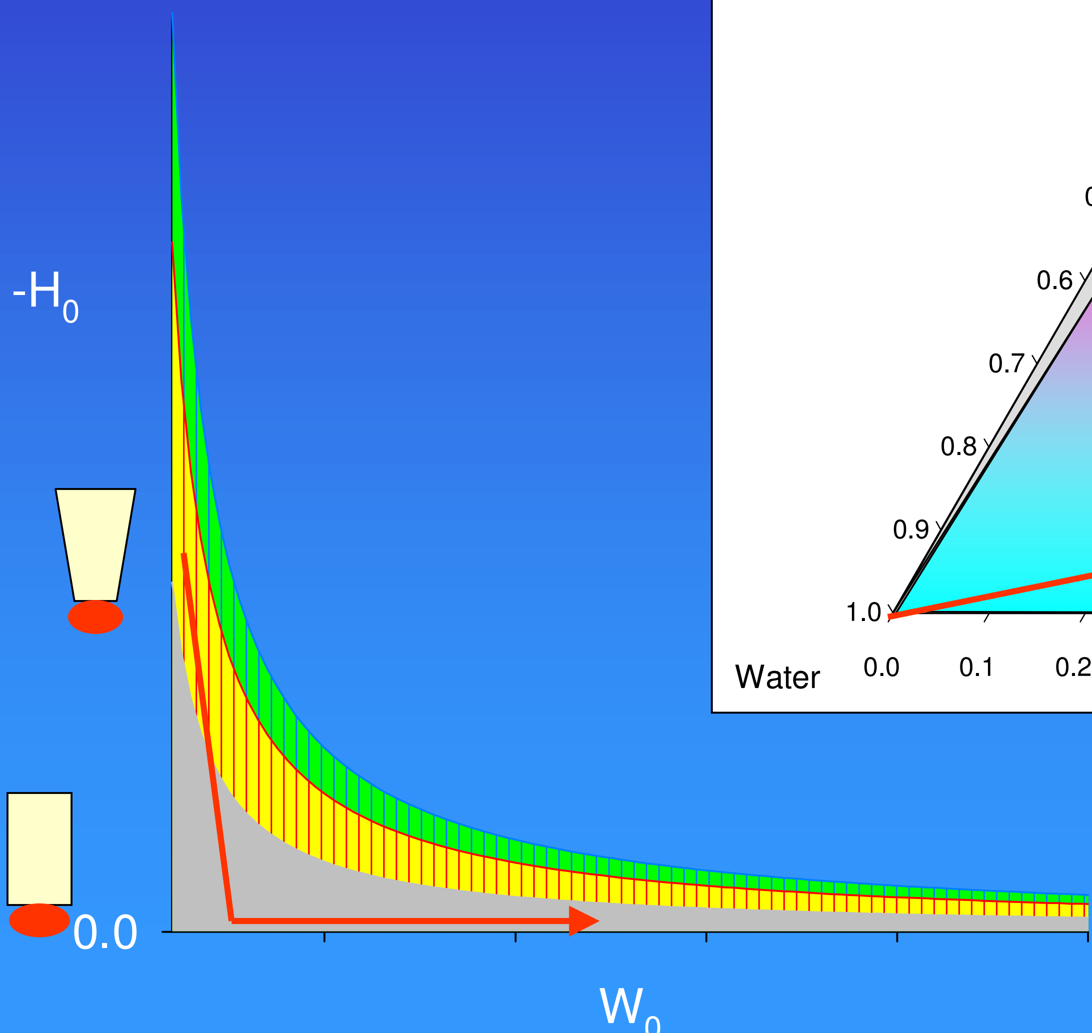


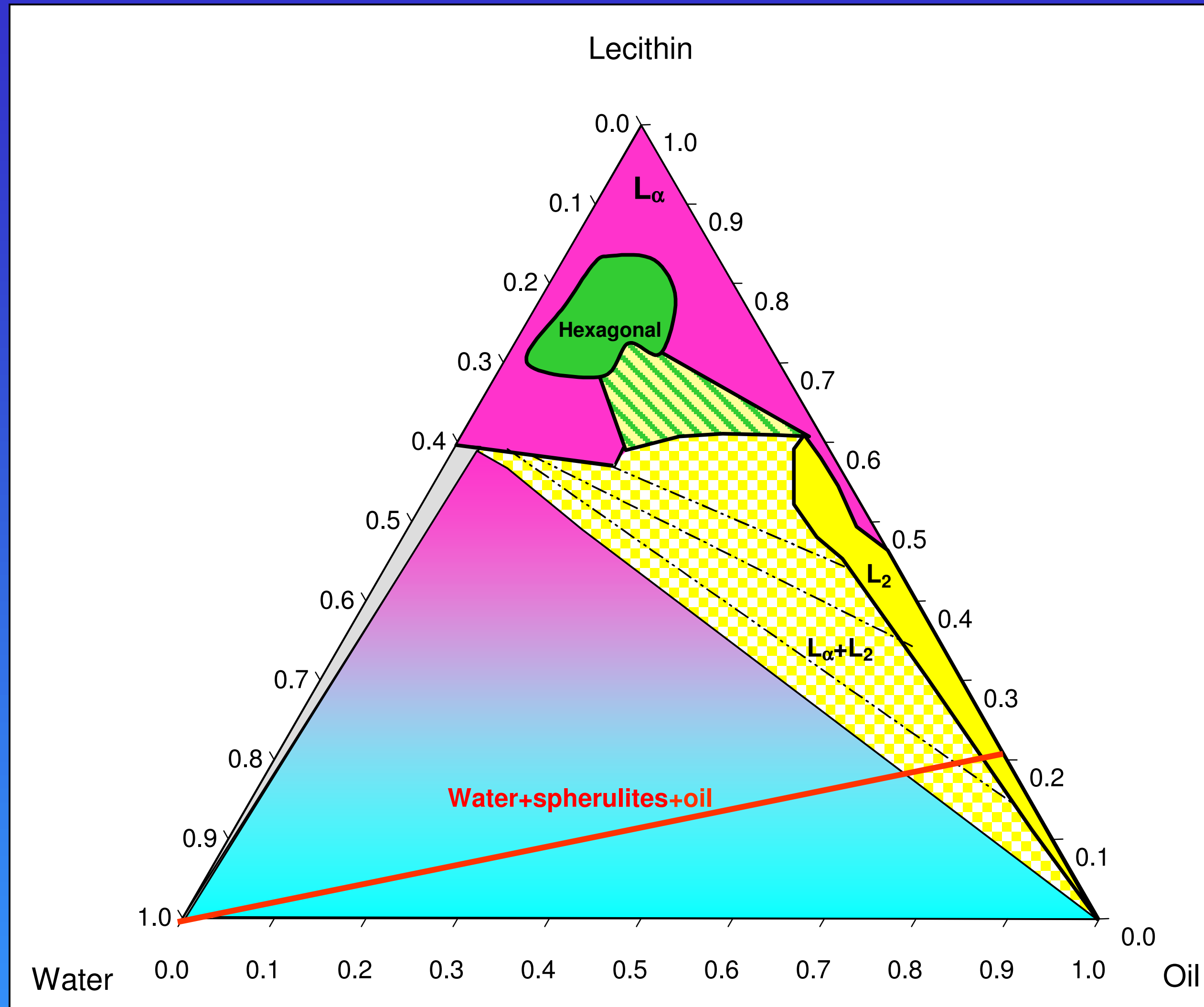
gel→gel+L_α →RM → Winsor II

W_0

Almost non-penetrable oil: isopropylpalmitate

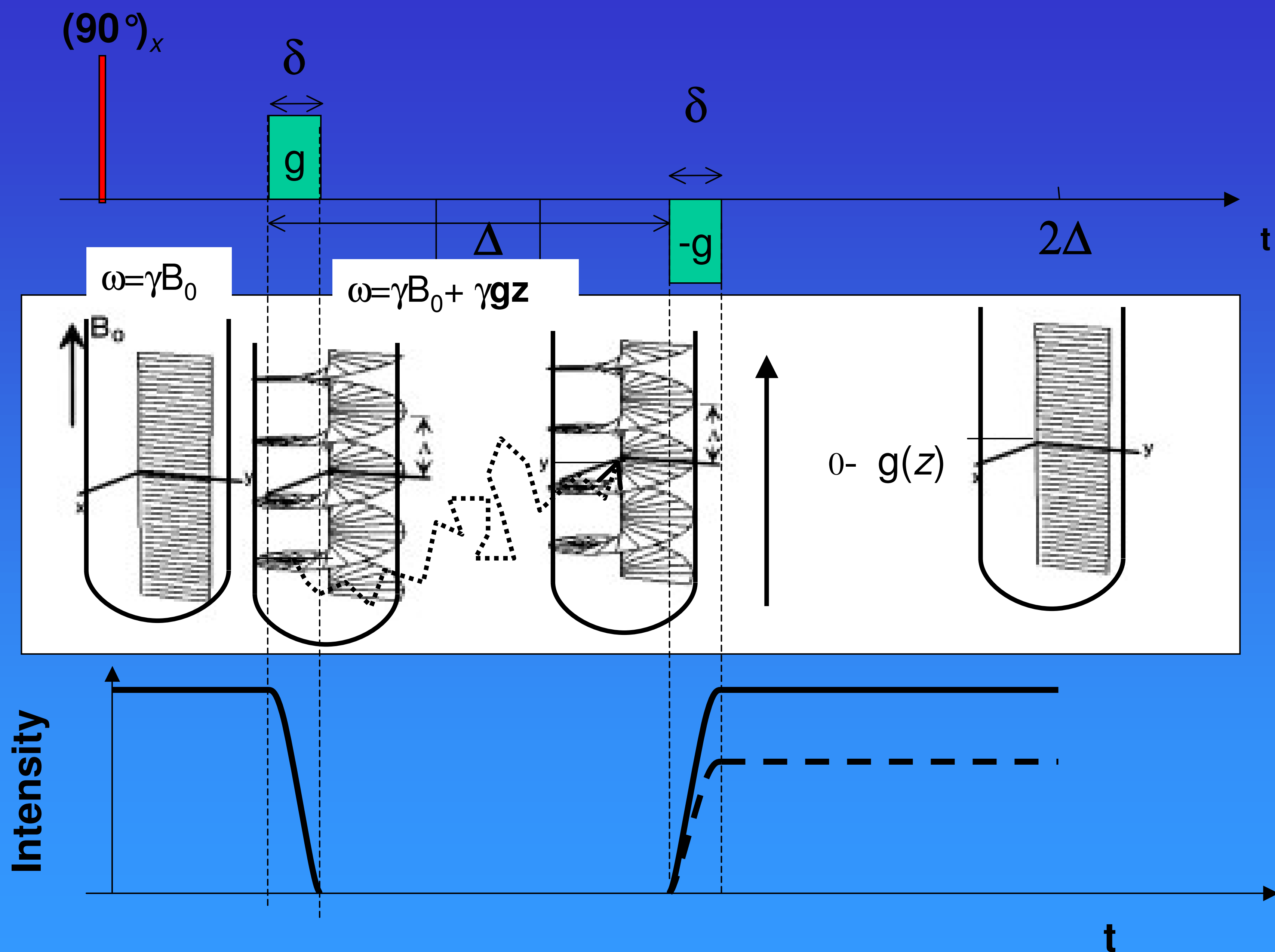
Angelico, Ceglie, Colafemmina, Lopez, Olsson, Palazzo
Langmuir 2005





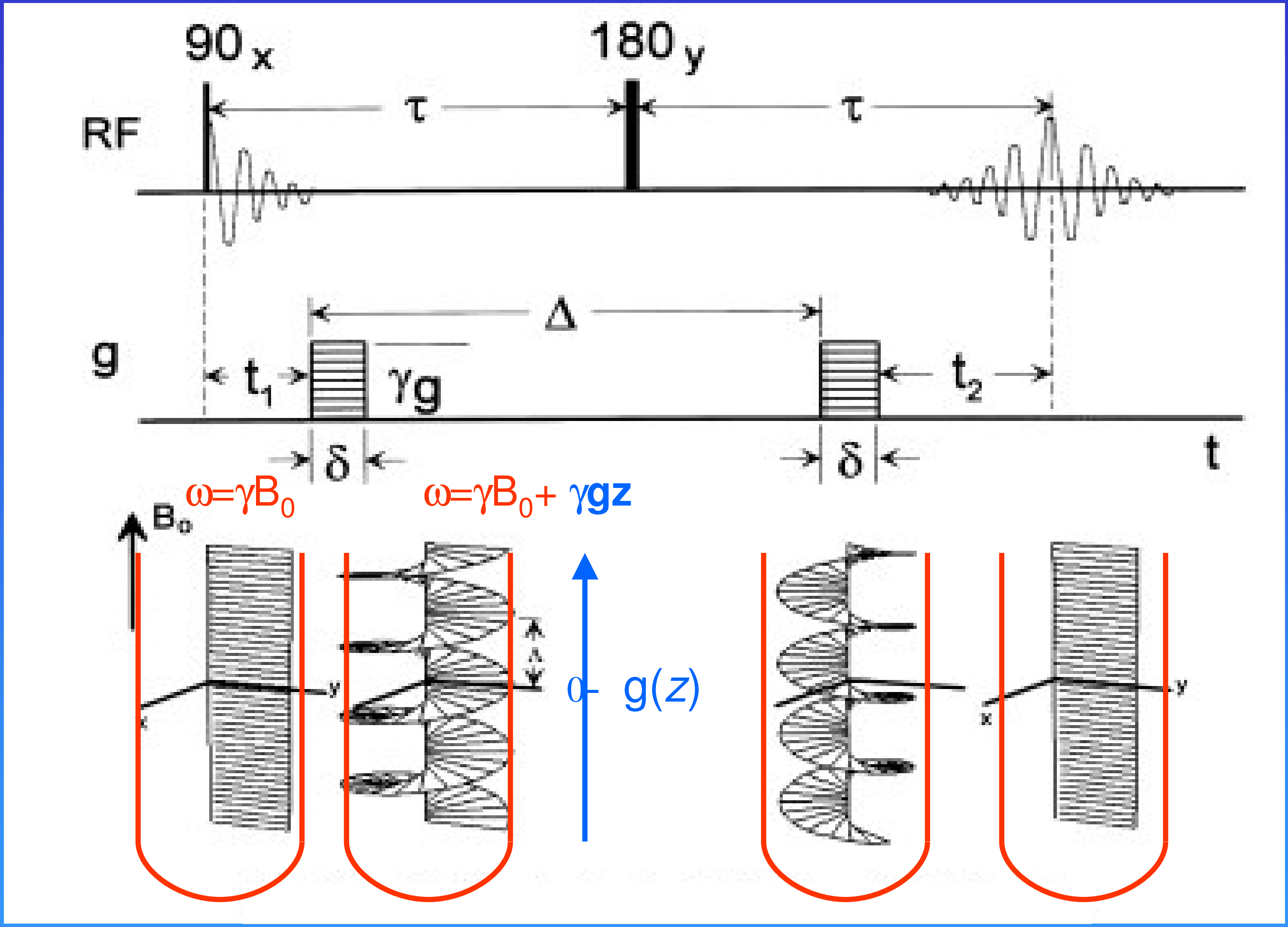
gel→gel+L_α → L_α → H_2O+ L_α +oil

W_0

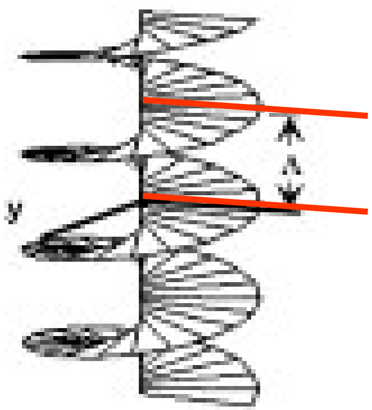


(90°)x
δ
g
δ
-g
Δ
2Δ
t
ω=γB0
ω=γB0+ γgz
B0
0- g(z)
Intensity
t

Determinazione di D via PGSE-NMR

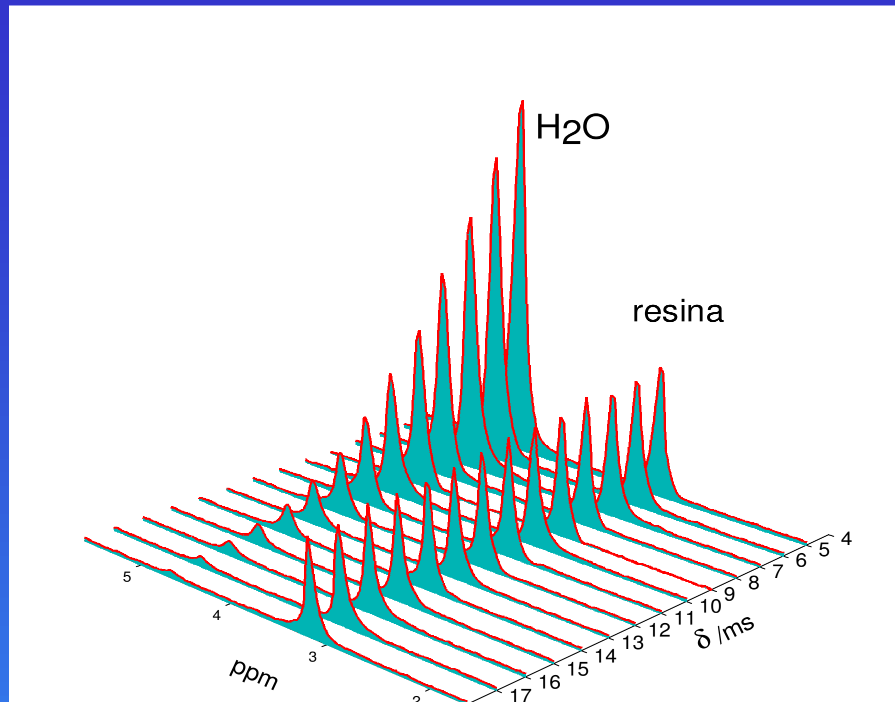


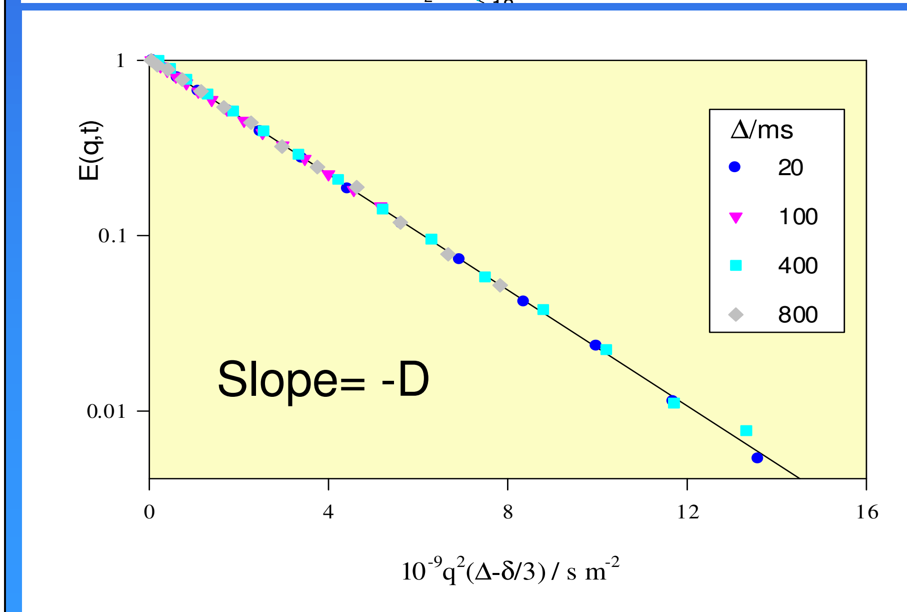
$$E(q,t) = \int_{-\infty}^{+\infty} \overline{P}(z,t) e^{iqz} dz$$



2π/q

q=γgδ

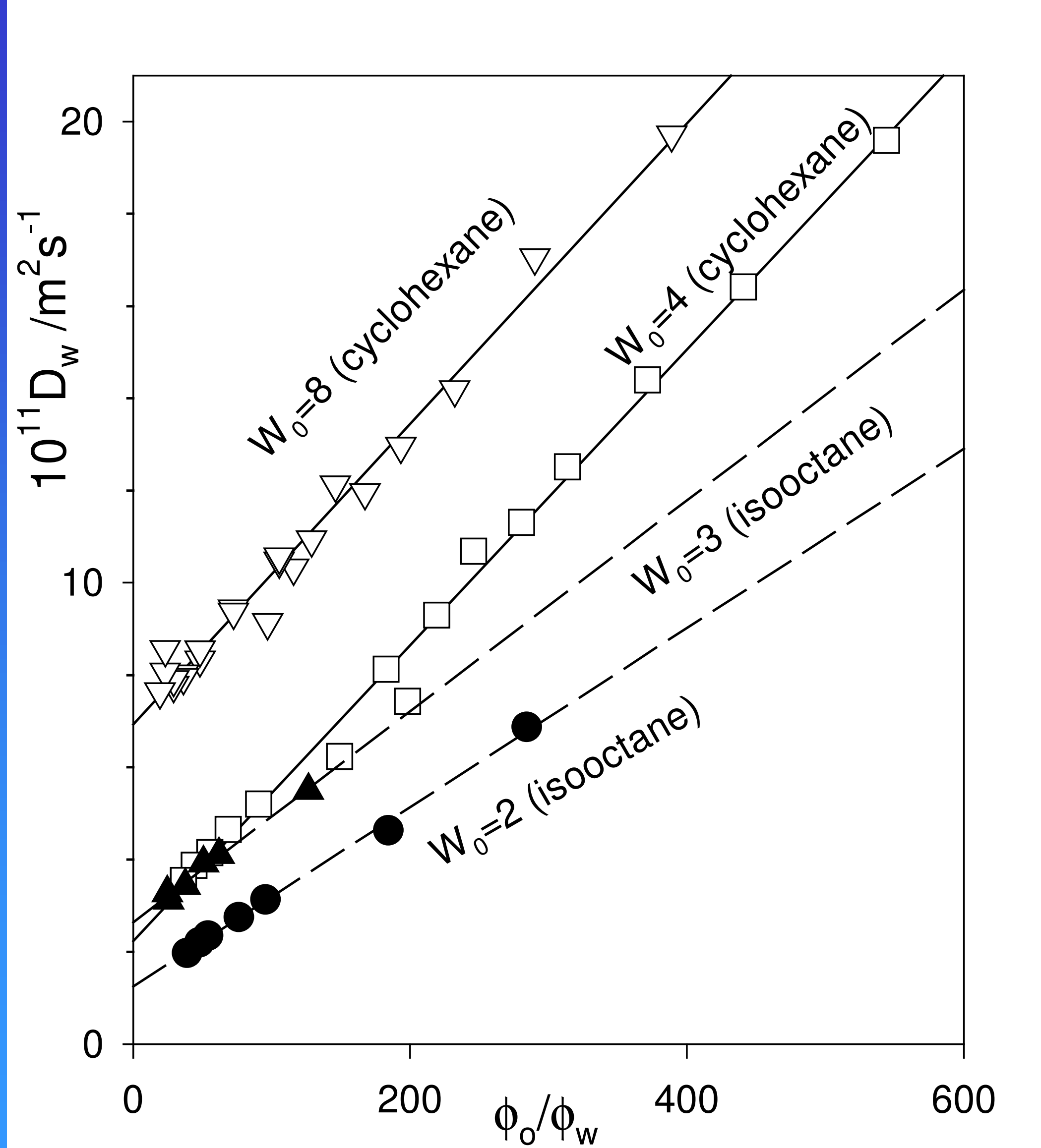




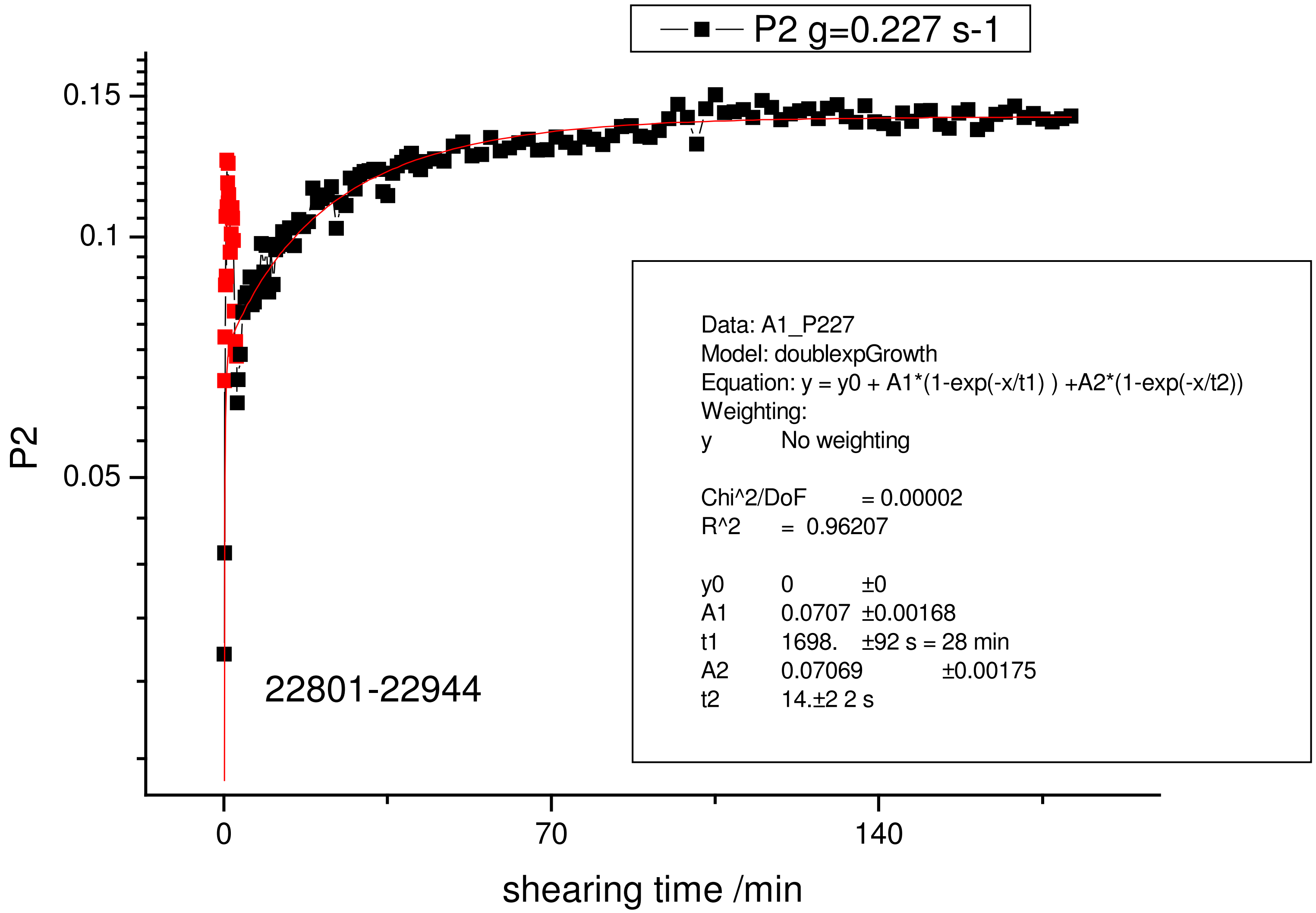
For a simple liquid

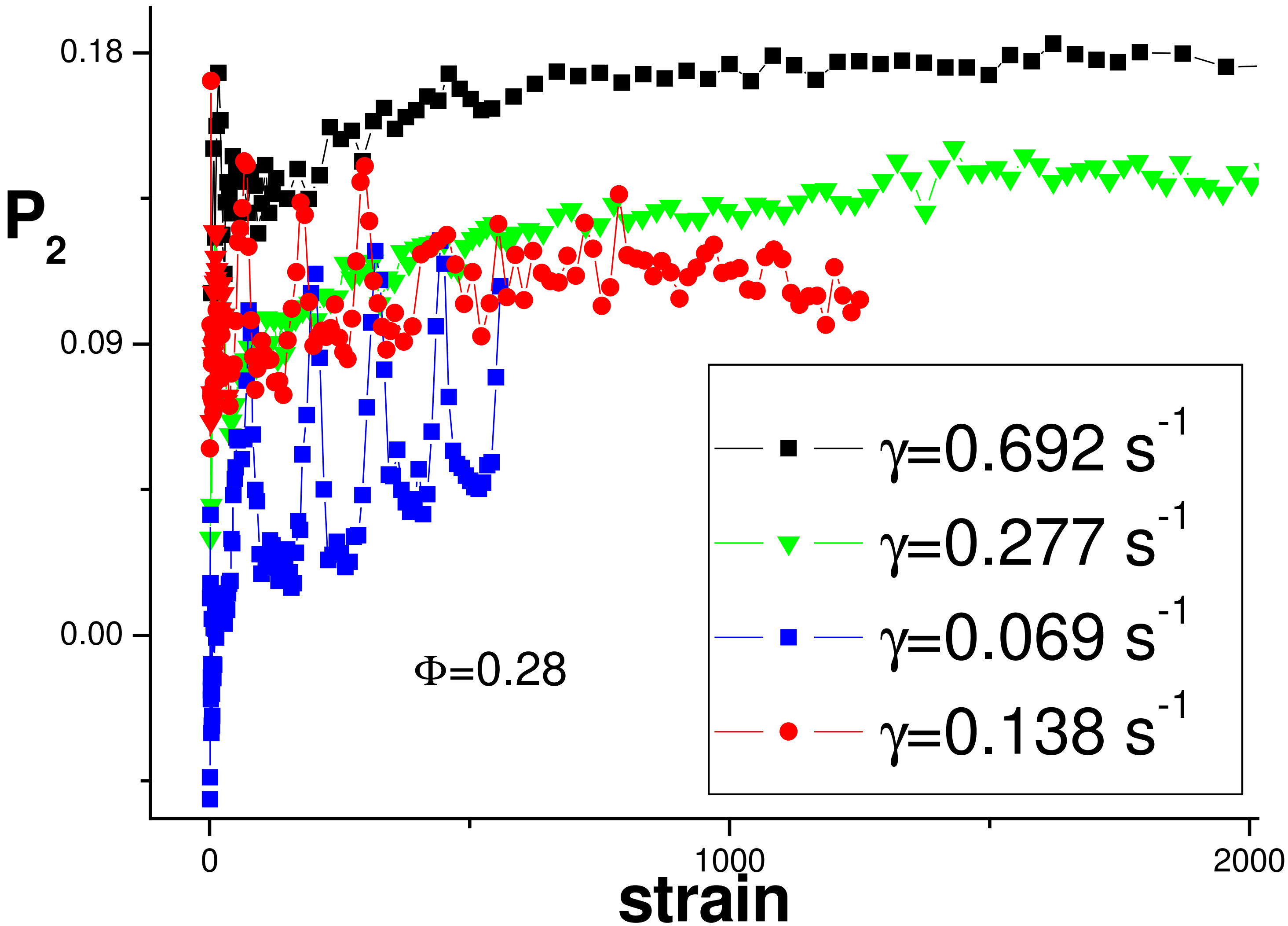
$$\overline{P}(z,t) = (4\pi Dt)^{-\frac{1}{2}} e^{-\frac{z^2}{4Dt}}$$

$$E(q,t) = e^{-q^2 Dt}$$



$10^{11}D_w$ /m^{2}s^{-1}
20
10
0
0
200
400
600
ϕ_o/ϕ_w
W_0=8 (cyclohexane)
W_0=4 (cyclohexane)
W_0=3 (isooctane)
W_0=2 (isooctane)


P2 g=0.227 s-1
0.15
0.1
0.05
P2
0
70
140
shearing time /min
22801-22944
Data: A1_P227
Model: doublexpGrowth
Equation: y = y0 + A1*(1-exp(-x/t1)) +A2*(1-exp(-x/t2))
Weighting:
y No weighting
Chi^2/DoF = 0.00002
R^2 = 0.96207
y0 0 ±0
A1 0.0707 ±0.00168
t1 1698. ±92 s = 28 min
A2 0.07069 ±0.00175
t2 14.±2 2 s



0.18
0.09
0.00
P2
0
1000
2000
strain
Φ=0.28
γ=0.692 s-1
γ=0.277 s-1
γ=0.069 s-1
γ=0.138 s-1